

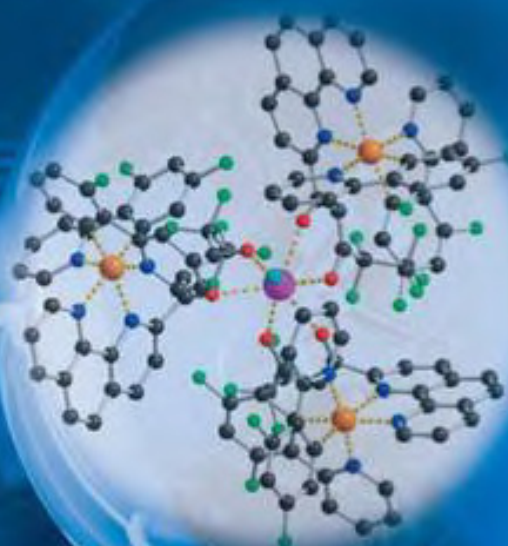
RARE EARTH COORDINATION CHEMISTRY

Fundamentals and Applications

Editor

CHUN-HUI HUANG

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RARE EARTH COORDINATION CHEMISTRY

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FUNDAMENTALS AND APPLICATIONS

Editor

Chunhui Huang

Peking University, China



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Contents

Author Biographies	xiii
Foreword	xxi
Preface	xxiii
1 Introduction	1
<i>Chunhui Huang and Zuqiang Bian</i>	
1.1 Electronic Configuration of Lanthanide Atoms in the Ground State	1
1.2 Lanthanide Contraction	2
1.3 Specificity of the Photophysical Properties of Rare Earth Compounds	6
1.3.1 Spectral Terms	7
1.3.2 Selection Rules for Atomic Spectra	8
1.3.3 Lifetime	9
1.3.4 Absorption Spectra	10
1.3.5 The Emission Spectra of Rare Earth Compounds	11
1.4 Specificities of Rare Earth Coordination Chemistry	13
1.4.1 Valence State of Rare Earth Elements	14
1.4.2 Chemical Bonding of Rare Earth Elements	15
1.4.3 Coordination Numbers of Rare Earth Complexes	15
1.4.4 Tetrad Effect of Lanthanide Elements – Changing Gradation Rules in Lanthanide Coordination Chemistry	21
1.5 Coordination Chemistry of Inorganic Compounds	25
1.5.1 Rare Earth Hydroxides	25
1.5.2 Rare Earth Halide and Perchlorate Compounds	26
1.5.3 Rare Earth Cyanide and Thiocyanate Compounds	27
1.5.4 Rare Earth Carbonate Compounds	28
1.5.5 Rare Earth Oxalate Compounds	30
1.5.6 Rare Earth Nitrate Compounds	31
1.5.7 Rare Earth Phosphate Compounds	32
1.5.8 Rare Earth Sulfate Compounds	34
1.5.9 Rare Earth Borate Compounds	36
1.6 Outlook	36
Acknowledgments	38
References	38
2 β-Diketonate Lanthanide Complexes	41
<i>Kezhi Wang</i>	
2.1 Introduction	41
2.2 Types of β -Diketones Used for Lanthanide Complexes	42

2.2.1	Mono(β -Diketone) Ligands	42
2.2.2	Bis(β -Diketones) Ligands	44
2.2.3	Dendritic β -Diketones Ligands	44
2.3	β -Diketonate Lanthanide Complexes	47
2.3.1	Mononuclear Lanthanide Complexes with β -Diketones	47
2.3.2	Polynuclear β -Diketonate Lanthanide Complexes	71
2.4	Summary and Outlook	83
	Acknowledgments	85
	References	85
3	Rare Earth Complexes with Carboxylic Acids, Polyaminopolycarboxylic Acids, and Amino Acids	91
	<i>Ruiyao Wang and Zhiping Zheng</i>	
3.1	Introduction	91
3.2	Rare Earth Complexes with Carboxylic Acids	92
3.2.1	Preparation of Rare Earth Complexes with Carboxylic Acids	92
3.2.2	Structural Chemistry of Rare Earth Complexes with Carboxylic Acids	94
3.2.3	Solution Chemistry of Rare Earth Complexes with Carboxylic Acids	114
3.3	Rare Earth Complexes with Polyaminopolycarboxylic Acids	115
3.3.1	Preparation of Rare Earth Complexes with Polyaminopolycarboxylic Acids	116
3.3.2	Structural Chemistry of Rare Earth Complexes with Polyaminopolycarboxylic Acids	116
3.3.3	Solution Chemistry of Rare Earth Complexes with Polyaminopolycarboxylic Acids	120
3.4	Rare Earth Complexes with Amino Acids	122
3.4.1	Preparation of Rare Earth Complexes with Amino Acids	122
3.4.2	Structural Chemistry of Rare Earth Complexes with Amino Acids	122
3.4.3	Solution Chemistry of Rare Earth Complexes with Amino Acids	127
3.5	Summary and Outlook	129
	References	130
4	N-Based Rare Earth Complexes	137
	<i>Xiaomei Zhang and Jianzhuang Jiang</i>	
4.1	Introduction	137
4.2	Rare Earth Complexes with Amide Type Ligands	137
4.2.1	Rare Earth Complexes with Aliphatic Amide Type Ligands	137
4.2.2	Rare Earth Complexes with Silyl Amide Type Ligands	142
4.3	Rare Earth Complexes with N-Heterocyclic Type Ligands	146
4.3.1	Rare Earth Complexes with Pyridine Type Ligands	146
4.3.2	Rare Earth Complexes with Imidazole Type Ligands	153
4.3.3	Rare Earth Complexes with Porphyrin Type Ligands	158
4.3.4	Rare Earth Complexes with Phthalocyanine Type Ligands	168

4.4	Rare Earth Complexes with Schiff Base Type Ligands	173
4.4.1	Rare Earth Complexes with Imine Type Ligands	174
4.4.2	Rare Earth Complexes with H_2Salen (30) Type Ligands	180
4.5	Outlook	185
	List of Abbreviations	185
	Acknowledgments	186
	References	186
5	Rare Earth Polyoxometalate Complexes	193
	<i>Ying Lu and Enbo Wang</i>	
5.1	Synthesis	193
5.2	Types and Structure Features	194
5.2.1	RE-POM Clusters	194
5.2.2	Extending Structural RE-POMs Complexes	208
5.2.3	RE–Organo Cation POM Supramolecule Complexes	217
5.3	Applications	218
5.3.1	Luminescence	218
5.3.2	Magnetism	221
5.3.3	Catalysis	221
5.3.4	Medicine	223
5.4	Outlook	223
	References	223
6	Coordination Chemistry of Rare Earth Alkoxides, Aryloxides, and Hydroxides	229
	<i>Zhiping Zheng and Ruiyao Wang</i>	
6.1	Introduction	229
6.2	Lanthanide Alkoxides, Aryloxides, and Macrocyclic Polyaryloxides	230
6.2.1	Preparative Methods	231
6.2.2	Structural Chemistry of Lanthanide Alkoxide Complexes	232
6.2.3	Applications of Lanthanide Alkoxides	246
6.3	Lanthanide Hydroxide Complexes	249
6.3.1	Rational Synthetic Methodologies for Lanthanide Hydroxide Complexes	250
6.3.2	Coordination Modes of Hydroxo Ligands and Key Lanthanide–Hydroxo Motifs	251
6.3.3	Properties and Possible Applications	263
6.4	Summary and Outlook	265
	Acknowledgments	265
	References	265
7	Rare Earth Metals Trapped Inside Fullerenes – Endohedral Metallofullerenes (EMFs)	273
	<i>Xing Lu, Takeshi Akasaka, and Shigeru Nagase</i>	
7.1	Introduction	273
7.1.1	History of Discovery	273

7.1.2	What Can Be Encapsulated Inside Fullerenes?	274
7.2	Preparation and Purification of EMFs	277
7.2.1	Production Methods	277
7.2.2	Extraction of EMFs from Raw Soot	279
7.2.3	Separation and Purification of EMFs	280
7.3	General Structures and Properties of EMFs Encapsulating Rare Earth Metals	282
7.3.1	Geometrical Structures	283
7.3.2	Electronic Structures of EMFs: Intramolecular Charge Transfer	284
7.4	Chemistry of EMFs	286
7.4.1	Chemical Reactions of EMFs: An Overview	286
7.4.2	Positional Control of Encapsulated Metals by Exohedral Modifications	292
7.4.3	Chemical Properties of Cage Carbons Dictated by the Encapsulated Metals	292
7.4.4	Chemical Behaviors of EMFs Bearing Fused Pentagons	293
7.5	Applications of EMFs and Their Derivatives	294
7.5.1	Applications in Biology and Medicine	295
7.5.2	Applications in Material Science	297
7.6	Perspectives: Challenge and Chance	299
	Acknowledgments	299
	References	300

8 Organometallic Chemistry of the Lanthanide Metals 309

Yingming Yao and Qi Shen

8.1	Introduction	309
8.2	Synthesis and Reactivity of Organolanthanide Complexes Containing Ln–C Bonds	310
8.2.1	Synthesis and Reactivity of Organolanthanide π -Complexes	310
8.2.2	Synthesis and Reactivity of Lanthanide Complexes Containing Ln–C σ -Bonds	314
8.2.3	Synthesis and Reactivity of Lanthanide N-Heterocyclic Carbene Complexes	320
8.2.4	Synthesis of Cationic Lanthanide Complexes	322
8.3	Synthesis and Reactivity of Lanthanide Hydride Complexes	325
8.3.1	Synthesis	325
8.3.2	Reactivity	328
8.4	Synthesis and Reactivity of Divalent Lanthanide Complexes	330
8.4.1	Synthesis of Classical Divalent Lanthanide Complexes	330
8.4.2	Synthesis of Non-classical Divalent Lanthanide Complexes	331
8.4.3	Reductive Reactivity	333
8.5	Organometallic Ce(IV) Complexes	334
8.6	Application in Homogeneous Catalysis	337
8.6.1	Organic Transformation	337
8.6.2	Polymerization	339

8.7	Summary and Outlook	345
	References	346
9	Lanthanide Based Magnetic Molecular Materials	355
	<i>Bingwu Wang, Shangda Jiang, Xiuteng Wang, and Song Gao</i>	
9.1	Introduction	355
9.2	Magnetic Coupling in Lanthanide Containing Molecular Materials	357
9.2.1	Magnetic Coupling Mechanism of Gd(III) Systems	357
9.2.2	Magnetic Coupling in Ln(III) Containing Systems with Orbital Moment Contribution	363
9.3	Magnetic Ordering in Lanthanide Based Molecular Materials	367
9.3.1	Lanthanide–Organic Radical Systems	367
9.3.2	4f–3d Heterometallic Systems	370
9.4	Magnetic Relaxation in Lanthanide Containing Molecular Materials	378
9.4.1	Introduction to Magnetic Relaxation	378
9.4.2	Magnetic Relaxation in Lanthanide Containing Complexes	381
9.5	Outlook	396
	Acknowledgments	397
	References	397
10	Gadolinium Complexes as MRI Contrast Agents for Diagnosis	407
	<i>Wingtak Wong and Kannie Waiyan Chan</i>	
10.1	Clinical Magnetic Resonance Imaging (MRI) Contrast Agents	407
10.1.1	Development of Clinical Contrast Agents	408
10.1.2	Clinical Contrast Agents	409
10.2	Chemistry of Gadolinium Based Contrast Agents	412
10.2.1	Relaxivity	412
10.2.2	Biomolecular Interactions	418
10.2.3	Toxicity and Safety Issues	420
10.3	Contrast Enhanced MRI for Disease Diagnosis	421
10.3.1	Magnetic Resonance Angiography (MRA)	422
10.3.2	Liver Disease	423
10.3.3	Oncology	424
10.4	Outlook	425
	References	426
11	Electroluminescence Based on Lanthanide Complexes	435
	<i>Zuqiang Bian and Chunhui Huang</i>	
11.1	Introduction	435
11.1.1	Operating Principles in OLEDs	436
11.1.2	History of OLEDs	438
11.1.3	Potential Advantages of Lanthanide Complexes Used in OLEDs	440
11.2	Lanthanide Complexes Used in OLEDs	441
11.2.1	Europium Complexes	442

11.2.2	Terbium Complexes	455
11.2.3	Other Lanthanide Complexes	464
11.3	Outlook	468
	Acknowledgments	468
	References	468
12	Near-Infrared (NIR) Luminescence from Lanthanide(III) Complexes	473
	<i>Zhongning Chen and Haibing Xu</i>	
12.1	Introduction	473
12.2	Organic Antenna Chromophores as Sensitizers	475
12.2.1	Acyclic Ligands as Antenna Chromophores	476
12.2.2	Macrocyclic Ligands as Antenna Chromophores	492
12.3	Metal–Organic Chromophores as Sensitizers	500
12.3.1	d-Block Chromophores	500
12.3.2	f-Block Chromophores	516
12.4	Outlook	517
	List of Abbreviations	518
	Acknowledgments	519
	References	519
13	Luminescent Rare Earth Complexes as Chemosensors and Bioimaging Probes	529
	<i>Fuyou Li, Hong Yang, and He Hu</i>	
13.1	Introduction	529
13.2	Rare Earth Complexes as Luminescent Chemosensors	531
13.2.1	Basic Concept	531
13.2.2	Rare Earth Complexes as Luminescent pH Chemosensors	532
13.2.3	Rare Earth Complexes as Luminescent Chemosensors for Cations	534
13.2.4	Rare Earth Complexes as Luminescent Chemosensors for Anions	537
13.2.5	Rare Earth Complexes as Luminescent Chemosensors for Small Molecules	540
13.3	Bioimaging Based on Luminescent Rare Earth Complexes	542
13.3.1	Time-Resolved Luminescence Imaging	542
13.3.2	Types of Luminescent Rare Earth Complexes for Bioimaging	543
13.3.3	Luminescent Rare Earth Complexes with “Privileged” Cyclen Core Structures as Bioimaging Probes	544
13.3.4	Luminescent Rare Earth Complexes with Bis(benzimidazole) pyridine Tridentate Units as Bioimaging Probes	549
13.3.5	Hybrid Rare Earth Complexes as Luminescent Probes in Bioimaging	552
13.4	Rare Earth Luminescent Chemosensors as Bioimaging Probes	552
13.4.1	Rare Earth Luminescent Chemosensors as Bioimaging Probes of Zn ²⁺	553

13.4.2	Rare Earth Luminescent Chemosensors as Bioimaging Probes of $^1\text{O}_2$	554
13.5	Rare Earth Complexes as Multiphoton Luminescence Probes for Bioimaging	556
13.6	Rare Earth Materials with Upconversion Luminescence for Bioimaging	558
13.6.1	General Concept of Upconversion Luminescence	558
13.6.2	Rare Earth Complexes with Upconversion Luminescence	558
13.6.3	Rare Earth Nanophosphors with Upconversion Luminescence	560
13.6.4	Rare Earth Upconversion Luminescence Nanophosphors as Bioimaging Nanoprobes	562
13.7	Outlook	565
	References	565
	Index	571

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Foreword

The rare earth adventure started in 1787 when Swedish artillery lieutenant Carl Axel Arrhenius discovered a heavy, black mineral in a feldspath quarry in the vicinity of Ytterby, located on a small island commanding the entrance to the harbor of Stockholm (Sweden). After suitable analysis, Professor Johan Gadolin, from the University of Åbo (today Turku), established that the black mineral contained a new element, which he named yttrium. His 1794 report in the *Proceedings of the Swedish Academy of Sciences* therefore represents the first paper on the rare earths. According to IUPAC nomenclature, the term “rare earths” includes Y, Sc, and La–Lu, with lanthanides being used for Ce–Lu and lanthanoids for La–Lu. However, the latter term is rarely used, and lanthanides is commonly used to refer to La–Lu. For a long time, rare earths remained laboratory curiosities, although Carl Auer von Welsbach initiated some applications in lighting, as he took patents out for the famous Auer mantle for gas lamps (1891) and for flint stones (1903), and founded two companies that are still active today. Another milestone is the discovery of the bright red emitting phosphor $\text{Y}_2\text{O}_3\text{:Eu}$ at the beginning of the twentieth century by Georges Urbain in Paris. However, rare earth chemistry really took off in the 1960s when efficient separation methods began to be available.

Rare earth coordination chemistry has also been slow to develop. For a long time most inorganic chemists were thinking that rare earths had a coordination number of six, by analogy with many 3d-transition elements. However, a crystal structure of neodymium bromate, published in 1939, revealed a coordination number of nine. Subsequent structural analyses performed in the 1960s on polyaminocarboxylates confirmed large coordination numbers, up to ten, which stirred interest in this intriguing field. This interest was further stimulated by several other important landmarks. The first one was the discovery by S. I. Weissman, in 1942, that metal-centered luminescence in β -diketonate, phenolate or salicylate complexes can be triggered by ligand absorption and subsequent energy transfer. Furthermore, lanthanide complexes of Pr, Eu, and Yb were found to be helpful in the elucidation of NMR spectra (the so-called shift reagents). Hence, in the 1980s when biomedical applications of lanthanide complexes in magnetic resonance imaging (Gd-based contrast agents) and time-resolved luminescence immunoassays were developed in Turku, rare earth coordination chemistry definitely took up a position as a major area of research.

Curiously enough, while numerous review articles, periodically renewed, cover one or another aspect of rare earth coordination chemistry, books with a wide coverage of the field are rather scarce. The present volume therefore meets a long-awaited expectation by presenting the basic and applied aspects of rare earth coordination chemistry. The introductory chapter sets the tone by describing the fundamentals of the field and reviewing inorganic complexes. Other chapters are devoted to the major classes of rare earth complexes, both classical, such as β -diketonates, polyaminocarboxylates, chelates with nitrogen-containing ligands, or polyoxometallates, as well as the more unusual, such as cluster compounds and lanthanidofullerenes.

Organometallics is another burgeoning aspect of rare earth chemistry, particularly now that the divalent state of all lanthanides can be mastered; the corresponding discussion gives a broad overview of all aspects of organolanthanides, including applications in homogeneous catalysis. Two chapters are devoted to the important luminescent properties of lanthanides with emphasis on electroluminescence and near-infrared emitting compounds. Applications are dealt with in chapters describing magnetic properties, contrast agents for magnetic resonance imaging and luminescent sensors for immunoassays and bio-imaging.

Altogether, graduate students and researchers should highly benefit from the reading of this book, which not only presents factual knowledge but, also, points to the amazing opportunities offered by lanthanides that stretch like a virgin land before us, to be discovered and exploited for the benefit of the whole of humanity.

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Preface

Lanthanide elements have atomic numbers ranging from 57 to 71. With the inclusion of scandium (Sc) and yttrium (Y), a total of 17 elements are referred to as the rare earth elements. A mixture of rare earths was discovered in 1794 by J. Gadolin and ytterbium was separated from this mixture in 1878 by Marignac, while the last rare earth element promethium (Pm) was separated by a nuclear reaction in 1974. Therefore, a period of more than 100 years separates the discovery of all the rare earth elements. In the latter part of the last century scientists started to focus on the applications of rare earth elements. Numerous interesting and important properties were found with respect to their magnetic, optical, and electronic behavior. This is the reason that many countries list all rare earth elements, except promethium (Pm), as strategic materials. Rare earth coordination chemistry, therefore, developed quickly as a result of this increased activity.

As a record of these scientific events, topical books have been published, among which the “*Handbook on the Physics and Chemistry of Rare Earths*” edited by K. A. Gschneidner and L. Eyring is most important. Volume 1 was published in 1978 and volume 37 in 2007, and consecutive volumes of this book will continue to be published. Besides this, “*Lanthanide and Actinide Chemistry*” written by S. Cotton in 2006 and “*Rare Earths*” edited by G. X. Xu in 1995 (second edition, in Chinese) have also been published. These are comprehensive books on this topic.

A book specializing in rare earth coordination chemistry and entitled “*Coordination Chemistry of Rare Earths*” was written in 1997 (in Chinese, Science Press), by myself. As a result of rapid developments in the coordination chemistry of rare earths, I was pleased to invite my colleagues, who are leading scientists in this field, to contribute to the present book and thus extend the contents of the former book from fundamental science to applications.

Chapters 1–8 cover fundamental work and basically constitute the characterization of ligands, namely: β -diketone ligands, carboxylic acids, poly-amino poly-carboxylic acids, amino acid ligands, alkoxide, aryloxides and hydroxide ligands, macrocyclic ligands, organometallic compounds, N-based complexes and polyoxometalate complexes. Chapters 9–13 cover applications and are either commercially viable applications, such as magnetic resonance imaging contrast agents, or promising practical applications, such as magnetic molecular materials, photoluminescent and electroluminescent materials, and materials for biological application. We believe this book will give people who are working or will work in either the fundamental or applied sectors of this field an insight into the coordination chemistry of the rare earths.

Finally, I wish to express my sincere thanks to all the contributors for their cooperation. Their contributions are so important that I will remember them forever. I also wish to express my sincere thanks to all the people who gave valuable help in different ways during the process of gathering materials, writing and publishing this book.

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1

Introduction

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Lanthanide elements (referred to as Ln) have atomic numbers that range from 57 to 71. They are lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). With the inclusion of scandium (Sc) and yttrium (Y), which are in the same subgroup, this total of 17 elements are referred to as the rare earth elements (RE). They are similar in some aspects but very different in many others. Based on the electronic configuration of the rare earth elements, in this chapter we will discuss the lanthanide contraction phenomenon and the consequential effects on the chemical and physical properties of these elements. The coordination chemistry of lanthanide complexes containing small inorganic ligands is also briefly introduced here [1–5].

1.1 Electronic Configuration of Lanthanide Atoms in the Ground State

The electronic configuration of an atom in the ground state is determined by its principal quantum number n and angular quantum number l . According to the principle of lowest energy, there are two types of electronic configurations for the lanthanide elements: $[\text{Xe}]4f^n6s^2$ and $[\text{Xe}]4f^{n-1}5d^16s^2$. Here $[\text{Xe}]$ represents the electronic configuration of xenon, which is $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^6$, where n represents a number from 1 to 14. Lanthanum, cerium, and gadolinium belong to the $[\text{Xe}]4f^n6s^2$ type, while praseodymium, neodymium, promethium, samarium, europium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium belong to the $[\text{Xe}]4f^{n-1}5d^16s^2$ type. Scandium and yttrium do not have 4f electrons but they do have similar chemical properties to lanthanide elements, because their outermost electrons have the $(n-1)d^1ns^2$ configuration. For this reason, they are generally regarded as being lanthanide elements.

Lanthanide elements adopt either the $[\text{Xe}]4f^n6s^2$ or $[\text{Xe}]4f^{n-1}5d^16s^2$ configuration depending on the relative energy level of these two electronic configurations. Figure 1.1 shows the

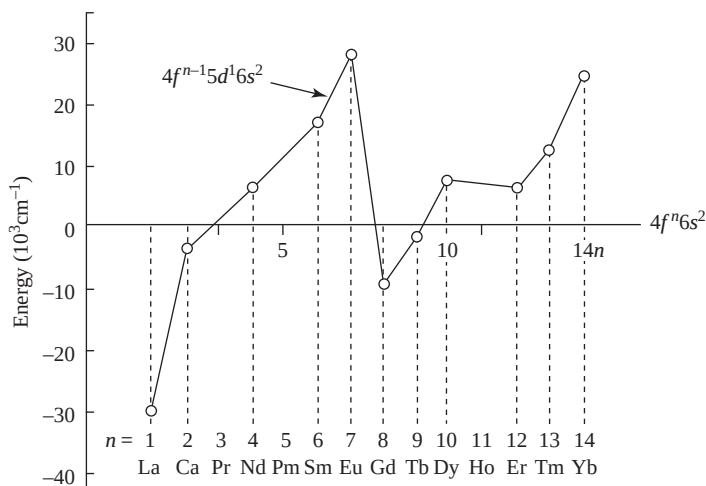


Figure 1.1 The relative energy level of the different electronic configurations, $4f^n 6s^2$ or $4f^{n-1} 5d^1 6s^2$ of neutral lanthanide atoms [5].

relative energy level of the neutral lanthanide atoms in the $4f^n 6s^2$ or $4f^{n-1} 5d^1 6s^2$ electronic configurations. For lanthanum, cerium, and gadolinium, the $[\text{Xe}]4f^{n-1} 5d^1 6s^2$ configuration is lower in energy than the $[\text{Xe}]4f^n 6s^2$ configuration, therefore, they adopt the former configuration. For terbium, the two configurations $[\text{Xe}]4f^9 6s^2$ and $[\text{Xe}]4f^8 5d^1 6s^2$ are energetically close to each other so terbium can adopt either one. Lutetium has 14 4f electrons and therefore its only possible configuration is $[\text{Xe}]4f^{14} 5d^1 6s^2$. The other elements all have a $[\text{Xe}]4f^n 6s^2$ configuration. All the electronic configurations of lanthanide elements are summarized in Table 1.1.

1.2 Lanthanide Contraction

For multi-electron atoms a decrease in atomic radius, brought about by an increase in nuclear charge, is partially offset by increasing electrostatic repulsion among the electrons. The shielding effect originates from the inner electrons and decreases according to: $s > p > d > f$. For lanthanide elements, as the atomic number increases an electron is not added to the outermost shell but rather to the inner 4f shell (Table 1.1). Because of their diffusive property, 4f electrons do not all distribute within the inner part of the 5s5p shell and this can be clearly seen in Figures 1.2 and 1.3. Figure 1.2 shows the radial distribution functions of 4f, 5s, 5p, 5d, 6s, and 6p electrons for cerium and Figure 1.3 illustrates the radial distribution functions of 4f, 5s, 5p electrons for Pr^{3+} . An increase in 4f electrons only partly shields the increase in nuclear charge. It is generally believed that the screening constant of 4f electrons in trivalent lanthanide ions is about 0.85. The 4f electron clouds in neutral atoms are not as diffusive as in trivalent lanthanide ions and the screening constant of 4f electrons is larger but still less than one. Therefore, as the atomic number increases the effective attraction between the nucleus and the outer electrons increases. This increased attraction causes shrinkage in the atomic or ionic radius. This phenomenon is referred to as “lanthanide contraction.”

Table 1.1 The electronic configurations of lanthanide elements.

Z	Element		Electronic configurations of neutral atoms					Electronic configurations of trivalent ions	Atomic radius (pm) (coordination number = 12)	Atomic weight
			4f	5s	5p	5d	6s			
57	La	The inner orbitals have been full-filled, 46 electrons in all	0	2	6	1	2	[Xe]4f ⁰	187.91	138.91
58	Ce		1	2	6	1	2	[Xe]4f ¹	182.47	140.12
59	Pr		3	2	6		2	[Xe]4f ²	182.80	140.91
60	Nd		4	2	6		2	[Xe]4f ³	182.14	144.24
61	Pm		5	2	6		2	[Xe]4f ⁴	(181.0)	(147)
62	Sm		6	2	6		2	[Xe]4f ⁵	180.41	150.36
63	Eu		7	2	6		2	[Xe]4f ⁶	204.20	151.96
64	Gd		7	2	6	1	2	[Xe]4f ⁷	180.13	157.25
65	Tb		9	2	6		2	[Xe]4f ⁸	178.33	158.93
66	Dy		10	2	6		2	[Xe]4f ⁹	177.40	162.50
67	Ho		11	2	6		2	[Xe]4f ¹⁰	176.61	164.93
68	Er		12	2	6		2	[Xe]4f ¹¹	175.66	167.26
69	Tm		13	2	6		2	[Xe]4f ¹²	174.62	168.93
70	Yb		14	2	6		2	[Xe]4f ¹³	193.92	173.04
71	Lu		14	2	6	1	2	[Xe]4f ¹⁴	173.49	174.97
			3d	4s	4p	4d	5s			
21	Sc	Inner 18 electrons	1	2				[Ar]	164.06	44.956
39	Y		10	2	6	1	2	[Kr]	180.12	88.906

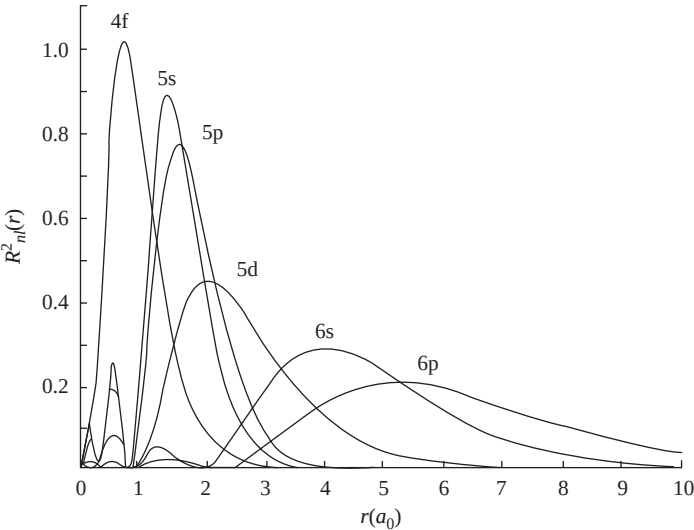


Figure 1.2 Radial distribution functions of 4f, 5s, 5p, 5d, 6s, and 6p electrons for cerium [2]. (Courtesy of Z.B. Goldschmidt, “Atomic properties (free atom),” in K.A. Gschneidner and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume I, 2nd edition, North Holland Publishing Company, Amsterdam. © 1978.)

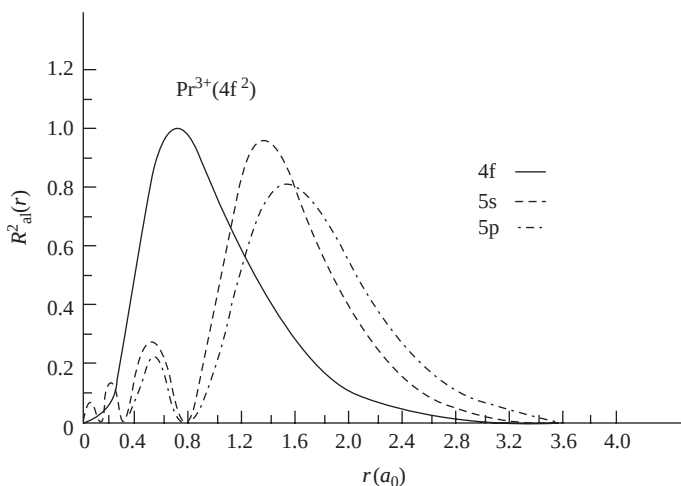


Figure 1.3 Radial distribution functions of 4f, 5s, 5p electrons for Pr^{3+} [6]. (With kind permission from Springer Science + Business Media: *Organometallics of the f Element*, © 1979, p. 38, T.J. Marks, and R.D. Fisher, figure 1, D. Reidel Publishing Company, Dordrecht.)

One effect of lanthanide contraction is that the radius of trivalent yttrium ion (Y^{3+}) is measured to be between that of Ho^{3+} and Er^{3+} , and the atomic radius of yttrium is between neodymium and samarium. This results in the chemical properties of yttrium being very similar to those of lanthanide elements. Yttrium is often found with lanthanide elements in natural minerals. The chemical properties of yttrium may be similar to the lighter or the heavier lanthanide elements in different systems and this depends on the level of covalent character of the chemical bonds in those systems.

Another effect of lanthanide contraction is that the third row of the d-block elements have only marginally larger atomic radii than the second transition series. For example, zirconium and hafnium, niobium and tantalum, or tungsten and molybdenum have similar ionic radii and chemical properties (Zr^{4+} 80 pm, Hf^{4+} 81 pm; Nb^{5+} 70 pm, Ta^{5+} 73 pm; Mo^{6+} 62 pm, W^{6+} 65 pm). These elements are also found in the same natural minerals and are difficult to separate.

Because of lanthanide contraction, the radius of lanthanide ions decreases gradually as the atomic number increases, resulting in regular changes in the properties of lanthanide elements as the atomic number increases. For example, the stability constant of lanthanide complexes usually increases as the atomic number increases; the alkalinity of lanthanide ions decreases as the atomic number increases; the pH at which hydrates start to precipitate from an aqueous solution decreases gradually as the atomic number increases.

Because of lanthanide contraction, the radius of lanthanide atoms also changes regularly. Because the shielding effect of 4f electrons in lanthanide atoms is not so strong as those in lanthanide ions, lanthanide contraction is weaker in lanthanide atoms than in ions. The atomic radius of a hexagonal crystal metal is defined as the average distance between adjacent atoms in a close-packed plane and in an adjacent close-packed plane (Table 1.1). The relationship between ionic radius and atomic number is shown in Figure 1.4. The atomic radius also exhibits lanthanide contraction, except for cerium, europium, and ytterbium. However, the contraction of lanthanide atoms is not so prominent as that of lanthanide ions (Figure 1.5).

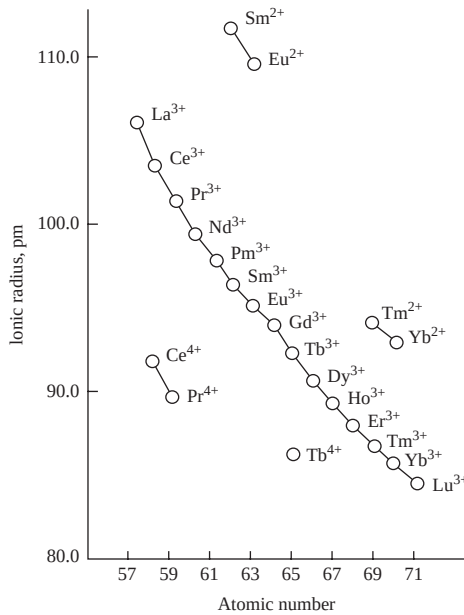


Figure 1.4 The relationship between ionic radius and atomic number of lanthanide ions [1, 5].

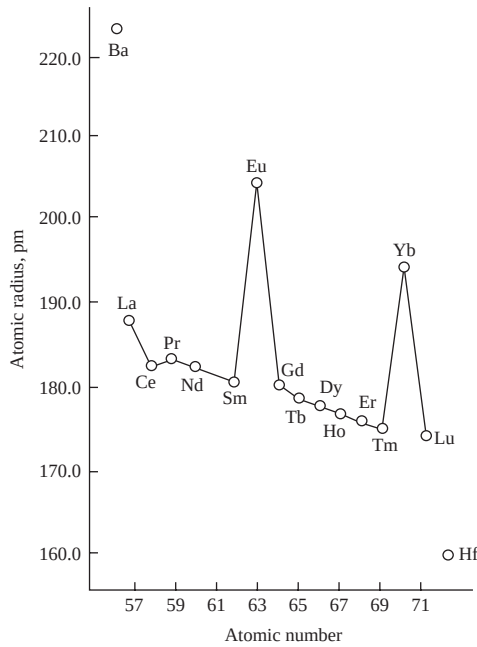


Figure 1.5 The relationship between atomic radius and atomic number of lanthanide atoms [1, 5].

The abnormal behavior for the atomic radii of cerium, europium, and ytterbium can be explained as follows. The atomic radius of a metal approximately equals the radius of the maxima of the outermost electron cloud density. Therefore, the outermost electron clouds overlap in metals. These electrons can move freely in the crystal lattice and become conducting electrons. Generally speaking, there are three conducting electrons in lanthanide metals. Europium and ytterbium tend to maintain a $4f^7$ and $4f^{14}$ electron configuration, respectively, and thus they provide only two conducting electrons. The overlapping part of the outermost electrons between adjacent atoms becomes smaller and the atomic radius becomes larger. On the contrary, a cerium atom has only one $4f$ electron and it tends to provide four conducting electrons to obtain a stable electronic configuration. The overlapping part of the outermost electrons becomes larger, which causes the distance between adjacent atoms to become smaller compared with other lanthanide elements.

1.3 Specificity of the Photophysical Properties of Rare Earth Compounds

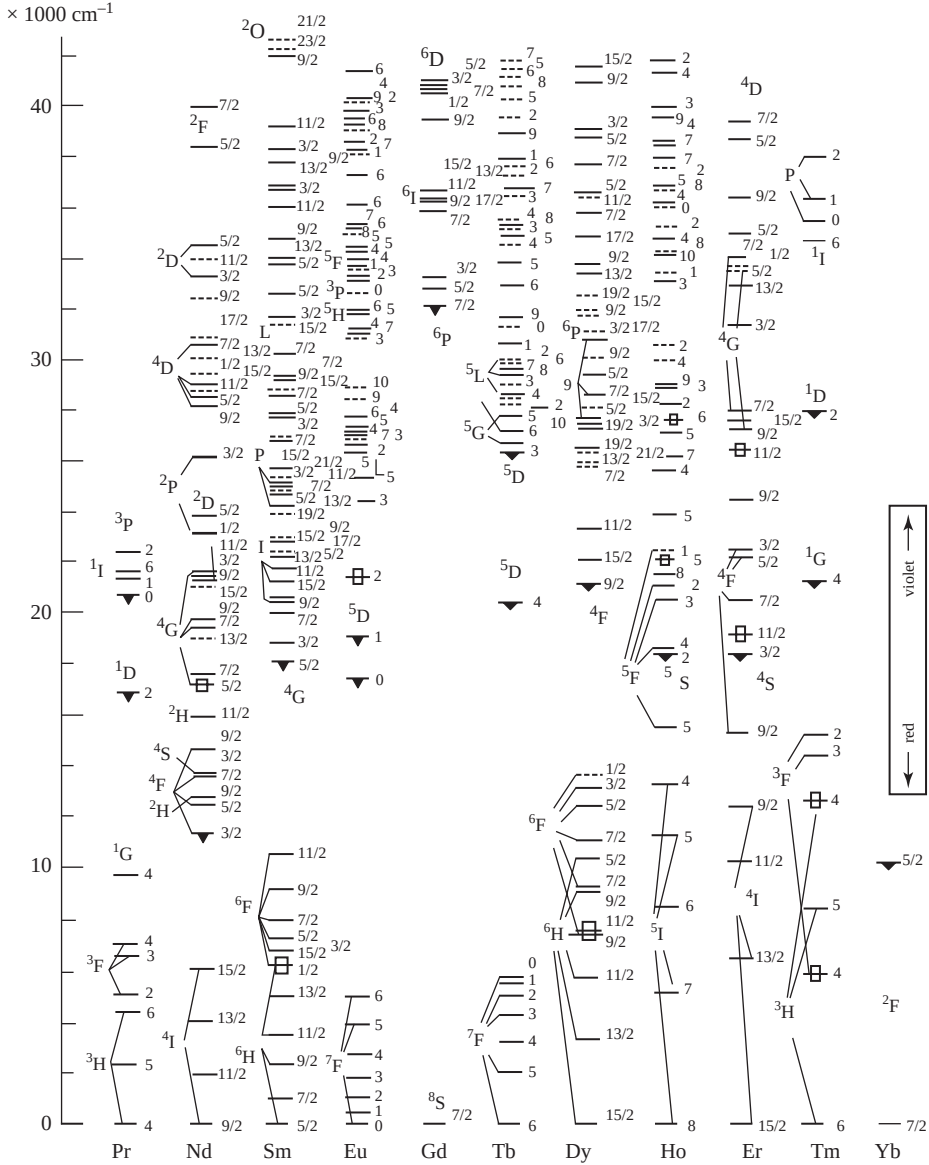
Because the $4f$ shells of lanthanide elements are unfilled, different arrangements of $4f$ electrons generate different energy levels. The $4f$ electron transitions, between the various energy levels, could generate numerous absorption and emission spectra.

Electronic configurations and spectral terms of ground state trivalent lanthanide ions are listed in Table 1.2. Figure 1.6 shows the energy level diagram for trivalent lanthanide ions.

Table 1.2 Electronic configurations and spectral terms of trivalent lanthanide ions in the ground state [5].

Ion	4f ^a	Magnetic quantum number of 4f orbital							L	S	J	Ground state spectral term	Δ (cm ⁻¹)	ζ _{4f} (cm ⁻¹)
		3	2	1	0	-1	-2	-3						
J = L - S														
La ³⁺	0								0	0	0	¹ S ₀		
Ce ³⁺	1	↑							3	1/2	5/2	² F _{5/2}	2200	640
Pr ³⁺	2	↑	↑						5	1	4	³ H ₄	2150	750
Nd ³⁺	3	↑	↑	↑					6	3/2	9/2	⁴ I _{9/2}	1900	900
Pm ³⁺	4	↑	↑	↑	↑				6	2	4	⁵ I ₄	1600	1070
Sm ³⁺	5	↑	↑	↑	↑	↑			5	5/2	5/2	⁶ H _{5/2}	1000	1200
Eu ³⁺	6	↑	↑	↑	↑	↑	↑		3	3	0	⁷ F ₀	350	1320
J = L + S														
Gd ³⁺	7	↑	↑	↑	↑	↑	↑	↑	0	7/2	7/2	⁸ S _{7/2}		1620
Tb ³⁺	8	↑↓	↑	↑	↑	↑	↑	↑	3	3	6	⁷ F ₆	2000	1700
Dy ³⁺	9	↑↓	↑↓	↑	↑	↑	↑	↑	5	5/2	15/2	⁶ H _{15/2}	3300	1900
Ho ³⁺	10	↑↓	↑↓	↑↓	↑	↑	↑	↑	6	2	8	⁵ I ₈	5200	2160
Er ³⁺	11	↑↓	↑↓	↑↓	↑↓	↑	↑	↑	6	3/2	15/2	⁴ I _{15/2}	6500	2440
Tm ³⁺	12	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	5	1	6	³ H ₆	8300	2640
Yb ³⁺	13	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	3	1/2	7/2	² F _{7/2}	10 300	2880
Lu ³⁺	14	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	0	0	0	¹ S ₀		

^aThe number of $4f$ electrons



number s , which takes the value of $1/2$; also, m_s is the spin magnetic quantum number. In addition, the electron in an atom has its spin movement, while also moving around the orbital. To describe this state, the overall angular quantum number, j was introduced. This is the vector sum momentum of l and s , that is, $j = l + s, l + s - 1, \dots, |l - s|$. m_j is the angular magnetic quantum number j along the magnetic field.

In a multi-electronic atom, the following quantum numbers can also be used to describe the energy levels, and the relationships between the quantum number of electrons are as follows.

1. Total spin quantum number $S = \Sigma m_s$.
2. Total orbital quantum number $L = \Sigma m_l$.
3. Total magnetic orbital quantum number M_L .
4. Total angular momentum quantum number J , which takes $L + S, L + S - 1, \dots, L - S$ when $L \geq S$, and can take $S + L, S + L - 1, \dots, S - L$ when $L \leq S$. M_J is the total magnetic angular quantum number J along the magnetic field.

The spectral term is a symbol which combines the azimuthal quantum number l and magnetic quantum number m to describe the energy level relationship between electronic configurations.

Seven orbitals are present in the 4f shell ($l = 3$). Their magnetic quantum numbers are $-3, -2, -1, 0, 1, 2$, and 3 , respectively. When lanthanide elements are in their ground states, the distribution of the 4f electrons in the orbitals are as shown in Table 1.2. Here, Δ represents the energy difference between the ground state and the J multiple state that lies right above the ground state; ζ_{4f} is the spin-orbital coupling coefficient.

In this table, M_L is the total magnetic quantum number of the ion. Its maximum is the total orbital angular quantum number L . M_s is the total spin quantum number along the magnetic field direction. Its maximum is the total spin quantum number S . $J = L \pm S$, is the total angular momentum quantum number of the ion and is the sum of the orbital and spin momentum. For the first seven ions (from La^{3+} to Eu^{3+}), $J = L - S$; for the last eight ions (from Gd^{3+} to Lu^{3+}), $J = L + S$. The spectral term consists of three quantum numbers, L , S , and J and may be expressed as $^{2S+1}L_J$. The value of L is indicated by S, P, D, F, G, H, and I for $L = 0, 1, 2, 3, 4, 5$, and 6 , respectively. The number on the top left represents the multiplicity of the spectral term. It equals $2S + 1$. The number on the bottom right is the total angular momentum quantum number J . Take Nd^{3+} as an example, $L = 6$ and its corresponding capital letter is I; $S = 3/2$ (three uncoupled electrons) so $2S + 1 = 4$; $J = L - S = 6 - 3/2 = 9/2$. Therefore, the spectral term for the ground state of Nd^{3+} is $^4\text{I}_{9/2}$.

1.3.2 Selection Rules for Atomic Spectra

The 4f electrons of lanthanide elements can be placed in any 4f orbital except for La^{3+} (empty) and Lu^{3+} (full) and this results in various spectral terms and energy levels for lanthanide elements. For example, praseodymium has 41 energy levels at the $4f^3, 6s^2$ configuration, 500 energy levels at the $4f^3, 6s^1, 6p^1$ configuration, 100 energy levels at the $4f^2, 5d^1, 6s^2$ configuration, 750 energy levels at the $4f^3, 5d^1, 6s^1$ configuration, and 1700 energy levels at the $4f^3, 5d^2$ configuration. Gadolinium has 3106 energy levels at the $4f^7, 5d^1, 6s^2$ configuration while its excited state $4f^7, 5d^1, 6s^1, 6p^1$ has as many as 36 000 energy levels. However, because of selection rule constraints many transitions between different energy levels are forbidden

transitions and the number of visible spectral lines is far less than expected. Experimental data, which has subsequently been proved by quantum mechanical theory, shows that only transitions that satisfy the following rules are allowed:

1. For $L - S$ coupling (so-called Russell–Saunders coupling), which is to combine the s of every electron to get S , and combine the l of every electron to obtain L initially and finally to combine S and L to get J :
 - $\Delta S = 0$
 - $\Delta L = \pm 1$
 - $\Delta J = 0, \pm 1$, (except $0 \rightarrow 0$)
 - $\Delta M_j = 0, \pm 1$ (for $\Delta J = 0$, except $0 \rightarrow 0$)
2. For $j-j$ coupling, which is firstly to combine s and l for every electron to obtain j , and then get the total angular quantum number J through $j-j$ coupling:
 - $\Delta j = 0, \pm 1$ (for the transition electron only), $\Delta j = 0$ (for the rest of the electrons)
 - $\Delta J = 0, \pm 1$, (except $0 \rightarrow 0$)
 - $\Delta M_j = 0, \pm 1$, (for $\Delta J = 0$, except $0 \rightarrow 0$)

In general, lanthanide atoms or ions with an unfilled 4f shell have about 30 000 visible spectral lines. Transition metals with an unfilled 5d shell have about 7000 visible spectral lines. Main group elements with an unfilled p shell only have about 1000 visible spectral lines. Lanthanide elements, therefore, have more electronic energy levels and spectral lines than the more common elements. They can absorb electromagnetic waves from the ultraviolet to the infrared and emit their characteristic spectra.

1.3.3 Lifetime

The lifetime (τ) of an excited state is an important term when the kinetic process is of concern. The lifetime of an excited molecule is not a time measuring the existence of the excited state but is rather the deactivation time needed for excited states to reduce to 1/e of its initial population. It is defined as follows:

$$\tau = 1/\Sigma k_f \quad (1.1)$$

where k_f is the rate constant of deactivation and Σk_f is the sum of all the rate constants of the deactivation processes, including radiative and non-radiative processes in the system.

Another characteristic of lanthanide elements is that some excited states have very long lifetimes ($10^{-2} \sim 10^{-6}$ s) while the average lifetimes of other typical atoms or ions range from 10^{-8} to 10^{-10} s. These long lifetime excited states are referred to as metastable states. These metastable states of lanthanide elements are caused by $4f \rightarrow 4f$ electronic transitions. According to the selection rules, these $\Delta l = 0$ electric dipole transitions are forbidden but are in fact observed. There are two major reasons for the forbidden transitions occurring: mixing between 4f configurations of opposite parity and the deviation of symmetry from an inversion center. Because lanthanide elements have many $4f \rightarrow 4f$ transitions between metastable states, the excited states of lanthanide elements have long lifetimes. This enables some lanthanide materials to be used in laser and fluorescence materials.

1.3.4 Absorption Spectra

In lanthanide elements, the $5s^2$ and $5p^6$ shells are on the outside of the $4f$ shell. The $5s^2$ and $5p^6$ electrons are shielded, any force field (the crystal field or coordinating field in crystals or complexes) of the surrounding elements in complexes have little effect on the electrons in the $4f$ shell of the lanthanide elements. Therefore, the absorption spectra of lanthanide compounds are line-like spectra similar to those of free ions. This is different from the absorption spectra of d-block compounds. In d-block compounds, spectra originate from $3d \rightarrow 3d$ transitions. The nd shell is on the outside of the atoms so no shielding effect exists. Therefore, the $3d$ electrons are easily affected by crystal or coordinating fields. As a result, d-block elements show different absorption spectra in different compounds. Because of a shift in the spectrum line in the d-block, absorption spectra change from line spectra in free ions to band spectra in compounds.

Most trivalent rare earth ions have no or very weak absorption in the visible range [8]. For example, Y^{3+} , La^{3+} , Gd^{3+} , Yb^{3+} , and Lu^{3+} in inorganic acid aqueous solutions are colorless. It is worth noting that colors of the aqueous solutions for ions having the $4f^n$ electronic configuration are usually similar to those that have the $4f^{14-n}$ configuration (Figure 1.7).

Another characteristic of rare earth ions (except for Ce^{3+} and Yb^{3+}) in absorption spectra are their linear-like behavior. This comes from f–f transitions where $4f$ electrons exchange between different $4f$ energy levels. However, no f–f transition is allowed for $Ce^{3+}(4f^1)$ or $Yb^{3+}(4f^{13})$. The broad absorption bands observed originates from configuration transitions, for example $4f^n$ to $4f^{n-1}5d^1$.

f–f transitions of lanthanide ions can be divided into magnetic dipole transitions and electric dipole transitions. In some cases an electric multi-dipole transition is also observed. According to the classic transition selection rule, a transition is forbidden when $\Delta L = 0$, that is, the f–f electric dipole transition is forbidden. However, it has been observed experimentally and this is because an odd parity term or an anti-parity electron is introduced into the $4f^n$ configuration to some extent.

The absorption spectra of rare earth complexes are mainly determined by the coordinated organic ligands.

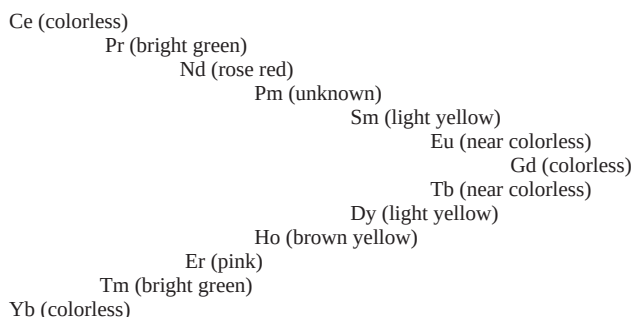


Figure 1.7 Similarity in color between ions with the electron configurations $4f^n$ and $4f^{14-n}$.

1.3.5 The Emission Spectra of Rare Earth Compounds

In the 1940s, emissions from rare earth complexes were observed and research into this phenomenon has received growing and lasting attention because of their potential application in optical communications, new generation displays, and sensors.

Since the dipole strength of f - f transitions are formally forbidden, typically, these extinction coefficients are of the order of $1 \text{ M}^{-1} \text{ cm}^{-1}$, an alternative path has to be used which is called luminescence sensitization or antenna effect, that is when the luminescent ion is coordinated with an organic ligand or imbedded into a matrix, then the energy absorbed will be transferred from the surrounding onto the luminescent ion and subsequently the ion emits characteristic light.

To quantitatively describe the effect of the emission, quantum yield Q is introduced, which has the following definition:

$$Q = \frac{\text{number of emitted photons}}{\text{number of absorbed photons}} \quad (1.2)$$

According to the emission properties, rare earth complexes can be divided into four groups as follows:

1. $\text{Sm}^{3+}(4f^5)$, $\text{Eu}^{3+}(4f^6)$, $\text{Tb}^{3+}(4f^8)$ and $\text{Dy}^{3+}(4f^9)$;
2. $\text{Pr}^{3+}(4f^2)$, $\text{Nd}^{3+}(4f^3)$, $\text{Ho}^{3+}(4f^{10})$, $\text{Er}^{3+}(4f^{11})$, $\text{Tm}^{3+}(4f^{12})$ and $\text{Yb}^{3+}(4f^{13})$;
3. $\text{Sm}^{2+}(4f^6)$, $\text{Eu}^{2+}(4f^7)$, $\text{Yb}^{2+}(4f^{14})$ and $\text{Ce}^{3+}(4f^1)$;
4. $\text{Sc}^{3+}(4f^0)$, $\text{Y}^{3+}(4f^0)$, $\text{La}^{3+}(4f^0)$, $\text{Gd}^{3+}(4f^7)$ and $\text{Lu}^{3+}(4f^{14})$.

For the first group, emissions originate because of the transition of $4f$ electrons from the lowest excited states to the ground states and the emissions are in the visible region. The probabilities of these transitions are relatively high and strong emissions may be observed. The lifetimes of these emissions are in the microsecond or milliseconds scale. For the second group, the energy levels of these ions are very close to one another. Thus, the emissions are often in the infrared region and their intensities are weaker than those of the first group by several orders of magnitude. All the ions in the third group exist in lower oxidation states and their emissions originate from d - f transitions and not f - f transitions, which would show broader emission bands. Obviously, the ions in the last group all have so-called stable electronic configurations, that is, their $4f$ orbitals are either “empty,” “half-filled” or “all-filled.” Therefore, no f - f transitions occur except in gadolinium complexes, which emit in the ultraviolet region. However, these complexes do sometimes emit when suitable ligands are coordinated to the central ions. In these cases, the emissions are caused by ligand emission complexes.

In 1990, Buono-core suggested a simplified diagram to show the three different mechanisms for intra-molecular energy transition in lanthanide complexes (Figure 1.8).

In Figure 1.8a, the ligands of the complex are excited from their ground state (S_0) to their excited singlet state (S_1) by the absorption of light energy. Energy is then transferred to the excited triplet state (T_1) through intersystem crossing. The energy could then transfer to the rare earth ion if the energy levels match each other and the electrons of the central ions can thus become excited. When the electrons return from the excited state to the ground state the complex emits with the characteristic wavelength of the central ion. In the case of Figure 1.8b, the ligands of the complex are excited from S_0 to S_1 and from there the energy absorbed could be transferred to the central ion directly but not through the T_1 state. In the case of Figure 1.8c, the ligands of the complex are excited from S_0 to S_1 and then the energy

absorbed can be transferred back and forth between S_1 and T_1 and then to the excited states, multiply, and finally transfer to the rare earth ion to excite it and then they return to the ground state. The complexes can then emit their characteristic emissions. Therefore, the theoretical emission yield is 100%.

It has been very difficult to unambiguously prove which state is responsible for the energy transfer processes because of the lack of information regarding the emission from the excited states of the coordinated ligand and the difficulties in determining ligand-localized triplet-triplet absorption spectra of lanthanide complexes. All the experimental work conducted seemed to support case (a) in Figure 1.8.

In 2004, Zhang and coworkers reported the first experimentally observed example of case (b) in Figure 1.8 by means of time-resolved luminescence spectroscopy with the system shown in Figure 1.9.

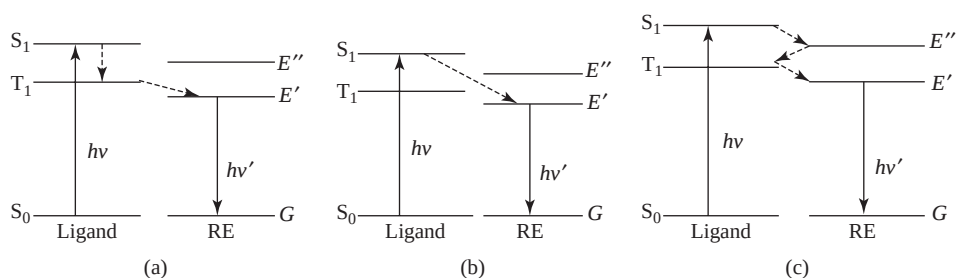


Figure 1.8 Three possible intra-molecular energy transition mechanisms [9]. (Reprinted from *Coordination Chemistry Reviews*, **99**, G.E. Buono-core, H. Li, and B. Marciniak, "Quenching of excited states by lanthanide ions and chelates in solution," 55–87, 1990, with permission from Elsevier.)

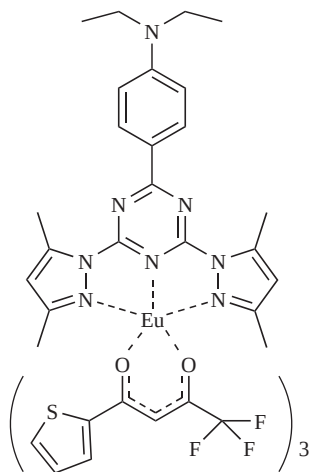


Figure 1.9 The molecular formula of $\text{Eu}(\text{tta})_3\text{L}$, $\text{L} = 4$ -[4, 6-bis(3, 5-dimethyl-1H-pyrazol-yl)-1, 3, 5-triazin-2-yl]-N,N-diethylbenzenamine, $\text{tta} = 2$ -thenoyltrifluoroacetate [10]. (Reprinted with permission from C. Yang, L.M. Fu, Y. Wang, Y. *et al.*, "Highly luminescent europium complex showing visible-light-sensitized red emission: Direct observation of the singlet pathway," *Angewandte Chemie International Edition*, 2004, **43**, 5010–5013. © Wiley-VCH Verlag GmbH & Co. KGaA.)

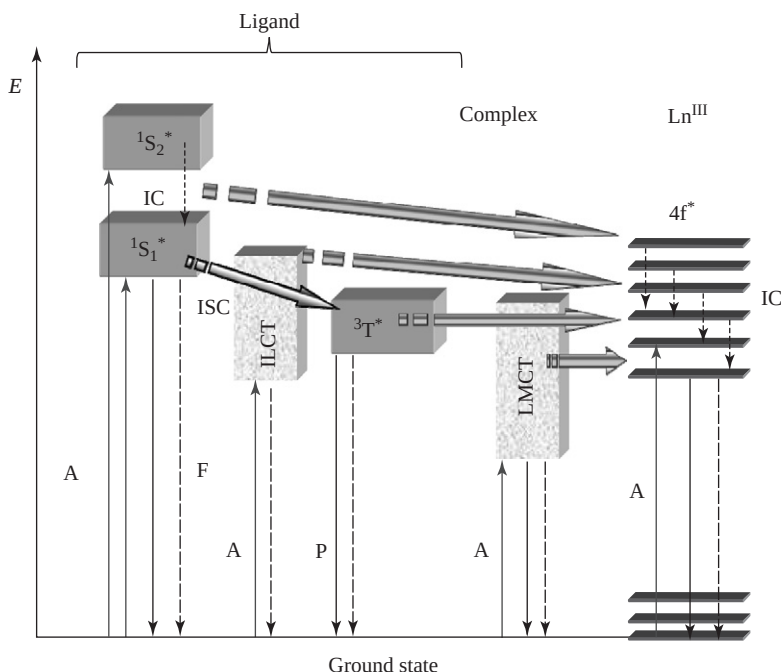


Figure 1.10 Schematic representation of energy absorption, migration, emission (solid arrows), and dissipation (dashed arrows) processes in a lanthanide complex. $^1S^*$ or S = singlet state, $^3T^*$ or T = triplet state, A = absorption, F = fluorescence, P = phosphorescence, IC = internal conversion, ISC = intersystem crossing, ILCT (or IL) = intra-ligand charge transfer, LMCT (or LM) = ligand-to-metal charge transfer. Back transfer processes are not drawn for the sake of clarity [11]. (Adapted with permission from Bünzli, J. C. G. and Eliseeva, S. V., “Basics of lanthanide photophysics,” in P. Hänninen and H. Härmä (eds.), *Springer Series on Fluorescence*, 7, Lanthanide Spectroscopy, Materials and Bio-Applications, © 2010, Springer-Verlag, Berlin.)

However, over the past ten years the situation has actually been found to be much more complicated. Bünzli summarized recent progress and proposed the diagram shown in Figure 1.10. In these cases, the complexes contain aromatic unsaturated ligands where they display a large energy absorption cross section and the energy is not usually transferred directly onto the emitting state, particularly in the case of a europium complex for which the 0–0 transition is strictly forbidden. In these processes, metal to ligand charge transfer (MLCT) and/or intra-ligand charge transfer (ILCT), even the triplet metal to ligand charge transfer (^3MLCT , where M stands for transition metals in a hetero-nuclear complex) may also emerge as important players.

1.4 Specificities of Rare Earth Coordination Chemistry

Rare earth coordination chemistry has many characteristic properties compared with d-block metal complexes. Four main issues will be discussed in this section: the valence state, chemical bonding, the coordination number, and the tetra effect – the changing gradation rules in rare earth coordination chemistry.

1.4.1 Valence State of Rare Earth Elements

Rare earth elements have similar configurations in the two outermost shells. They exhibit typical metallic properties in chemical reactions. They tend to lose three electrons and exhibit a 3+ valence state. From the Periodic Table of the elements, rare earth elements are classed as less reactive than alkali metals and alkaline earth metals but more reactive than other metals. They should be stored in an inert liquid otherwise they will be oxidized and lose their metal luster. The metal reactivity increases gradually from scandium to lanthanum and decreases gradually from lanthanum to lutetium. That is to say, lanthanum is the most reactive metal of the 17 rare earth elements. Rare earth metals can react with water and release hydrogen. They react more vigorously with acids but do not react with bases.

According to Hund's rule, electron shells are stable when empty, full or half-full. For example, the configurations $4f^0$ (La^{3+}), $4f^7$ (Gd^{3+}), and $4f^{14}$ (Lu^{3+}) are stable. Ce^{3+} , Pr^{3+} , and Tb^{3+} have one or two more electrons than required for stable electronic configurations so they can be further oxidized to a 4+ state. In contrast, Sm^{3+} , Eu^{3+} , and Yb^{3+} have one or two less electrons than required for a stable electronic configuration and they, therefore, tend to receive one or two electrons and undergo a reduction to a 2+ state. These are the reasons for these elements having abnormal valence states.

Standard reduction potentials, $E_{\text{Ln}^{4+}/\text{Ln}^{3+}}^\circ$ and $E_{\text{Ln}^{3+}/\text{Ln}^{2+}}^\circ$, represent the driving force stability of the reduction state. The more positive the value of E_{red}° , the greater the driving force for reduction. The standard reduction potentials of rare earths are shown in Table 1.3.

Table 1.3 Standard reduction potentials E_{red}° of rare earths.

Electro-pair	$E^\circ(\text{V})$	Electro-pair	$E^\circ(\text{V})$
$\text{Ce}^{4+}/\text{Ce}^{3+}$	+1.74	$\text{Eu}^{3+}/\text{Eu}^{2+}$	−0.35
$\text{Tb}^{4+}/\text{Tb}^{3+}$	+3.1 ± 0.2	$\text{Yb}^{3+}/\text{Yb}^{2+}$	−1.15
$\text{Pr}^{4+}/\text{Pr}^{3+}$	+3.2 ± 0.2	$\text{Sm}^{3+}/\text{Sm}^{2+}$	−1.55
$\text{Nd}^{4+}/\text{Nd}^{3+}$	+5.0 ± 0.4	$\text{Tm}^{3+}/\text{Tm}^{2+}$	−2.3 ± 0.2
$\text{Dy}^{4+}/\text{Dy}^{3+}$	+5.2 ± 0.4		

The data shown in the table indicate that when comparing $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^\circ$ with $E_{\text{Tb}^{4+}/\text{Tb}^{3+}}^\circ$ electronic pairs, to act as an oxidizing agent, Tb^{4+} is stronger than Ce^{4+} ; to act as a reducing agent Ce^{3+} is stronger than Tb^{3+} . When comparing $E_{\text{Eu}^{3+}/\text{Eu}^{2+}}^\circ$ with $E_{\text{Yb}^{3+}/\text{Yb}^{2+}}^\circ$, to act an oxidizing agent Yb^{2+} is stronger than Eu^{2+} under the standard conditions. Figure 1.11 visualizes this

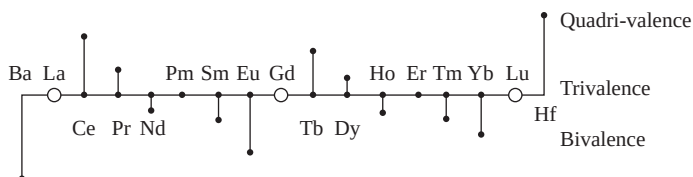


Figure 1.11 Valence states of lanthanide elements.

trend. The transverse axis is the atomic number and the length of the short lines along the vertical axis represents the trend of valence state variation.

1.4.2 Chemical Bonding of Rare Earth Elements

As a group of typical metal elements, lanthanide elements can form chemical bonds with most nonmetal elements. Some low-valence lanthanide elements can form chemical bonds in organometallic or atom cluster compounds. Because lanthanide elements lack sufficient electrons and show a strong repulsive force towards a positive charge, chemical bonds between lanthanide metals have not yet been observed. Table 1.4 shows that 1391 structure-characterized lanthanide complexes were reported in publications between 1935 and 1995 and these are sorted by chemical bond type.

From a soft–hard acid–base point of view, lanthanide elements are hard bases. Thus, they tend to form chemical bonds with atoms that belong to the hard acid group. For example, oxygen and lanthanide elements tend to form RE–O bonds. The data in Table 1.4 show that 1080 complexes (77.6% of the 1391 complexes) contain RE–O bonds. Among these, 587 complexes (42.2% of the 1391 complexes) contain RE–O bonds only. On the other hand, only 46 complexes contain RE–S bonds, 7 complexes contain RE–Se bonds, and 10 complexes contain RE–Te bonds. Lanthanide elements can also form chemical bonds with nitrogen group atoms. There are 318 lanthanide complexes that contain RE–N bonds and 15 complexes that contain RE–P bonds. No complex containing a RE–As bond has been observed yet. Lanthanide complexes containing RE–C bonds are not stable under normal conditions. However, 407 complexes containing RE–C bonds are stable under water-free conditions. Complexes containing RE–Si bonds are very rare.

The nature of chemical bonds in lanthanide complexes and whether 4f electrons contribute to bonding in these complexes has been a long and controversial problem. To further understand the electronic structure of lanthanide complexes, scientists have investigated the nature of their molecular bonding by quantum chemistry. It is now generally believed that chemical bonds in lanthanide complexes exhibit polar covalent bond properties and that 4f electrons do not contribute to bonding, with the major contribution being from the 5d and 6s orbitals, while the 4f orbital is highly localized [12].

1.4.3 Coordination Numbers of Rare Earth Complexes

1.4.3.1 Definition of Coordination Number

The coordination number is a well known concept. However, its definition is not standard. For example, the Cambridge database defines the coordination number of cyclopentadiene as one. It defines the coordination number as the number of ligands coordinated to a central atom. Cotton reported the coordination number of $(C_5H_5)_2ZrCl_2$ to be four, which also adopts this definition. However, the coordination numbers of butadiene and bipyridine are defined as two in some sources. This obviously conflicts with the former definition. Guangxian Xu defined the coordination number of the central atom to be the number of coordinating atoms for σ ligands or the number of π electron pairs provided by π ligands. According to this definition 2,6-xylene provides four σ coordinating atoms to the central lutetium atom in $[Li(THF)_4][Lu-(2,6-Me_2C_6H_3)_4]$ and the coordination number of Lu^{3+} is four. As another

Table 1.4 The chemical bonding of lanthanide complexes.

Chemical bond	Compound				Sum total
	Sc	Y	Ln	Subtotal	
RE–O	13	54	520	587	719
RE–N	1	1	25	27	
RE–C	4	6	64	74	
RE–L (L = halogen)	0	2	6	8	
RE–S	0	0	21	21	
RE–P	1	0	1	2	
RE–O, RE–N	5	13	183	201	412
RE–O, RE–C	1	15	92	108	
RE–O, RE–L	4	10	58	72	
RE–O, RE–S	0	0	17	17	
RE–O, RE–P	0	1	1	2	
RE–O, RE–H	0	4	3	7	
RE–O, RE–Te	0	0	3	3	
RE–O, RE–Si	0	0	1	1	
RE–O, RE–Ge	0	0	1	1	
RE–N, RE–C	4	7	40	51	64
RE–N, RE–L	0	1	5	6	
RE–N, RE–S	0	0	2	2	
RE–N, RE–P	0	0	1	1	
RE–N, RE–H	0	0	1	1	
RE–N, RE–Se	0	0	2	2	
RE–N, RE–Te	0	0	1	1	
RE–C, RE–L	2	6	58	66	109
RE–C, RE–P	0	0	5	5	
RE–C, RE–S	0	0	5	5	
RE–C, RE–H	2	9	12	23	
RE–C, RE–Te	0	0	2	2	
RE–C, RE–Se	0	0	2	2	
RE–C, RE–Si	0	0	2	2	
RE–L, RE–H	0	3	1	4	
RE–O, RE–N, RE–C	0	2	12	14	80
RE–O, RE–N, RE–P	0	0	1	1	
RE–O, RE–N, RE–L	0	1	5	6	
RE–O, RE–C, RE–L	1	2	39	42	
RE–O, RE–C, RE–H	0	5	5	10	
RE–O, RE–C, RE–Se	0	0	3	3	
RE–O, RE–C, RE–Te	0	0	3	3	
RE–O, RE–C, RE–S	0	0	1	1	
RE–N, RE–C, RE–P	0	1	0	1	2
RE–N, RE–C, RE–L	0	0	1	1	
RE–C, RE–L, RE–H	0	1	0	1	2
RE–C, RE–P, RE–Te	1	0	0	1	
RE–N, RE–C, RE–P, RE–H	1	0	0	1	3
RE–N, RE–C, RE–P, RE–Cl	0	1	0	1	
RE–N, RE–O, RE–C, RE–L	0	0	1	1	
					1391

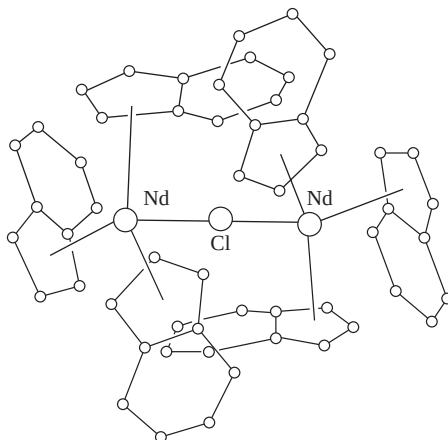


Figure 1.12 The structure of the anion in the complex $[\text{Nd}(\eta^5\text{-C}_9\text{H}_7)_3(\mu_2\text{-Cl})\text{Nd}(\eta^5\text{-C}_9\text{H}_7)_3][\text{Na}(\text{THF})_6]$ [13]. (Adapted with permission from M.Q. Chen, G. Wu, Z. Huang, *et al.*, “Studies on rare earth-indenyl compounds. 2. Synthesis and crystal structure of hexakis(tetrahydrofuran)sodium (.mu.-chloro)bis(triindenylneodymate),” *Organometallics*, **7**, no. 4, 802–806, 1988. © 1988 American Chemical Society.)

example, $\text{Ce}(\text{C}_9\text{H}_7)_3\text{Py}$ (C_9H_7 represents indene, Py represents pyridine) has an X-ray single crystal structure which shows that every indene ligand provides three pairs of π electrons and, therefore, the coordination number of Ce^{3+} in this complex is ten. According to this definition, the coordination numbers contributed by the π ligands $\text{CH}_2=\text{CH}_2$, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, C_6H_6 , C_5H_5^- , and $(\text{C}_8\text{H}_8)^{2-}$ are one, two, three, three, and five, respectively. In $[\text{Ce}(\text{C}_8\text{H}_8)_2]^-$, C_8H_8 has a planar structure and according to the $4n+2$ rule, only those annular structures that have 6, 10, 14, or 18 π electrons are aromatic. When C_8H_8 exists as an anion, it has ten π electrons and it can provide the central atom with five pairs of π coordinating electrons. Therefore, the coordination number of cerium in $[\text{Ce}(\text{C}_8\text{H}_8)_2]^-$ is ten. In the complex $[\text{Nd}(\eta^5\text{-C}_9\text{H}_7)_3(\mu_2\text{-Cl})\text{Nd}(\eta^5\text{-C}_9\text{H}_7)_3][\text{Na}(\text{THF})_6]$, each of the C_9H_7^- groups provide three coordination sites and, therefore, the coordination number of each neodymium ion is ten (Figure 1.12).

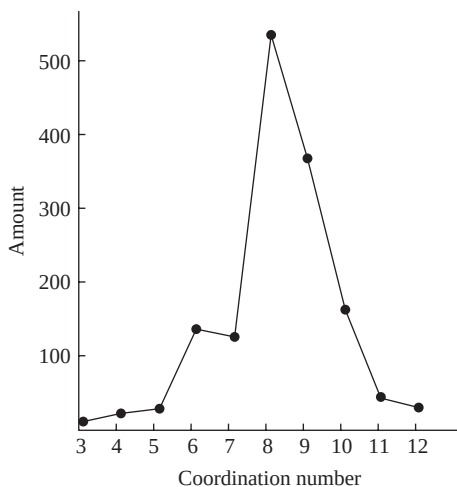
1.4.3.2 Large and Variable Coordination Number

Based on the 1391 complexes that have been structurally characterized and published between 1935 and 1995, we compiled data on the central atoms and their coordination numbers. These results are summarized in Table 1.5 and Figure 1.13. All the coordination numbers are between 3 and 12 and the most common coordination number is eight (37%). Compared with transition metals, lanthanide elements have two distinct characteristics in terms of their coordination number:

1. **Large coordination numbers.** For example, the coordination number of 3d transition metals is generally four or six. However, the most common coordination number of lanthanide complexes is eight or nine. This number is close to the sum of the 6s, 6p, and 5d orbitals. Another fact responsible for the large coordination number of lanthanide complexes

Table 1.5 The statistic number of rare earth complexes with different coordination number [5].

CN ^a	Subtotal	Sc	Y	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
3	10	2	1		1		1		1	2		1						1
4	18			3	3				1		1	1					7	2
5	25		4	3	3	3	4				1				3		3	1
6	133	9	19	8	7	12	8		15	10	7		3	1	6	1	20	7
7	121	12	20	10	7	5	10		12	7	6	1	5	1	5	1	13	6
8	534	18	51	31	36	27	53		73	34	24	6	13	16	39	5	68	40
9	367	3	33	31	17	26	61		36	32	25	11	16	12	25	5	21	13
10	160		5	33	20	16	32		18	13	4	1	3	2	2	1	9	1
11	37			14	5	6	4		2	3				1			2	
12	28		1	11	7	2	4			1	1		1					
Sum total	1433	44	134	144	106	97	177		158	102	69	21	41	33	80	13	144	70

^aCN = coordination number.**Figure 1.13** The distribution of rare earth complexes according to coordination number, which were collected from 1391 structurally-characterized coordination complexes reported between 1935 and 1995 [5].

is the large ionic radius of the lanthanide elements. When its coordination number is six, the ionic radius of Fe^{3+} and Co^{3+} are 55 and 54 pm, respectively. However, the ionic radius of La^{3+} , Gd^{3+} , and Lu^{3+} are 103.2, 93.8, and 86.1 pm, respectively.

2. **Variable coordination numbers.** The coordinating stabilization energy (about $4.18 \text{ kJ}\cdot\text{mol}^{-1}$) of lanthanide ions is much smaller than the crystal field stabilization energy of transition metals (typically $\geq 418 \text{ kJ}\cdot\text{mol}^{-1}$). Therefore, the coordinating bonds of lanthanide complexes are not directional and the coordination number varies from 3 to 12.

From Table 1.5 we gather that the number of complexes sorted by their central atoms is 1433. This number is larger than 1391. Two reasons are responsible for this disagreement: (1) the existence of hetero-nuclear lanthanide complexes such as $\{[\text{LaY}(\text{C}_6\text{H}_{11}\text{COO})_4]\text{Cl}_2(\text{CH}_3\text{COCH}_3)_2(\text{H}_2\text{O})_2\}_n$, $\{[\text{ErY}(\text{Gly})_6(\text{H}_2\text{O})_4](\text{ClO}_4)_6(\text{H}_2\text{O})_4\}_n$, and $\{[\text{H}[\text{EuLa}_2(\text{DPA})_5(\text{H}_2\text{O})_8](\text{H}_2\text{O})_8\}_n$, and so on, where Gly is glycine and DPA is 2,6-pyridinedicarboxylic acid. (2) In some binuclear or multi-nuclear complexes, the same central ion may have different coordination environments. For example, in the 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-(8,8,8)-hexacosane (denoted 222) complex $[(222)(\text{NO}_3)\text{RE}][\text{RE}(\text{NO}_3)_5(\text{H}_2\text{O})]$ ($\text{RE} = \text{Nd}, \text{Sm}$ or Eu), when the central ion is a cation the coordination number is 10 and when the central ion is an anion the coordination number is 11.

1.4.3.3 Coordination Number and Effective Ionic Radius

Recently, by assuming that the distance between different ions is the sum of the ionic radius of the anion and the cation, the distance between anions and cations in thousands of nitrides and oxides have been examined. The influence of coordination number, electron spin, and the geometry of the coordination polyhedron on the ionic radius have also been considered. Under certain conditions, differences in the type of structure will not influence the ionic radius. The crystal cell volume of complexes that have the same anion in a series of analog compounds will be proportional to the cation's radius. Based on the ionic radius proposed by Pauling (O^{2-} , 140 pm; F^- , 133 pm), a suggested set of ionic data was proposed by dividing the distance between different ions using the "Goldschmidt method." This radius was designated the "effective radius." "Effective" implies that these data were deduced from experimental data. The sum of the ionic radii agrees fairly well with the distance between the ions. Table 1.6 lists the effective radii of lanthanide ions for different coordination numbers and at different valence states. For the sake of convenience, some elements that directly bond to lanthanide elements are also listed. These data show that:

1. For the same ion, a larger coordination number leads to a larger effective ionic radius. For example, when the coordination number is 6, 7, 8, 9, 10, and 12 the effective radius of La^{3+} is 103.2, 110, 116.0, 121.6, 127, and 136 pm, respectively.
2. For the same element with the same coordination number, the effective radius will decrease if the valence state increases. For example, when the coordination number is six the effective radius of Ce^{3+} is 101 pm while the effective radius of Ce^{4+} is 87 pm. When the coordination number is eight, the effective radius of Sm^{2+} is 127 pm while that of Sm^{3+} is 102 pm. The reason for this is that one more electron is present in the outer shell for the lower valence ion compared with the higher valence one.
3. When the coordination number and the valence state remain the same, the effective ionic radius will decrease as the atomic number increases. This is caused by lanthanide contraction.

Some ions (for example, H^+ with a coordination number of one or two, C^{4+} with a coordination number of three) show effective radii below zero. This is because they coordinate very tightly to other anions when bonding to them. This strong attraction decreases the distance between the anions and cations even more than the radii of the anions.

Table 1.6 Effective ionic radii of lanthanide ions and other related ions (pm).

Ion	CN ^a	Radii	Ion	CN ^a	Radii	Ion	CN ^a	Radii
La ³⁺	6	103.2	Tb ³⁺	7	98.0	Br ⁻	6	196
	7	110.0		8	104.0	Br ³⁺	4	59
	8	116.0		9	109.5	Br ⁵⁺	3	31
	9	121.6	Tb ⁴⁺	6	76.0	Br ⁷⁺	4	25
	10	127.0		8	88.0		6	39
Ce ³⁺	12	136.0	Dy ²⁺	6	107.0	I ⁻	6	220
	6	101.0		7	113.0	O ²⁻	2	135.0
	7	107.0		8	119.0		3	136.0
	8	114.3	Dy ³⁺	6	91.2		4	138.0
	9	119.6		7	97.0		6	140.0
Ce ⁴⁺	10	125.0		8	102.7		8	142.0
	12	134.0	Ho ³⁺	9	108.3	S ²⁻	6	182.0
	6	87.0		6	90.1	S ⁴⁺	6	34.0
	8	97.0		8	101.5	S ⁶⁺	4	12.0
	10	107.0		9	107.2		6	29.0
Pr ³⁺	12	114.0		10	112.0	Se ²⁻	6	198.0
	6	99.0	Er ³⁺	6	89.0	Se ⁴⁺	6	50.0
	8	112.6		7	94.5	Se ⁶⁺	4	28.0
	9	117.9		8	100.4		6	42.0
Pr ⁴⁺	6	85.0	Tm ²⁺	9	106.2	Te ²⁻	6	221.0
	8	96.0		6	103.0	Te ⁴⁺	3	52.0
Nd ²⁺	8	129.0	Tm ³⁺	7	109.0		4	66.0
	9	135.0		6	88.0		6	97.0
Nd ³⁺	6	98.3		8	99.4	Te ⁶⁺	4	43.0
	8	110.9	Yb ²⁺	9	105.2		6	56.0
	9	116.3		6	102.0	N ³⁻	4	146.0
	12	127.0		7	108.0	N ³⁺	6	16.0
Sm ²⁺	7	122.0	Yb ³⁺	8	114.0	N ⁵⁺	3	-10.4
	8	127.0		6	86.8		6	13.0
	9	132.0		7	92.5	P ³⁺	6	44
Sm ³⁺	6	95.8	Lu ³⁺	8	98.5	P ³⁺	4	17
	7	102.0		9	104.2		5	29
	8	107.9		6	86.1		6	38
	9	113.2		8	97.7	As ³⁺	6	58
	12	124.0		9	103.2	As ³⁺	4	33.5
Eu ²⁺	6	117.0	Sc ³⁺	6	74.5		6	46
	7	120.0		8	87.0	C ⁴⁺	3	-8
	8	125.0		6	90.0		4	15
	9	130.0	Y ³⁺	7	96.0		6	16
	10	135.0		8	101.9	Si ⁴⁺	4	26.0
Eu ³⁺	6	94.7		9	107.5		6	40.0
	7	101.0	F ⁻	2	128.5	Ge ²⁺	6	73
	8	106.6		3	130.0	Ge ⁴⁺	4	39
	9	112.0		4	131.0		6	53
	6	93.8	Cl ⁻	6	133.0	Sn ⁴⁺	4	55
Gd ³⁺	7	100.0		6	181.0		5	62
	8	105.3		3	12.0		6	69.0
	9	110.7		4	8.0	H ⁺	1	-38
	6	92.3		6	27		2	-18

^aCN = coordination number.

1.4.4 Tetrad Effect of Lanthanide Elements – Changing Gradation Rules in Lanthanide Coordination Chemistry

Because of gradation filling of electrons into the 4f shell, the properties of many lanthanide compounds show changing gradation with an increase in the atomic number. The lanthanide tetrad effect is an important phenomenon and has also been well studied. Because the separation of lanthanide elements was required before a study of the properties of individual lanthanide elements was possible, the discovery of the lanthanide tetrad effect was related to the separation of lanthanide elements.

It was found that when extracting lanthanide elements with tributyl phosphate at low pH, $\lg D-Z$ showed an “odd–even effect,” which is observed when plotting the logarithm of distribution coefficient D versus the atomic number Z . Straight lines are plotted when Z is odd or even but the odd line is above the even one. Since this report, a lot of data have been reported and presented differently. Figure 1.14 shows typical curves for the change in lanthanide gradation. The lanthanide tetrad effect will also be very clear if the y-axis is not $\lg D$ but $\lg K_{\text{ex}}$

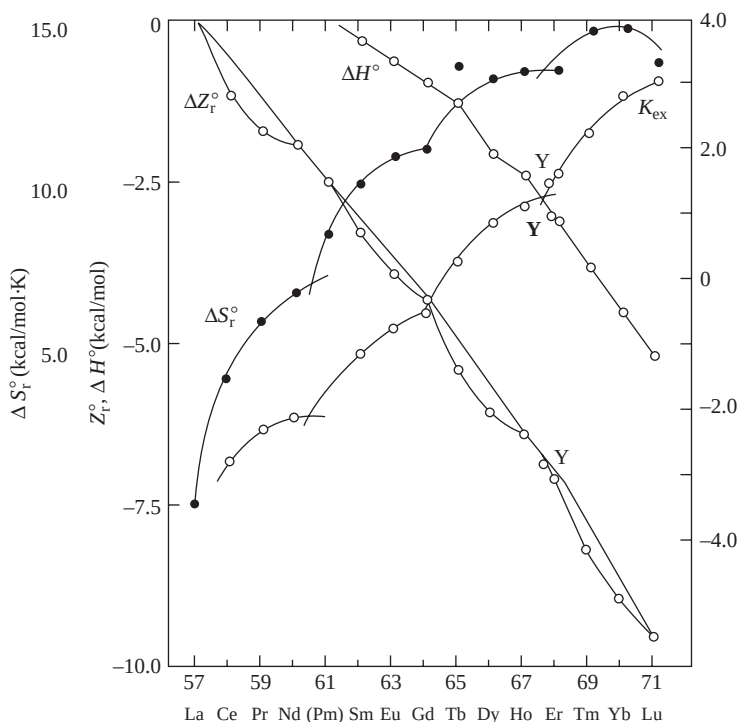


Figure 1.14 The relationship between the atomic number of lanthanides and thermodynamic functions (K_{ex} , ΔH , ΔZ_r° , and ΔS_r°) from the extraction system consisting of 2-ethyl hexyl mono(2-ethyl hexyl) ester phosphinate in a dodecane solution [14]. (Reprinted from E.X. Ma, X.M. Yan, S.Y. Wang, *et al.*, “The extraction chemistry of lanthanides with 2-ethyl-hexyle mono (2-ethyl-hexyle) phosphinate oxide,” *Scientia Sinica B: Chemistry* (in Chinese), **5**, 565–573, © 1981, with permission from Science in China Press.)

(extraction equilibrium constant), ΔH (enthalpy variation), ΔZ_r° (free energy variation), and ΔS_r° (entropy variation) of an extraction reaction.

There is a similar phenomenon for trivalent actinide elements. Thus, the tetrad effect is a common characteristic of f-group elements.

Many scientists have shown great interest in the essence of the tetrad effect. Spectral terms and electronic repulsive energies related to constants of the trivalent lanthanide elements are listed in Table 1.7. The ground state spectral terms of lanthanide elements can be sorted into two categories and these are divided by gadolinium: the first category consists of elements before gadolinium, which includes lanthanum, cerium, praseodymium, neodymium and promethium, samarium, europium, and gadolinium, while the second category contains the elements after gadolinium, which includes gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. As described previously, if one plotted the total orbital angular momentum quantum number L of the ground state versus the atomic number Z the curves will exhibit a tilted W shape as shown in Figure 1.15. Therefore, the tetrad effect can be regarded as a reflection of 4f electronic configuration variations.

To discuss the tetrad effect quantitatively, Nugent analyzed lanthanide and actinide elements using the approximate electronic repulsive energy equation proposed by Jørgensen [15]. He suggested that the electronic repulsive energy H_r between the electrons of the f^q configuration is related to the electron number q . In fact, the macro tetrad effect is a representation of the relationship between H_r and q .

The Jørgensen equation is:

$$H_r = e_0 E^0 + e_1 E^1 + e_2 E^2 + e_3 E^3 \quad (1.3)$$

Table 1.7 Ground state spectral terms and electronic repulsive energy related constants of trivalent lanthanide ions [15].

Trivalent ions	4f electrons	Total angular momentum L	Ground state spectral term	E^1 (eV)	E^3 (eV)	e_1	e_3
La	0	0	$^1S_0$				
Ce	1	3	$^2F_{5/2}$			0	0
Pr	2	5	$^3H_4$	0.56 389	0.0 579	-9/13	-9
Nd	3	6	$^4I_{9/2}$	0.58 758	0.0 602	-27/13	-21
Pm	4	6	$^5I_4$	0.61 019	0.0 652	-54/13	-21
Sm	5	5	$^6H_{5/2}$	0.68 152	0.0 689	-90/13	-9
Eu	6	3	$^7F_0$	0.69 095	0.0 691	-135/13	0
Gd	7	0	$^8S_{7/2}$	0.71 420	0.0 722	-189/13	0
Tb	8	3	$^7F_6$	0.74 655	0.0 755	-135/13	0
Dy	9	5	$^6H_{15/2}$	0.75 872	0.0 756	-90/13	-9
Ho	10	6	$^5I_8$	0.79 851	0.0 774	-54/13	-21
Er	11	6	$^4I_{15/2}$	0.83 934	0.0 802	-27/13	-21
Tm	12	5	$^3H_6$	0.88 552	0.0 836	-9/13	-9
Yb	13	3	$^2F_{7/2}$			0	0
Lu	14	0	$^1S_0$				

(Reprinted from *Journal of Inorganic and Nuclear Chemistry*, 32, L.J. Nugent, "Theory of the tetrad effect in the lanthanide(III) and actinide(III) series," 3485-3491, 1970, with permission from Elsevier).

where

e_0, e_1, e_2 , and e_3 are all constants obtained from a quantum mechanics calculation
 E^0, E^1, E^2 , and E^3 are obtained from hyperfine emission and absorption spectra

Among them,

$$e_0 = \frac{q(q-1)}{2}$$

(1.4)

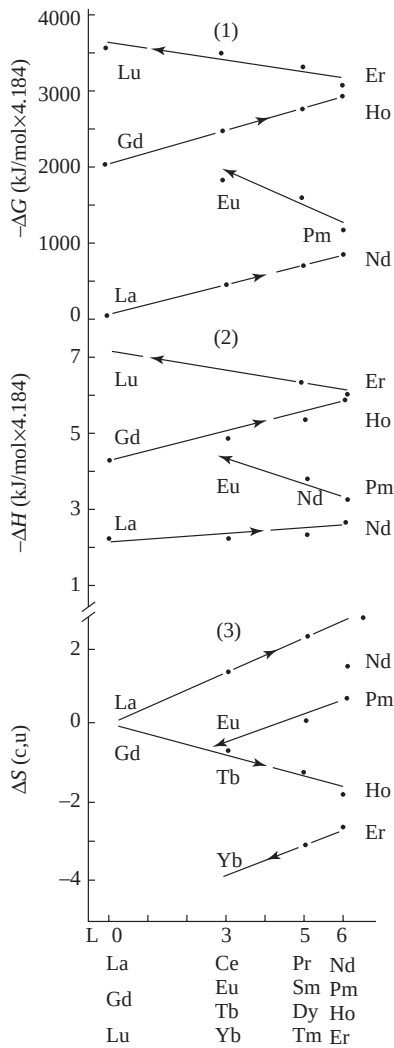


Figure 1.15 The relationship between ΔS , ΔH , ΔG , and L . ΔS , ΔH , and ΔG are thermodynamic constants for the extraction system of N236-xylene/ $\text{RE}(\text{NO}_3)_3\text{-HNO}_3$. L is the orbital angular momentum quantum number of the lanthanide elements [14]. (Reprinted from E.X. Ma, X.M. Yan, S.Y. Wang, *et al.*, “The extraction chemistry of tanthanides with 2-ethyl-hexyle mono (2-ethyl-hexyle) phosphinate oxide,” *Scientia Sinica B: Chemistry* (in Chinese), 5, 565–573, © 1981, with permission from Science in China Press.)

The first term of H_r increases regularly as q increases. Therefore, it does not contribute to a periodic change in H_r . The term $e_2 E^2$ can be ignored because all functions related to this term approach zero in the ground state. Additionally,

$$e_1 = 9/8\{ \langle S(S-1) \rangle - S(S+1) \} \quad (1.5)$$

where

$\langle S(S+1) \rangle$ is the weighting of a spectral term with a total spin quantum number S

l is the angular quantum number

and

$$\langle S(S+1) \rangle = \frac{3}{4}q \left[1 - \frac{(q-1)}{4l+1} \right] \quad (1.6)$$

for f electrons $l = 3$, and thus

$$\langle S(S+1) \rangle = \frac{3}{4}q \left[1 - \frac{(q-1)}{13} \right] \quad (1.7)$$

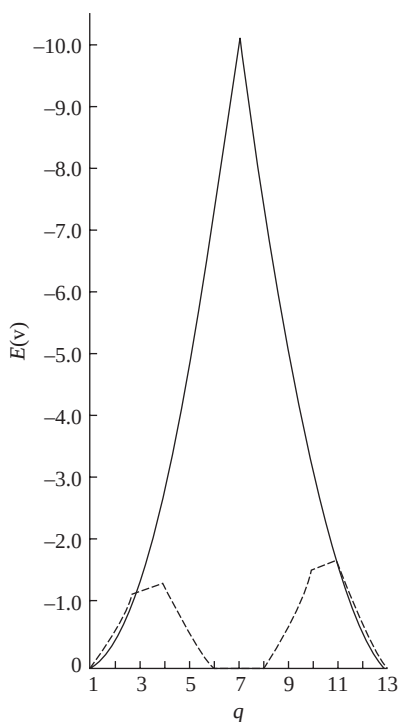


Figure 1.16 The ground state electronic repulsive stabilization energy E as a function of the $4f$ electron number q (the contribution from the E^1 term in Equation 1.3, solid line; the contribution from the E^3 term in Equation 1.3, dashed line) [15]. (Reprinted from *Journal of Inorganic and Nuclear Chemistry*, 32, L.J. Nugent, "Theory of the tetrad effect in the lanthanide(III) and actinide(III) series," 3485–3491, 1970, with permission from Elsevier.)

From Table 1.7 we can see that e_1 changes with the 4f electron number q . e_1 reaches a maximum when $q = 7$. By plotting $e_1 E$ versus q we get Figure 1.16. The solid line in Figure 1.16 reaches a maximum at f^7 (Gd^{3+}). This is an obvious reflection of the half-full effect of its 4f orbital. It is generally referred as the “gadolinium broken effect.”

It can be seen from Table 1.7 that although E^3 increases regularly as q increases, e_3 changes periodically. The dashed line in Figure 1.16 shows the plot of $e_3 E^3$ versus q . Two maxima are observed at f^{3-4} (Nd^{3+} – Pm^{3+}) and f^{10-11} (Ho^{3+} – Er^{3+}), respectively. This result implies that three steady states are present at f^7 , f^{3-4} , and f^{10-11} , respectively. This explains the tetrad effect because the three intersections in the tetrad effect are in the same position. However, the two maxima at f^{3-4} and f^{10-11} are six times smaller than the one at f^7 . It is very difficult to observe such small stabilization energies in chemical reactions. This explains why the tetrad effect was discovered so much later than the gadolinium broken effect.

It should be pointed out that not all the ions discussed here are affected by the outer fields. In fact, lanthanide ions may be affected by solvents or coordination fields in chemical reactions. For example, E^1 and E^3 will change because of the coordination effect of water or organic molecules in an extraction. In addition, the amount of change would be different in different media. The tetrad effect would thus be different in different systems. The tetrad effect not only relates to the electronic configurations of lanthanide elements but is also affected by the surrounding conditions. Currently it is still not possible to predict the tetrad effect or to calculate it quantitatively. Tetrad effect theory still needs to be improved and further data need to be accumulated.

1.5 Coordination Chemistry of Inorganic Compounds

1.5.1 Rare Earth Hydroxides

Under general conditions, rare earth hydroxides $RE(OH)_3 \cdot nH_2O$ precipitate from a high pH solution as a gel. However, they are unstable during heating and usually lose water to become $REO(OH)$ or RE_2O_3 when the temperature approaches or exceeds 200 °C. From lanthanum to lutetium, the dehydration temperature decreases with an increase in atomic number because of a decrease in the ionic ratio.

Single crystals of rare earth hydroxides can be obtained by a hydrothermal method. At 190–420 °C and from 1.2×10^6 to 7×10^7 Pa, rare earth hydroxides can be grown from RE_2O_3 – H_2O – $NaOH$ systems after prolonged treatment.

Structure: $Lu(OH)_3$ and $Sc(OH)_3$ have a cubic system but all the other rare earth single crystals have hexagonal systems. In the hexagonal system, two $RE(OH)_3$ units are present in each cell. As a μ_3 -bridge, each hydroxide group links three rare earth ions and there are thus nine oxygen atoms around each RE^{3+} ion and their coordination number is nine. No hydrogen bonds exist in the cells as all three lone pair electrons of the oxygen atoms are occupied by rare earth ions and form a tri-capped tri-angular prism polyhedron. In cubic systems, there are eight $RE(OH)_3$ units in each cell. As a μ_2 -bridge, each hydroxide group links two rare earth ions and the rare earth ions are six coordinated by six oxygen atoms and form an octa-polyhedron. In this infinite network, strong hydrogen bonds exist between the hydroxide groups (Figure 1.17).

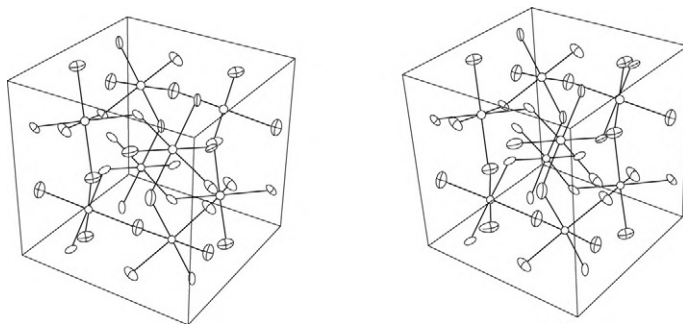


Figure 1.17 Crystal structures of $\text{Lu}(\text{OH})_3$ [16]. (Reprinted from *Journal of Inorganic and Nuclear Chemistry*, **42**, D.F. Mullica, and W.O. Milligan, "Structural refinement of cubic $\text{Lu}(\text{OH})_3$," 223–227, 1980, with permission from Elsevier.)

1.5.2 Rare Earth Halide and Perchlorate Compounds

Rare earth halide compounds easily absorb water from their surroundings to form hydrates, $\text{RECl}_3 \cdot n\text{H}_2\text{O}$. For lanthanum, cerium, praseodymium, $n = 7$, while for neodymium to lutetium and scandium, yttrium, $n = 6$. Non-hydrated rare earth halides can be directly obtained by the reaction of rare earth metals with corresponding halide gases or by substitution reactions of rare earth metals with halide mercury. They can not, however, be obtained by heating the hydrated halide because the hydrate will hydrolyze to form REOX , where X represents the corresponding halide. Another commonly used method is to mix $\text{REX}_3 \cdot n\text{H}_2\text{O}$ and excess NH_4X ($\text{RECl}_3/\text{NH}_4\text{Cl} = 6$, $\text{REI}_3/\text{NH}_4\text{I} = 12$) into a solution and slowly heat under vacuum to remove all the water, upon which heating is slowly continued up to 300°C and until all the ammonium halide is entirely sublimated.

The solubility of rare earth fluorides REF_3 is very low, the $\text{p}K_{\text{sp}}$ ranges from 19 to 15 for lighter rare earth lanthanum, cerium, praseodymium, and neodymium to heavier rare earth ytterbium and lutetium, respectively.

Structure: Non-hydrated rare earth fluorides have two different crystal systems, a hexagonal system (lanthanum to terbium) and an orthorhombic system (dysprosium to lutetium, yttrium). In the crystal of LaF_3 , the central ion is nine coordinated by nine fluoride atoms. Each fluoride atom further connects with two lanthanum atoms through a μ_3 -bridge to form an infinite polymer.

Hydrates of rare earth chlorides also have two different crystal systems: a triclinic system for lanthanum, cerium, and praseodymium, as well as a monoclinic system for neodymium to lutetium and yttrium. $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, as an example of the former system, is different from the above infinite polymer as two cerium atoms are connected by two μ_2 -bridges to form a dimer. The formula for this dimer is $[(\text{H}_2\text{O})_7\text{Ce}(\mu_2\text{-Cl})_2\text{Ce}(\text{H}_2\text{O})_7]\text{Cl}_4$ as shown in Figure 1.18. Therefore, the coordination number of cerium is nine and the polyhedron takes on a destroyed mono-capped square antiprism configuration.

$\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ exists as a single molecule and can be represented as $[\text{GdCl}_2 \cdot 6\text{H}_2\text{O}] \cdot \text{Cl}$. The coordination number of gadolinium is eight and the uncoordinated chloride is present in the lattice because it forms six hydrogen bonds with coordinated water molecules.

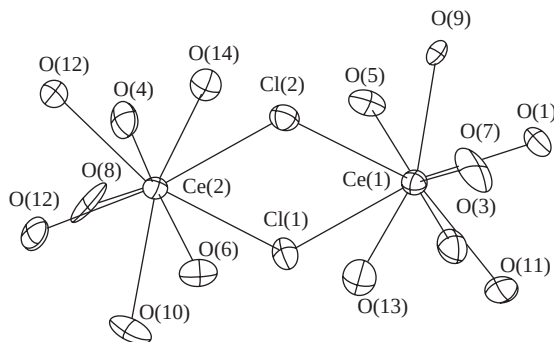


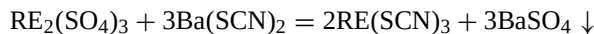
Figure 1.18 Structure of the $[(\text{H}_2\text{O})_7\text{Ce}(\mu_2\text{-Cl})_2\text{Ce}(\text{H}_2\text{O})_7]^{4+}$ in hydrated cerium chloride [17]. (Reprinted from E.J. Peterson, E.I. Onstott, and R.B.V. Dreele, “A refinement of cerium(III) trichloride heptahydrate in space group $P1$,” *Acta Crystallographica*, **B35**, no. 4, 805–809, 1979, with permission from International Union of Crystallography.)

Because its ionic potential Z/R is relatively small, the coordination capability of the perchlorate group to rare earth ions is relatively weak compared with other oxygen containing acid groups. For example, in $\text{RE}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ the central ion is coordinated to water molecules and all the perchlorate anions only exist in the lattice and are not connected to the rare earth central ion. However, it does coordinate to rare earth ions by adopting mono- or bidentate modes depending on the coordination capability of the competitive ligands. For example, in the complex $[\text{Nd}(\text{ClO}_4)_2(\text{ph}_3\text{PO})_4]\text{ClO}_4 \cdot \text{C}_2\text{H}_5\text{OH}$, two perchlorate groups adopt a bidentate mode to coordinate to the neodymium ion, while the third one exists in the lattice (Figure 1.19).

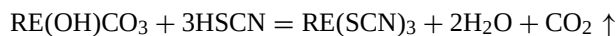
1.5.3 Rare Earth Cyanide and Thiocyanate Compounds

Rare earth cyanide compounds can be obtained by a reaction between the corresponding metal and cyanic acid in liquid ammonia, but when rare earth metals react with cyanic acid directly under ambient conditions the related cyanide compounds can not be obtained, but the products will be rare earth nitride and carbide.

The non-hydrated rare earth thiocyanate can be obtained by a reaction between the corresponding metal and NH_4SCN in liquid ammonia or by the dehydration of the corresponding hydrated thiocyanate at 1333 Pa and 50 °C. However, the hydrated thiocyanate can be prepared by the following double replacement reactions:



or



Structures: In rare earth cyanides the rare earth ions prefer to coordinate to carbon and not nitrogen because of the negative charge of the cyanide anion that is present at the carbon side

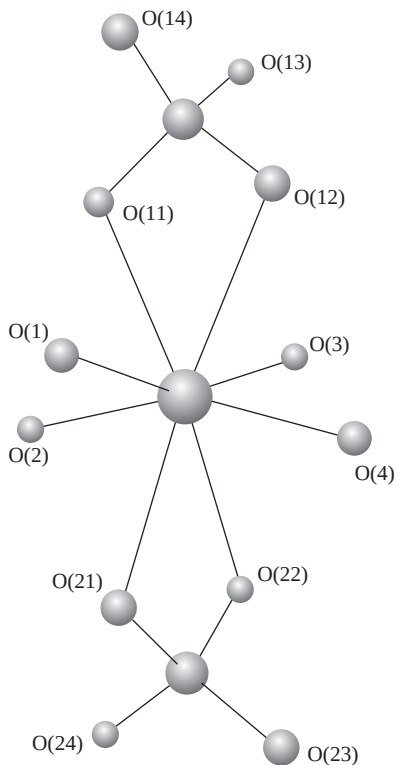


Figure 1.19 The cation structure in the complex $[\text{Nd}(\text{ClO}_4)_2(\text{ph}_3\text{PO})_4]\text{ClO}_4 \cdot \text{C}_2\text{H}_5\text{OH}$ [18].

[19] (Figure 1.20). On the other hand, when rare earth thiocyanates are the ligands, the rare earth ions prefer to coordinate to the nitrogen and not the sulfur (Figure 1.21).

1.5.4 Rare Earth Carbonate Compounds

The solubility of rare earth carbonates is fairly low and ranges from 10^{-5} to 10^{-6} mol L^{-1} . Rare earth carbonates can be obtained by the addition of ammonium carbonate to a solution of a rare earth water-soluble salt. In this case, the precipitates will all be hydrates. Lanthanum to neodymium carbonates contain eight water molecules while neodymium to lutetium carbonates contain two water molecules only. Rare earth carbonates can be dissolved in alkali metal carbonate solutions and form a double salt of alkali metals.

Structure: The coordination modes of carbonates are fairly abundant and they can be monodentate, bidentate, or multidentate when coordinated to the central ion (Figure 1.22). For instance, in the crystal of $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ the carbonate groups have modes a, b, and c as shown in Figure 1.22 when coordinated to the lanthanum ion. In the $\text{Nd}(\text{OH})\text{CO}_3$ crystal, the carbonate groups have the d mode when coordinating to neodymium ions. In this compound, the coordination number of neodymium ion is nine. A layer-like polymer is formed by hydroxyl linkages and a carbonate bridge. The $\text{Y}(\text{OH})\text{CO}_3$ crystal belongs to the orthorhombic system

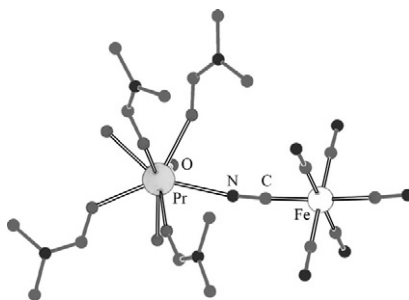


Figure 1.20 A projection of the bi-nuclear unit of $[\text{Pr}(\text{dmf})_4\text{Fe}(\text{CN})_6(\text{H}_2\text{O})_4]$. Lattice water molecules have been omitted for clarity [19a] (Reprinted from *Coordination Chemistry Review*, **250**, S. Tanase and J. Reedijk, “Chemistry and magnetism of cyanido-bridged d-f assemblies,” 2501–2510, 2006, with permission from Elsevier.)

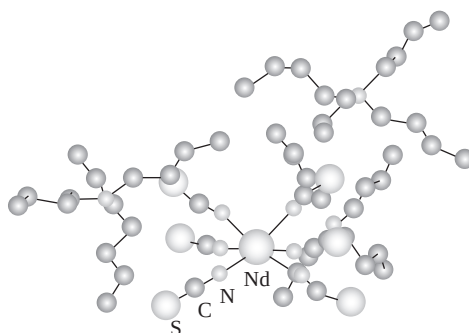


Figure 1.21 The structure of the complex $[(\text{C}_4\text{H}_9)_4\text{N}]_3\text{Nd}(\text{NCS})_6$ [20].

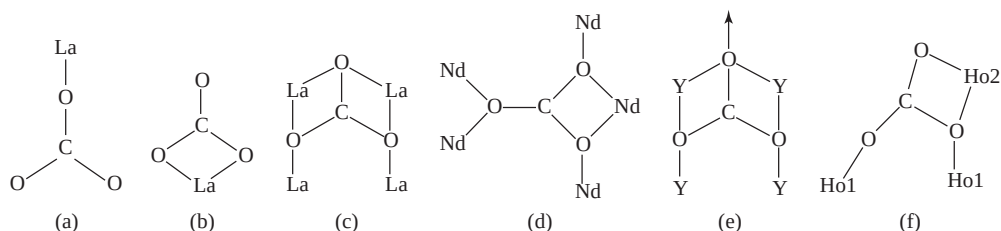


Figure 1.22 Six coordination modes for different rare earth carbonates.

and the coordination number of yttrium is nine (Figure 1.23). Two coordination places are taken up by hydroxyls through a μ_2 -bridge and the other seven are taken up by one carbonate group each (see Figure 1.22e) to form a polymer. Under thermo-hydration (250–300 °C) conditions, the heavier rare earth carbonates will end up as $\text{RE}_2(\text{OH})_4\text{CO}_3$, where RE = yttrium, holmium, erbium, thulium, or ytterbium. In the crystal of $\text{Ho}_2(\text{OH})_4\text{CO}_3$ (Figure 1.22f), holmium ions have two different coordination numbers: Ho1 ions have seven while Ho2 ions have eight, and the hydroxyls adopt μ_2 and μ_3 coordination modes to connect to the holmium ions.

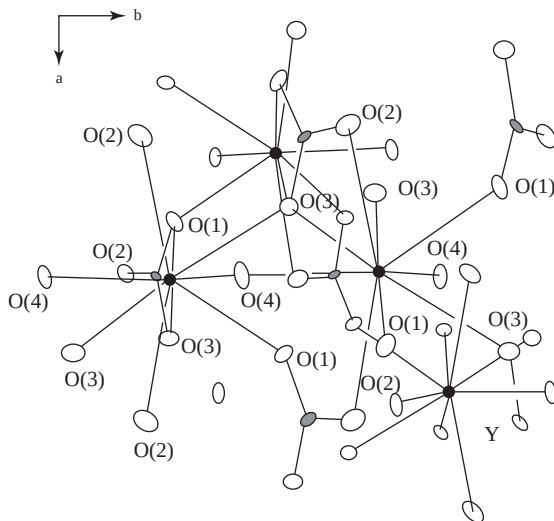


Figure 1.23 The structure of Y(OH)CO_3 [21]. (Reprinted from G.W. Beall, W.O. Milligan, and S. Mroczkowski, "Yttrium carbonate hydroxide," *Acta Crystallographica*, **B32**, no. 11, 3143–3144, 1976, with permission from International Union of Crystallography.)

1.5.5 Rare Earth Oxalate Compounds

Oxalic acid is a precipitation agent for rare earth ions. The solubility of rare earth oxalates range from 10^{-3} to 10^{-4} mol L^{-1} in neutral solutions. The precipitate usually contains coordinated and/or lattice water molecules, $\text{RE}_2(\text{C}_2\text{O}_4)_3 \cdot n \text{H}_2\text{O}$, where $n = 10$ for lanthanum to erbium and yttrium while $n = 6$ for holmium, erbium, thulium, ytterbium to lutetium and scandium.

Structure: In the $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ molecule, the central neodymium ion is nine coordinated by nine oxygen atoms of which six are contributed by the three oxalic groups and the other three come from water molecules. The coordinated polyhedron can be described as a destroyed tri-capped triangular prism. In this molecule, each oxalic group is bidentate coordinated from both sides and acts as a bridge to connect two neodymium ions. Therefore, the molecular formula is represented by $\{[\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}] \cdot 4\text{H}_2\text{O}\}_n$ (Figure 1.24).

In alkali metal salt solutions, the solubility of rare earth oxalates is higher compared with that in water and this is due to the formation of a double salt. Depending on their formation conditions, they exist in different forms. At least three of these forms have been structurally characterized: $\text{NH}_4\text{RE}(\text{C}_2\text{O}_4)_2 \cdot n\text{H}_2\text{O}$, where $n = 3$ for lanthanum to neodymium, $n = 1$ for samarium to thulium; $\text{K}_3\text{RE}(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ and $\text{K}_8\text{RE}_2(\text{C}_2\text{O}_4)_7 \cdot 14\text{H}_2\text{O}$ for the latter, $\text{RE} =$ terbium, dysprosium, erbium, ytterbium, and yttrium are analogs. The structure of the anion in $\text{K}_8[\text{RE}_2(\text{C}_2\text{O}_4)_7] \cdot 14\text{H}_2\text{O}$ is represented in Figure 1.25. It is worth noting that in this anion two different coordination modes are present for the oxalate group. One is a bidentate coordination from both sides of the oxalate group and the other is coordination by the bidentate ligand from one side only.

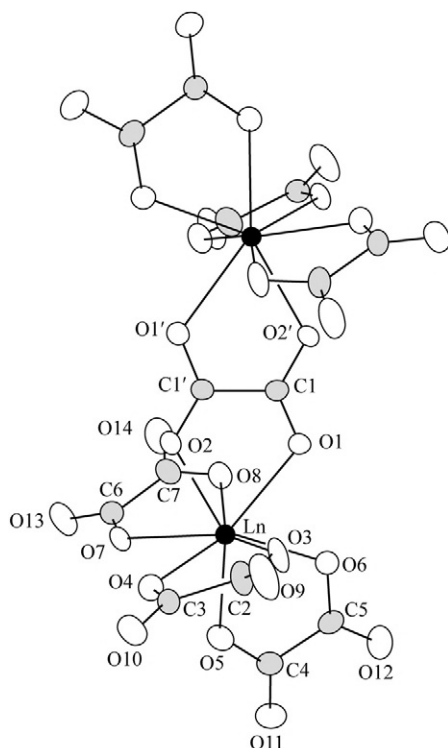


Figure 1.25 The anion structure in the complex $K_8RE_2(C_2O_4)_7 \cdot 14H_2O$ [23]. (Reprinted from *Inorganica Chimica Acta*, **82**, no. 2, I.A. Kahwa, F.R. Fronczek, and J. Selbin, "The crystal and molecular structures of potassium- μ -oxalato-di [tris-oxalato-lanthanate(III)]-14-hydrates $K_8[Ox_3LnOxLnOx_3]14H_2O$ [$Ln = Tb, Dy, Er, Yb, Y$]," 167–172, 1984, with permission from Elsevier.)

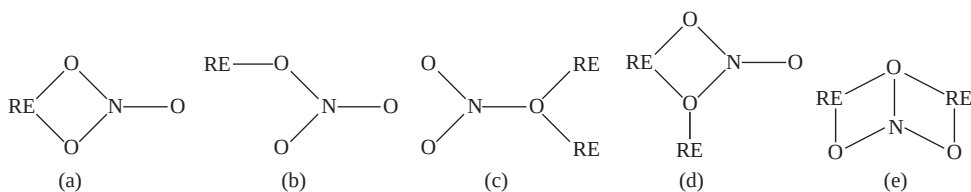


Figure 1.26 Five coordination modes in different rare earth compounds.

1.5.7 Rare Earth Phosphate Compounds

The solubility of rare earth phosphates is fairly low in neutral or acidic aqueous solutions, for example, the K_{sp} values for $LaPO_4$ and $CePO_4$ are 4.0×10^{-23} and 1.6×10^{-23} , respectively. Therefore, rare earth phosphates can be obtained by the reaction of soluble rare earth salts with alkali metal phosphates. Usually, the product has the following formula: $REPO_4 \cdot nH_2O$

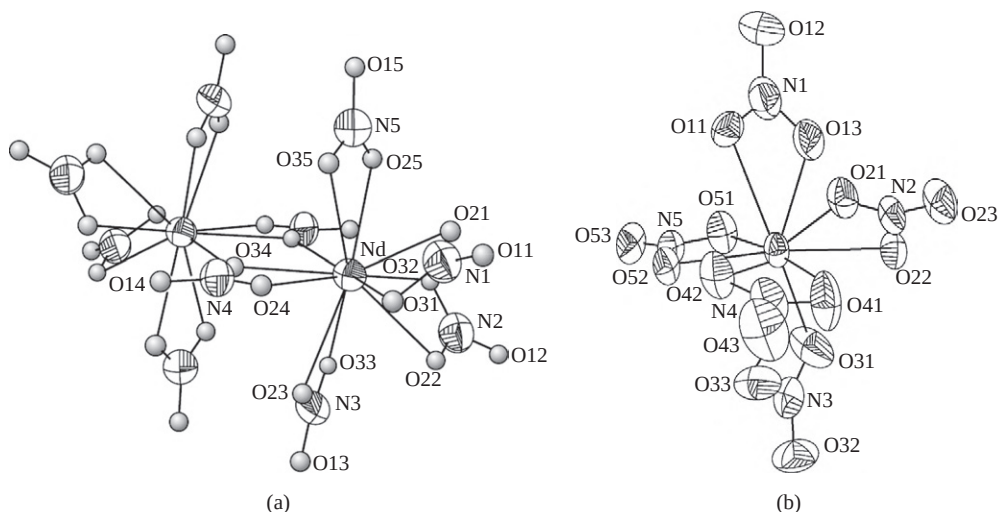


Figure 1.27 Anion structures in the complexes $\{[(\text{CH}_3)_3\text{NC}_{16}\text{H}_{33}]_3\text{Nd}(\text{NO}_3)_6\}_2$ (a) and $[(\text{C}_4\text{H}_9)_4\text{N}]_3\text{Nd}(\text{NO}_3)_6$ (b) [24].

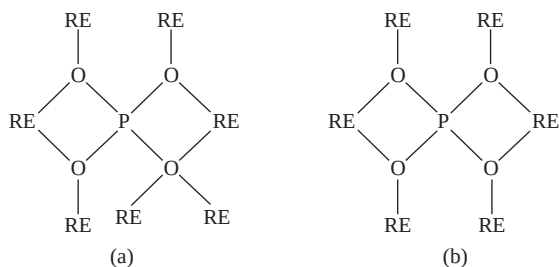


Figure 1.28 Two coordination modes for REPO_4 .

where $n = 0.5\text{--}4$. Single crystals of these phosphates may be obtained by melting them at high temperatures using lead pyro-phosphate as a medium.

Structure: These compounds can be divided into two groups according to structure.

For the lighter rare earth elements (lanthanum to gadolinium), REPO_4 belongs to the monoclinic system. The coordination number of the central ions is nine. All nine oxygen atoms are contributed by the phosphate groups. The coordination modes of the phosphate group is shown in Figure 1.28a. The coordination polyhedron has a destroyed pentagonal di-pyramid configuration. Five oxygen atoms form an equatorial plane with a rare earth ion in the center and two phosphate groups capped on the top and bottom of the equatorial plane. The coordination status of the central ion and the crystal structure of the REPO_4 compounds are shown in Figure 1.29.

The REPO_4 structure for the heavier rare earth elements (terbium to lutetium, yttrium, and scandium) belong to the tetragonal system. The coordination number of the central ions is

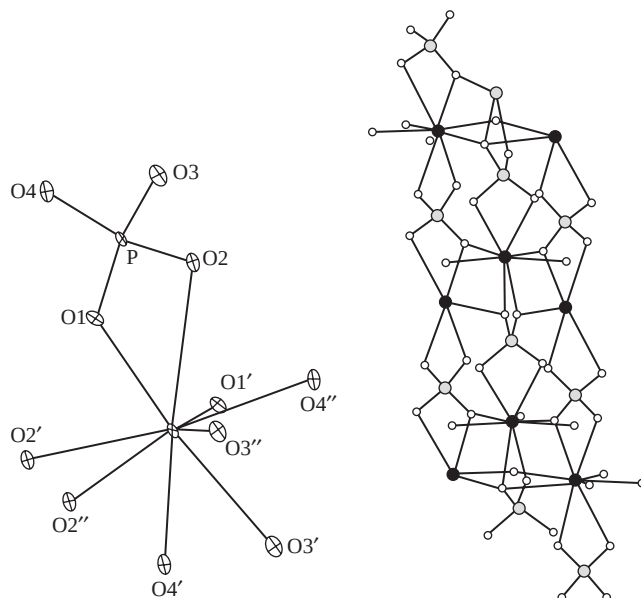


Figure 1.29 The coordination status of the central ion and the crystal structure of the REPO_4 (RE = lanthanum to gadolinium) compounds [25]. (Reprinted from *Inorganica Chimica Acta*, **109**, no. 2, D.F. Mullica, D.A. Grossie, and L.A. Boatner, "Coordination geometry and structural determinations of SmPO_4 , EuPO_4 and GdPO_4 ," 105–110, 1985, with permission from Elsevier.)

eight and they are filled by the phosphate, which forms a three-dimensional polymer. The coordination mode of the phosphate group is shown in Figure 1.28b.

1.5.8 Rare Earth Sulfate Compounds

When rare earth oxides, hydroxides, or carbonates react with dilute sulfuric acid, rare earth sulfate hydrates are obtained and they have the formula $\text{RE}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ where $n = 3, 4, 5, 6, 8$, and 9. The most common is $n = 9$ for lanthanum and cerium and $n = 8$ for praseodymium to lutetium and yttrium. Anhydrous compounds may be obtained by heating the respective rare earth sulfate hydrate at 155–260 °C, however, they easily absorb water to become hydrated again.

Structure: The $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ structure consists of an infinite network. In this molecule, lanthanum ions have two coordination environments (La1 and La2 in Figure 1.30a). La1 is coordinated to 12 oxygen atoms from six bidentate sulfate groups, while for La2 the coordination number is nine and consists of six oxygen atoms that are contributed from six water molecules and the other three are occupied by three monohapto sulfate groups. The coordination polyhedron has a tri-capped triangular prism configuration. The rest of the water molecules exist in the network through hydrogen bonds connected to oxygen atoms. Therefore, the formula may be represented as $\{[\text{La}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}\}_n$.

$\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ is also an infinite network. In this molecule, the coordination number of praseodymium is eight, among which four of the oxygen atoms come from four water molecules

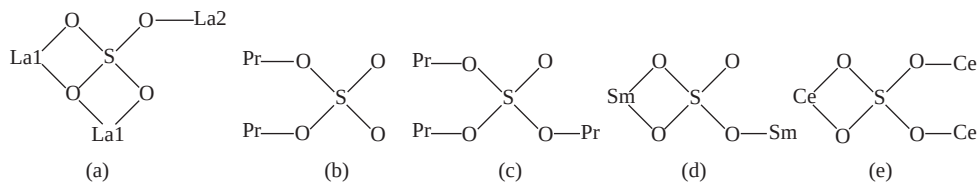


Figure 1.30 Five coordination modes of the sulfate group in different rare earth compounds.

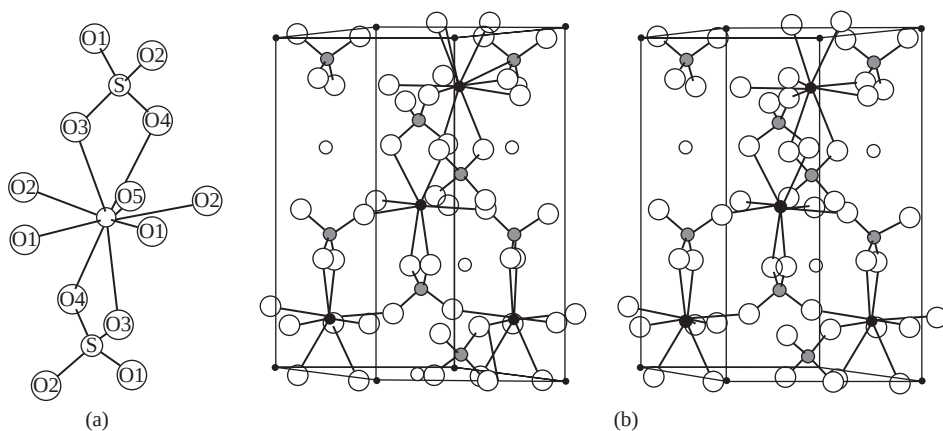


Figure 1.31 (a) The coordination status of the central cerium ion in $\text{NaCe}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$; (b) the crystal structure of $\text{NaCe}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ [26]. (Reprinted from O. Lindgren, "The crystal structure of sodium cerium(III) sulfate hydrate, $\text{NaCe}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, *Acta Chemica Scandinavica*, **A31**, 591–594, 1977, with permission from Forlagsforeningen Acta Chemica Scandinavica.)

and the rest come from four monohapto sulfate groups. The coordination polyhedron takes on a square antiprism configuration. In this molecule, the sulfate groups adopt two different coordination modes to coordinate to the central ions and they are present as bidentate (Figure 1.30b) and tridentate bridges (Figure 1.30c).

Rare earth double salts can be formed by the reaction of rare earth sulfates with a corresponding alkali or alkaline earth sulfate. For the former, the general formula is $\text{RE}_2(\text{SO}_4)_3 \cdot \text{M}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$, where $n = 0, 2$ or 8 . $\text{NH}_4\text{Sm}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ has an infinite chain-like configuration. In this molecule, samarium is coordinated to nine oxygen atoms, where three of them come from three water molecules and the rest come from two bidentate sulfate groups and two monohapto sulfate groups. The sulfate groups adopt a bridging coordination mode as shown in Figure 1.30d. The molecular formula should thus be $\{\text{NH}_4[\text{Sm}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}] \cdot \text{H}_2\text{O}\}_n$.

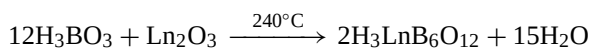
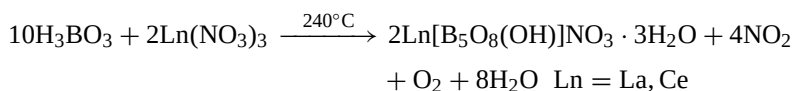
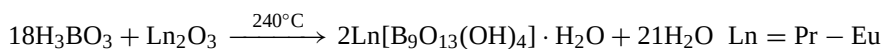
The crystal structure of $\text{NaCe}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ has a trigonal system and the central cerium ion is coordinated to nine oxygen atoms. The oxygen atoms, four from monohapto sulfate groups and one from a water molecule form an equatorial plane, and each bidentate sulfate group cap the top and bottom positions of the equatorial plane (Figure 1.31a). Sodium ions are coordinated to six oxygen atoms from the sulfate groups and they bridge between the cerium ions to form an infinite network (Figure 1.31b).

1.5.9 Rare Earth Borate Compounds

Many borate structures exist and are fairly interesting. They are stable in air and have been considered for use as important nonlinear optical materials and as hosts for luminescent materials, particularly when the excitation of high energy photons is required, for example, $\text{LuMgB}_5\text{O}_{11}$: Tb, Ce and SrB_4O_7 : Eu.

In the borates, the boron atoms are coordinated to oxygen atoms forming either a tetrahedral or a triangular configuration. $[\text{BO}_4]$ or $[\text{BO}_3]$ units can exist individually in the borate. However, it is more common for them to form a one-dimensional chain, two-dimensional plane, or three-dimensional network by sharing corners and by sharing edges in a few instances.

In 2001 Lin and coworkers found that in a sealed reaction system containing melted boric acid and trivalent rare earth cations, a series of new rare earth polyborates were obtained. The structure of these resulting products was found to be highly dependent on reaction conditions, such as the starting materials used, the temperature, the water content, the ratio of RE/B, and the radius of the rare earth ions. The lighter rare earth elements, lanthanum, cerium, praseodymium or neodymium, prefer to form $\text{Ln}[\text{B}_5\text{O}_8(\text{OH})_2]$ or $\text{Ln}[\text{B}_8\text{O}_{11}(\text{OH})_5]$. When the radius is contracted further $\text{Ln}[\text{B}_6\text{O}_9(\text{OH})_3]$ ($\text{Ln} = \text{Sm} - \text{Lu}$) is formed. These formation reactions can be summarized as follows:



As representative examples the $[\text{LnB}_6\text{O}_{11}]$ layer in $\text{Ln}[\text{B}_8\text{O}_{11}(\text{OH})_5]$ or $\text{Ln}[\text{B}_9\text{O}_{13}(\text{OH})_4] \cdot \text{H}_2\text{O}$, and the $[\text{LnB}_5\text{O}_9]$ layer in $\text{Ce}[\text{B}_5\text{O}_8(\text{OH})]\text{NO}_3 \cdot 3\text{H}_2\text{O}$ are presented in Figure 1.32. The fundamental building blocks of (a) $\text{Ln}[\text{B}_8\text{O}_{11}(\text{OH})_5]$, (b) $\text{Ln}[\text{B}_9\text{O}_{13}(\text{OH})_4] \cdot \text{H}_2\text{O}$, and (c) $\text{Ce}[\text{B}_5\text{O}_8(\text{OH})]\text{NO}_3 \cdot 3\text{H}_2\text{O}$ are shown in Figure 1.33.

1.6 Outlook

The unique properties of rare earth elements, for instance, the hard Lewis acid character, the sharp, wide-range (from near IR to UV) long-lived luminescence, and the high magnetic moment with long electron-spin relaxation time, etc. and the potential applications of their complexes, are the main driving forces for the development of the coordination chemistry of rare earth. In this chapter, fundamental rules for rare earth complexes and the coordination chemistry of rare earth with some simple but important ligands are briefly discussed. At present, some of these aspects are still not clear enough. There is no doubt that the inherent properties of these complexes will be understood more quantitatively as research tools and technologies are improved.

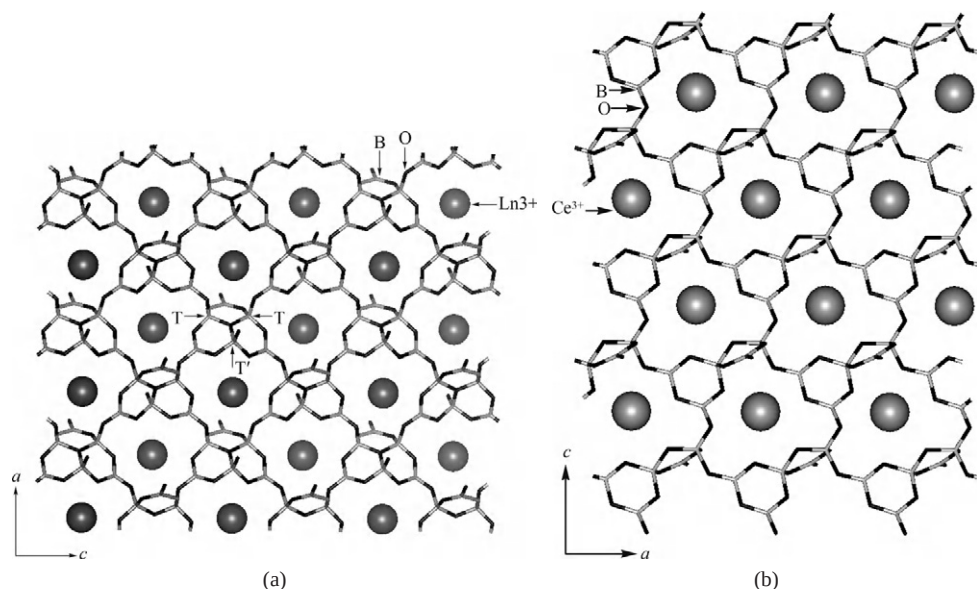


Figure 1.32 (a) The $[\text{LnB}_6\text{O}_{11}]$ layer in $\text{Ln}[\text{B}_8\text{O}_{11}(\text{OH})_5]$ and $\text{Ln}[\text{B}_9\text{O}_{13}(\text{OH})_4]\cdot\text{H}_2\text{O}$; (b) the $[\text{LnB}_5\text{O}_9]$ layer in $\text{Ce}[\text{B}_5\text{O}_8(\text{OH})]\text{NO}_3\cdot 3\text{H}_2\text{O}$. The borate network is displayed in stick style and the balls represent the rare earth cations [27]. (Reprinted with permission from J.H. Lin, Y.X. Wang, L.Y. Li, *et al.*, “Rare earth borates: an overview from the structural chemistry viewpoint,” in G. Meyer, D. Naumann and L. Wesemann (eds.), *Inorganic Chemistry in Focus II*, 293–378 (Figure 16.21). © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. © 2005.)

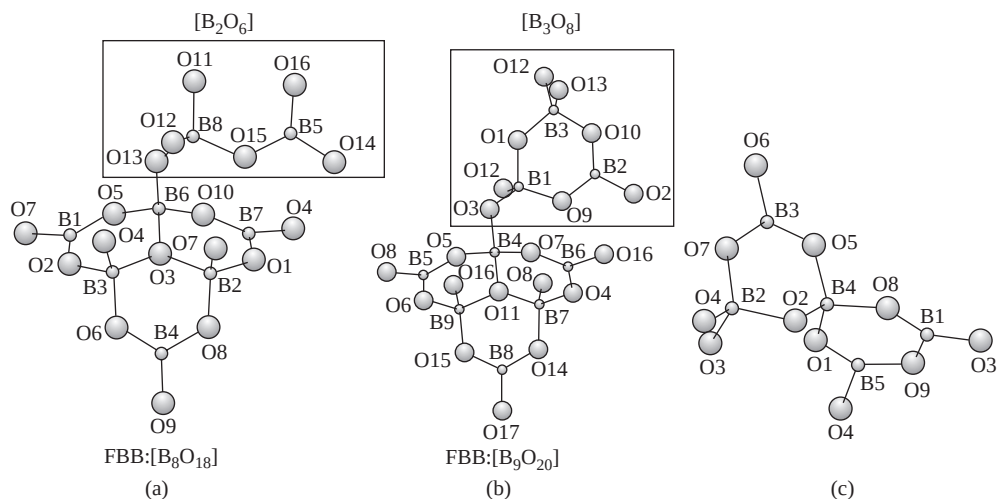


Figure 1.33 The fundamental building block of: (a) $\text{Ln}[\text{B}_8\text{O}_{11}(\text{OH})_5]$; (b) $\text{Ln}[\text{B}_9\text{O}_{13}(\text{OH})_4]\cdot\text{H}_2\text{O}$; and (c) $\text{Ce}[\text{B}_5\text{O}_8(\text{OH})]\text{NO}_3\cdot 3\text{H}_2\text{O}$ [28]. (Reprinted with permission from L.Y. Li, X.L. Jin, G.B. Li, *et al.*, “Novel rare earth polyborates. 2. Syntheses and structures,” *Chemistry of Materials*, **15**, 2253–2260, 2003. © 2003 American Chemical Society.)

Acknowledgments

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β -Diketonate Lanthanide Complexes

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2.1 Introduction

1,3-Diketones, also frequently known as β -diketones, are a family of the most widely investigated ligands in lanthanide complexes [1–9]. They usually occur as prototropic tautomerisms, the so called keto–enol tautomerisms, in solutions and in solids, as evidenced by solution ^1H NMR (nuclear magnetic resonance) spectroscopy and single-crystal structural determinations. A simple example is the keto–enol tautomerism equilibrium of acetylacetone (HL^1) as shown in Figure 2.1. Figure 2.2 shows the keto–enol tautomerism equilibria between three species of beta-diketo, beta-keto–enol, and beta-enol–keto, where the substitutes R_1 and R_2 are different. The positions of the keto–enol tautomerism equilibria are determined by the solvent polarities and the substituents. The presence of bulkier substituents seems to be the driving force capable of shifting the tautomeric equilibrium toward the less stabilized β -diketo form, as revealed by a systematic study recently carried out by Bertolasi and coworkers [10], where the β -diketones occurred as only a small percentage of the beta-diketo tautomer in the solution, as opposed to in the solid where they were almost exclusively in the beta-keto–enol form.

A β -diketone behaves as a monobasic acid, as the proton on the α -carbon of its beta-diketo form or the enol proton of beta-keto–enol form can readily be deprotonated in an appropriate pH range, depending on the $\text{p}K_a$ values of the β -diketones. Thus the β -diketone acts as a mononegative O–O' bidentate ligand to coordinate to a lanthanide ion, and forms stable lanthanide complexes. As tris(β -diketonate) lanthanide(III) complexes are electrically neutral, and can dissolve in some water immiscible organic solvents, such as chloroform and benzene, in early work many β -diketones were synthesized as lanthanide extractants [11]. The β -diketones have been recognized as efficient sensitizers, so called “antennae,” to achieving high harvest lanthanide emissions, owing to the effectiveness of the energy transfer from the β -diketonate



Figure 2.1 Keto–enol tautomerism equilibrium of acetylacetone.

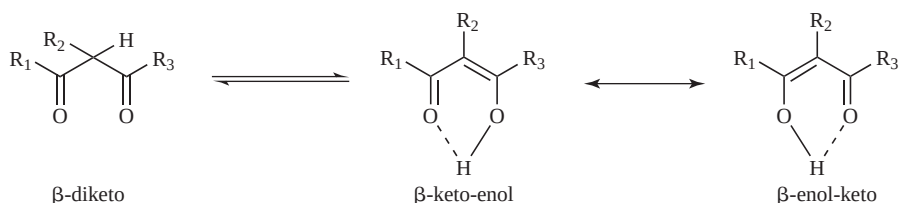


Figure 2.2 Keto–enol tautomerism equilibrium of acetylacetone derivatives.

to the Ln^{3+} cation. Thus this family of complexes have developed rapidly, and attracted long-lasting interest, due partially to their easy synthesis, but mainly to their promising prospects in widespread applications, ranging from materials science to biomedical analysis. In the past few decades, many of the intriguing applications envisioned for lanthanide β -diketonates have included light conversion molecular devices, nuclear resonance shift reagents, organic–inorganic hybrid photonic and nanobiophotonic devices, molecular switching and sensing devices, organic electroluminescent devices, liquid-crystalline materials, stains and labels for immunoassays and the imaging of biological cells, diode lasers, optical fibers, and supramolecular assemblies. These topics have been covered in many reviews [1–9, 12–21]. The structural characterization plays an important role in the development of the chemistry of β -diketonate lanthanide complexes. In the following discussions, the main attention will be focused on recent developments of structurally characterized β -diketonate lanthanide complexes.

2.2 Types of β -Diketones Used for Lanthanide Complexes

2.2.1 Mono(β -Diketone) Ligands

2,4-Pentanedione (HL^1) (also known as acetylacetone), which was prepared by Claisen more than 100 years ago, is the simplest aliphatic (mono) β -diketone ligand. Its development and important properties and applications have recently been elegantly reviewed by Reedijk [8]. A vast number of HL^1 derivatives have been synthesized so far. Among them, fluorinated β -diketones have received special attention [22–35], and are summarized in Figure 2.3. This type of ligands were synthesized with the purposes of enhancing the extraction power, by reducing the acidity of the β -diketones [22], and of improving photoluminescence and electroluminescence properties, by reducing the level of the higher energy frequency oscillator C–H vibrational quenching [23]. Additional advantages of using fluorinated β -diketone ligands

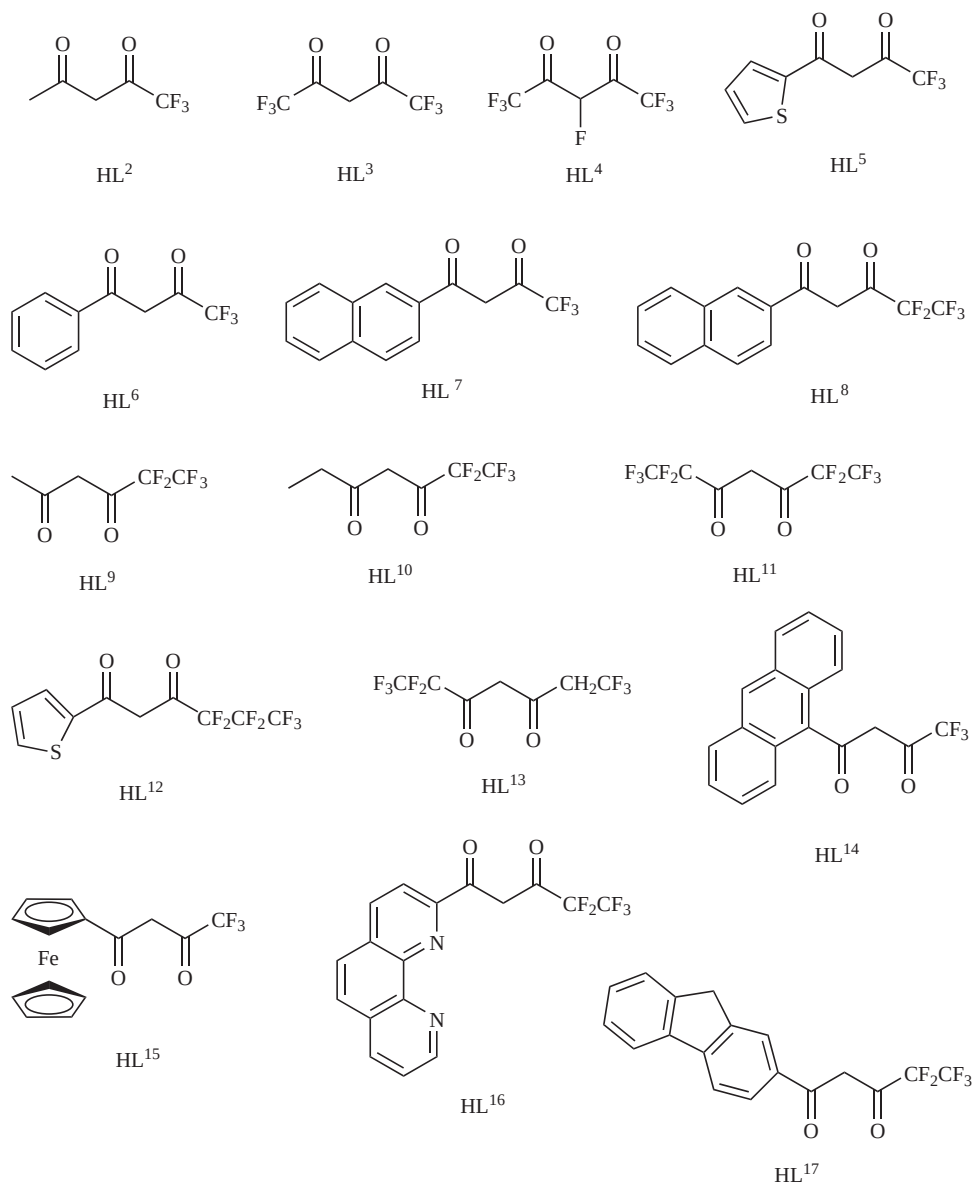


Figure 2.3 Some representative fluorinated β -diketones.

include enhanced thermal stability and volatility of their lanthanide complexes, which are of significance in practical applications.

Although lanthanide emitters have the potential advantages of sharp emission bands, with high purities of colors ranging from blue to red, compared with fluorescent organic

emitters in photonic electroluminescent (EL) applications, the emission intensity of lanthanide ions is usually very weak due to the poor charge transportation capabilities of the lanthanide complexes, hindering their applications in EL displays. In order to improve the performance, many lanthanide β -diketonates, grafted with hole-transporting carbazole and triphenylamine, or electron-transporting 1,3,4-oxadiazole groups, have been reported. Some representative nonfluorinated β -diketones [36–45] based on the parent 1,3-propanedione are shown in Figure 2.4. If the β -diketones were grafted with H-bond forming groups such as hydroxyl, for example H_2L ²⁷ as shown in Figure 2.4, a high dimensional supramolecular network could be formed [40]. If the β -diketones have additional coordination groups like pyridine, such as HL ^{31,32,35} [43, 45], they could often function as useful building blocks for the construction of supramolecular assemblies.

The next category of β -diketones are 4-acyl-1-phenyl-3-methyl-5-pyrazolones (see Figure 2.5) and their analogs of 3-phenyl-4-acyl-5-isoxazolones (see Figure 2.6). The latter type of β -diketones have stronger acidities (lower pK_a values) than the former, and have recently been studied as promising light conversion molecular devices [46–51].

Figure 2.7 shows a family of inorganic analogs of β -diketonates, aryl-functionalized imidodiphosphinate ligands (HL ^{46–48}) [52], which are bulky ligands around the lanthanide ion, providing shell-type protection of the ion from coordinated solvent molecules. HL ⁴⁸ consists of fully fluorinated *N*-(*P,P*-di(pentafluorophinoyl))-*P,P*-dipentafluorophenylphosphinimidic acid, and can form ideal fluorinated shells around all visible and NIR (near-infrared) emitting lanthanides [52c].

2.2.2 Bis(β -Diketones) Ligands

Molecular structures of some representative bis(β -diketones) ligands are shown in Figure 2.8.

Bis(β -diketones) ligands, were proved to be efficient motifs or structural elements for self-assembling highly luminescent metallo-supramolecular lanthanide complexes [53–59] and representative examples (H_2L ^{49–61}) are shown in Figure 2.8. Special attention has also been paid to the use of enantiomerically pure bis- β -diketones of H_2L ^{54–56} [58]. H_2L ⁵⁰ in Figure 2.8 was shown to have the ability to form d–f–d molecular magnetic materials [60].

2.2.3 Dendritic β -Diketones Ligands

Dendrimers are tree-like branched macromolecules that consist of a core, one or more dendrons, and surface groups [61]. Several recently reported dendrimer β -diketones are shown in Figure 2.9. They have attracted special interest due to their unique structures and properties. The tree-like shape of dendrimers provides a large surface area that can be grafted with chromophores such as carbazole, resulting in a large absorption cross-section and, accordingly, the efficient capture of photons, as well as a tuning of the carrier-transporting capability and site-isolation effect [62].

The other interesting properties of dendritic molecules are the site-isolation effect of dendrons, creating a micro-environment to prevent the intermolecular interaction and avoiding a self-quenching effect. Indeed, it was found that the dendritic shell could achieve site isolation of the Ln^{3+} cation and maximize the luminescent characteristics. The introduction of such functional groups as carrier-transporting carbazole groups into the dendrimer diketone

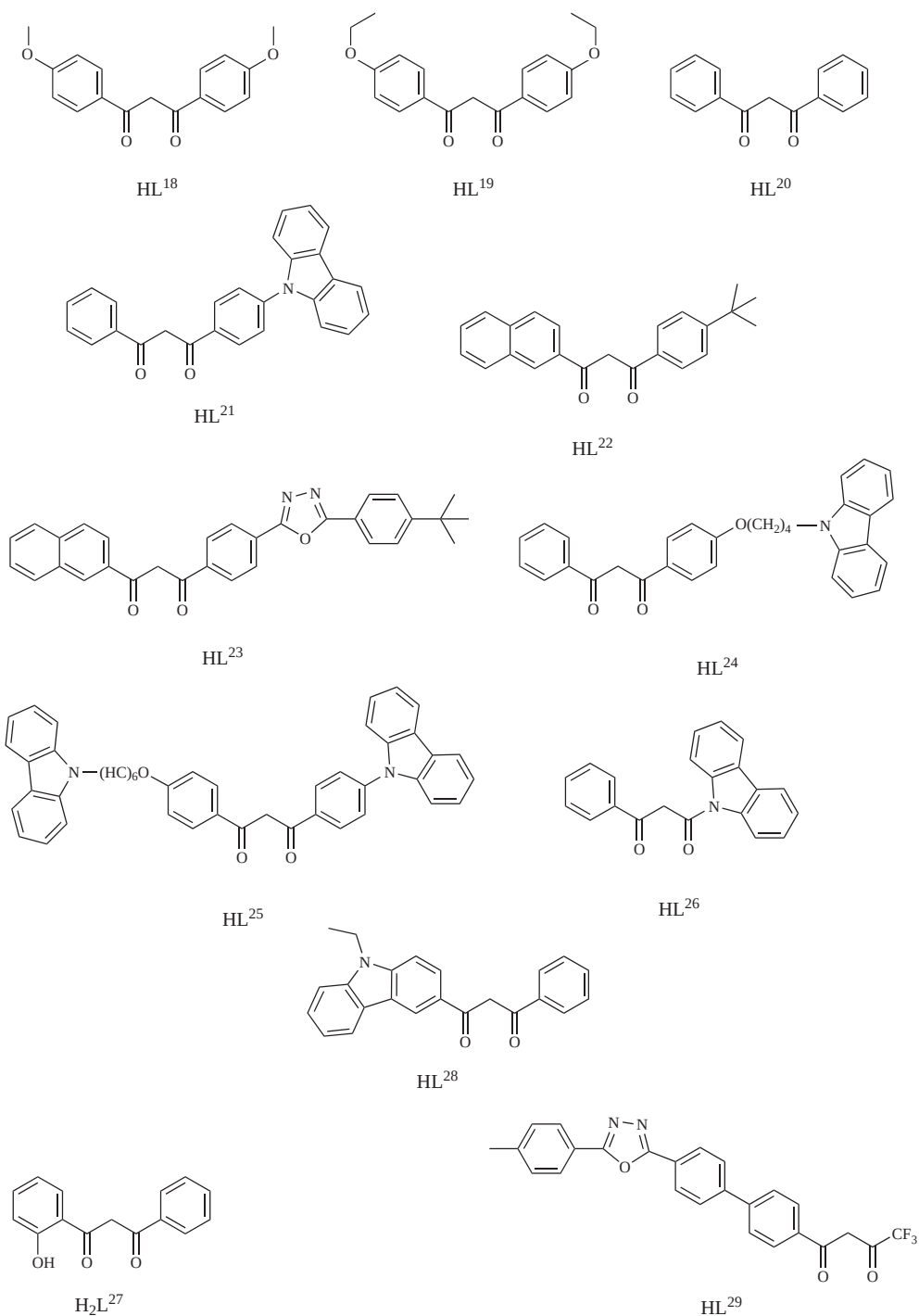


Figure 2.4 Some representative nonfluorinated β -diketones based on parent 1,3-propanedione.

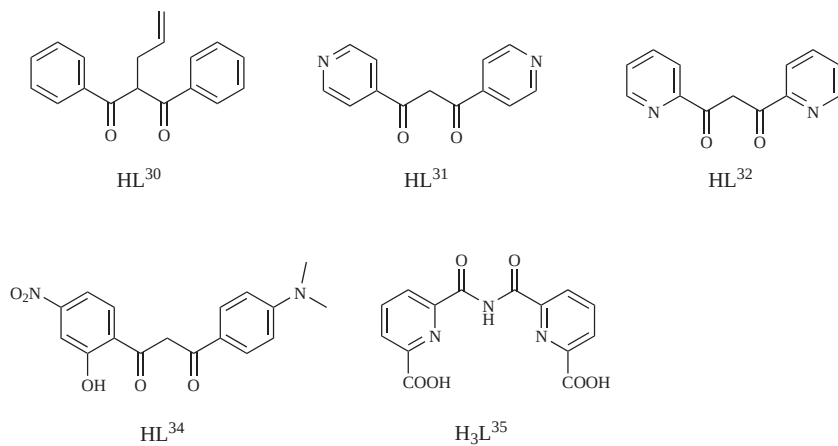


Figure 2.4 (Continued)

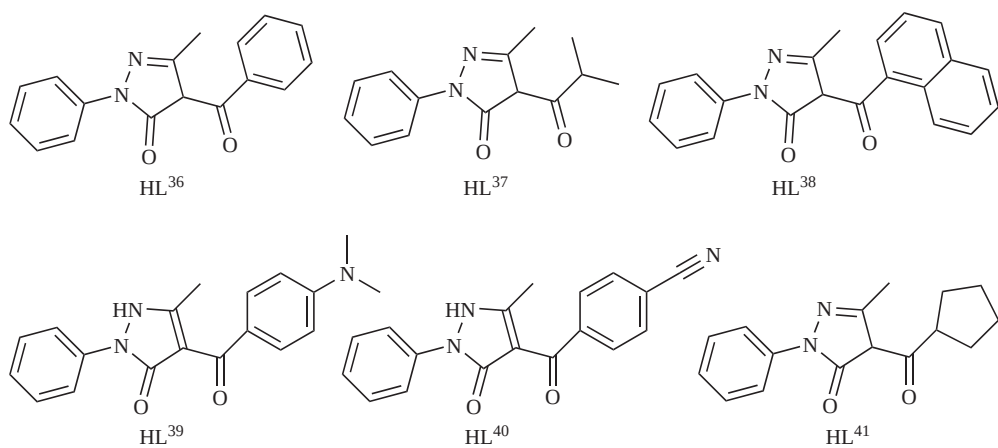


Figure 2.5 Molecular structures of 1-phenyl-3-methyl-4-acyl-5-pyrazolones.

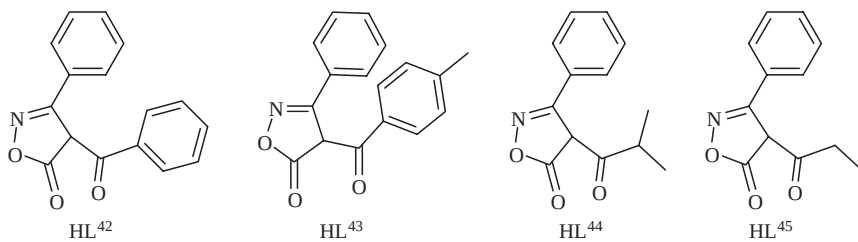


Figure 2.6 Molecular structures of 3-phenyl-4-acyl-5-isoxazolones.

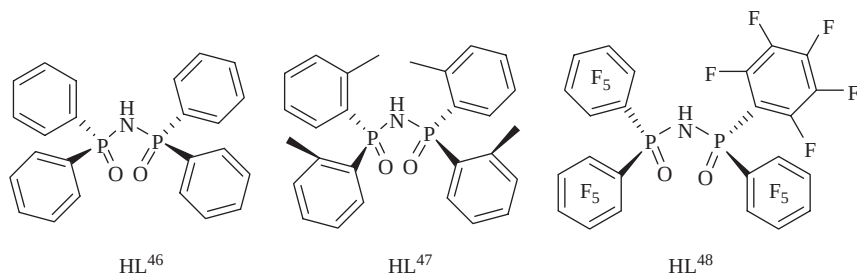


Figure 2.7 Aryl-functionalized imidodiphosphinate ligands.

lanthanide complexes would be an attractive aspect of dendrimer chemistry. The dendritic β -diketonate ligands consisting of dibenzoylmethane cores, Fréchet-type poly(aryl ether) dendrons, and the carrier-transporting group-grafted peripheral functional groups may not only tune the triplet energy level, but also exhibit a strong light-harvesting potential, resulting in an intense emission from the central lanthanide(III) ion via sensitization. Therefore, some dendritic β -diketonates (see Figure 2.9) and their corresponding lanthanide complexes have been synthesized [62–65]. Among such wide ranging applications as drug delivery, light harvesting, solar cells, organic light-emitting diode (OLED)s, and sensors [66–68], the application of β -diketone lanthanide dendrimer as (OLED) materials have attracted particular attention, due to the presence of controllable key features such as intermolecular interactions and charge transport, which are important for all OLED.

2.3 β -Diketonate Lanthanide Complexes

2.3.1 Mononuclear Lanthanide Complexes with β -Diketones

Coordination numbers of mononuclear β -diketonate lanthanides complexes are generally high, varying from 6 to 10, and strictly depend on the ionic radii of the lanthanide ions, the β -diketones, and the reaction medium and conditions, such as temperature or ligand to metal ratio. As lanthanide ions have large ionic radii, and are typically hard Lewis acids, the bonding in their complexes is thus electrostatic and non-directional. As a result, the coordination geometries are often irregular, and are governed by steric factors. In the following section, particular attention will be paid to the crystal structure studies of representative mononuclear β -diketonate lanthanide complexes recently reported.

2.3.1.1 Six-Coordinated Lanthanide Complexes with β -Diketones

Pikramenou and coworkers structurally characterized six-coordinated $[\text{Tb}(\text{L}^{46})_3]$, $[\text{Eu}(\text{L}^{47})_3]$, and $[\text{Tb}(\text{L}^{47})_3]$, [52a,b] in addition to $[\text{Ln}(\text{L}^{48})_3]$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Er}, \text{Yb}, \text{Y}, \text{Gd}$) [52c]. The crystal structures of $\text{Eu}(\text{L}^{46})_3$ and $\text{Eu}(\text{L}^{47})_3$ (see Figure 2.10) revealed that three anionic L^{46} or L^{47} ligands adopt a bidentate coordination mode to produce a six-coordinate metal ion as there are no coordinated solvent molecules. The low coordination number is stabilized by a hydrophobic shell around the central metal ion formed by the 12 *o*-tolyl groups

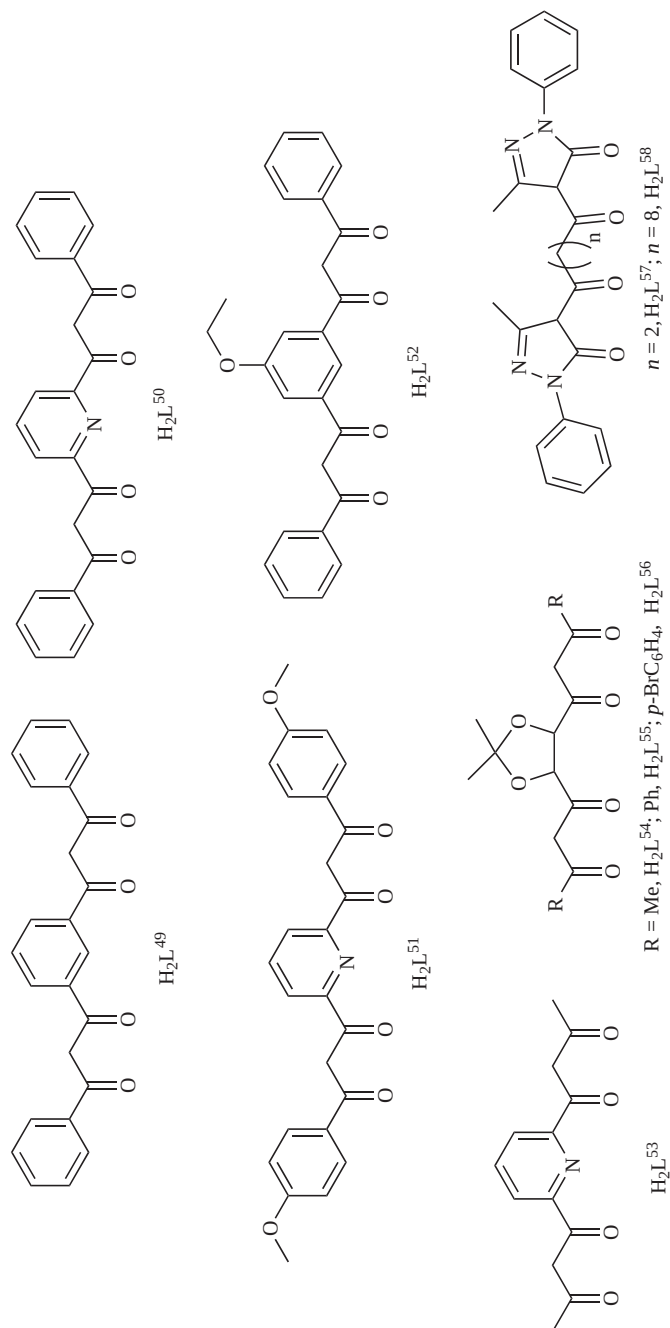


Figure 2.8 Molecular structures of some representative bis(β-diketones) ligands.

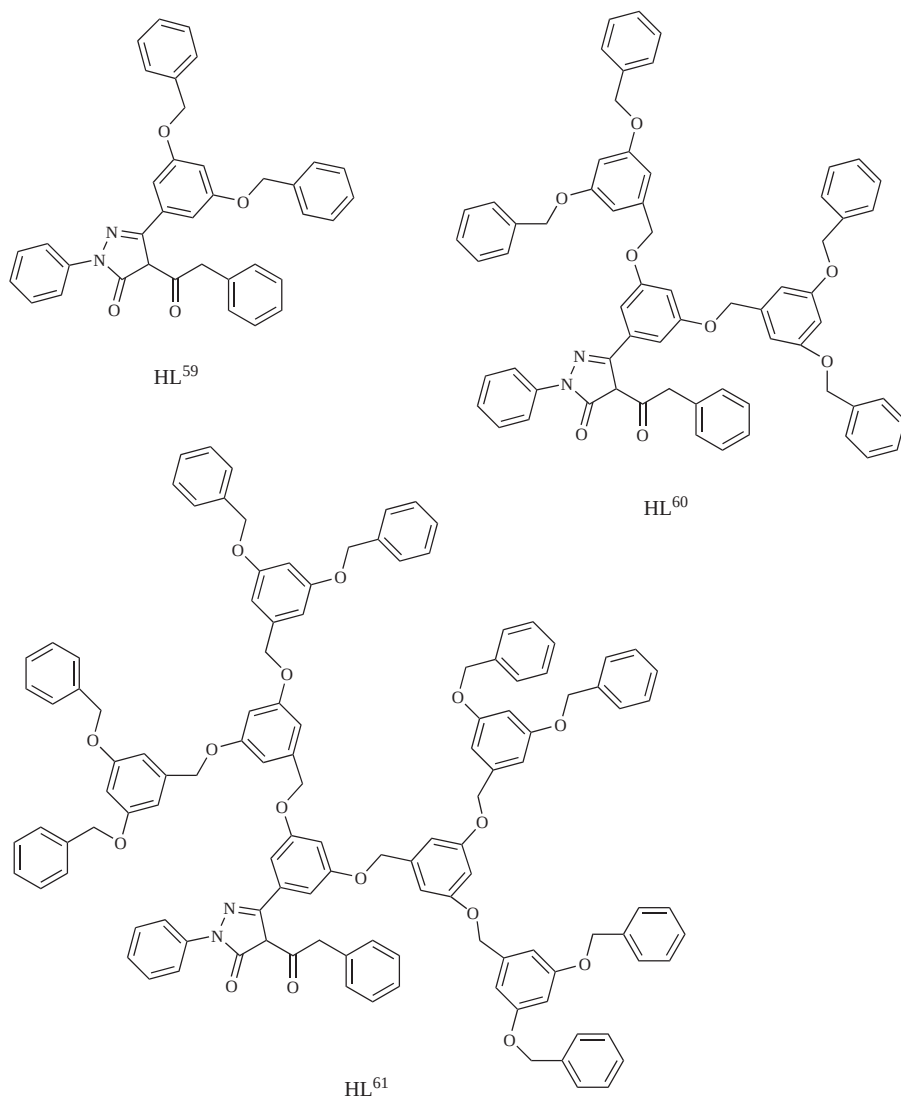


Figure 2.9 Molecular structures of some representative dendrimer dendritic β -diketonates ligands.

with 6 of the 12 methyl groups being located above the faces of the distorted octahedron defined by the oxygen atoms, shielding the approach of any solvent molecules. The average Eu–O bond length for the structure is 2.28 Å, with average P–N and P–O bond lengths of 1.59 and 1.51 Å, respectively. The lifetimes of [Eu(L^{46,47})₃] and [Tb(L^{46,47})₃] in the solid state are of the orders of magnitude of milliseconds. These very long lifetimes are characteristic of an absence of deactivating, non-radiative pathways. Luminescence quantum yields measured for [Eu(L⁴⁶)₃] and [Tb(L⁴⁶)₃] in dry CH₃CN upon excitation at 273 nm were derived to be 1.3%

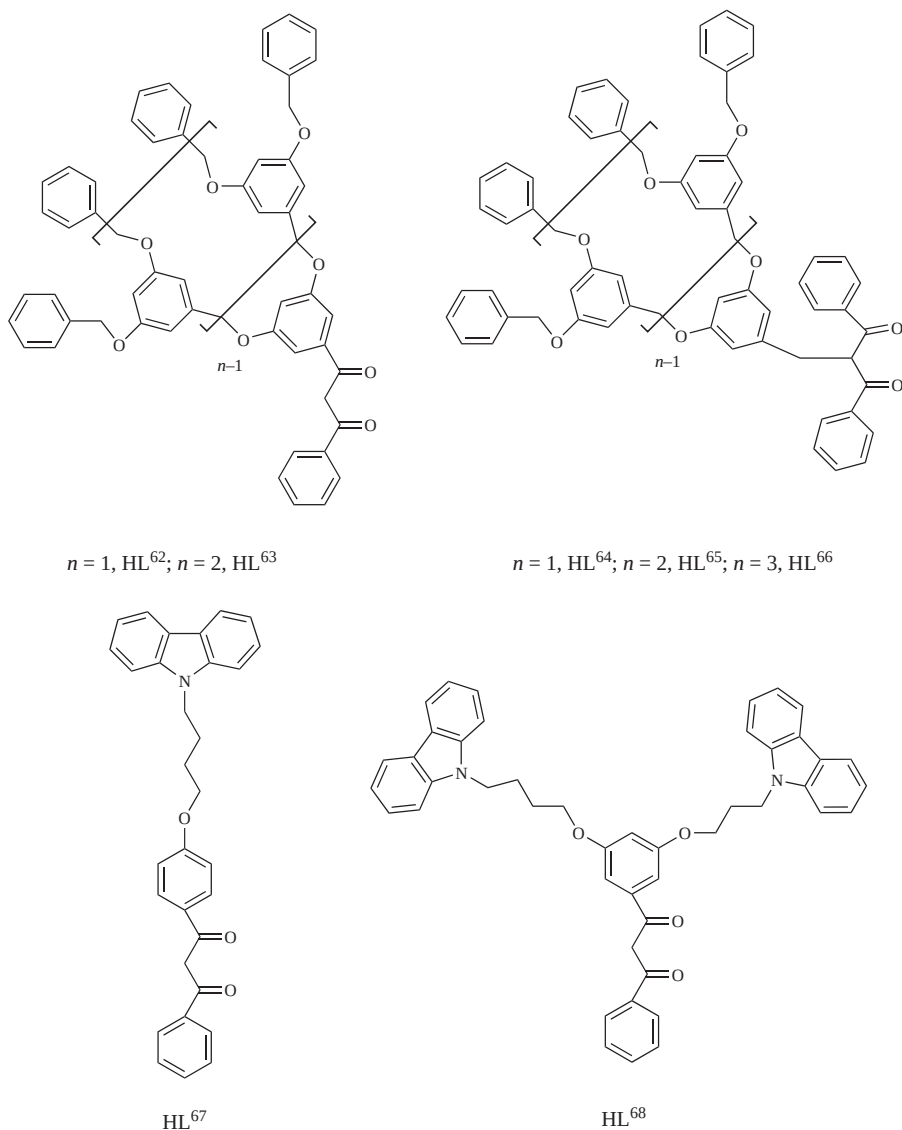
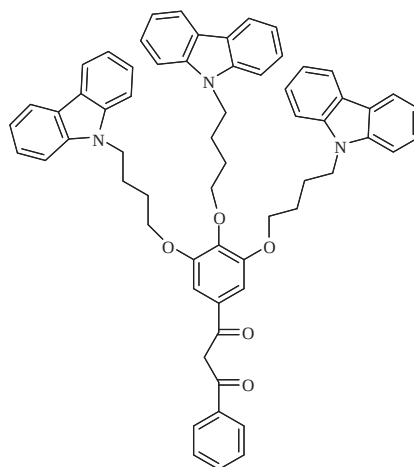
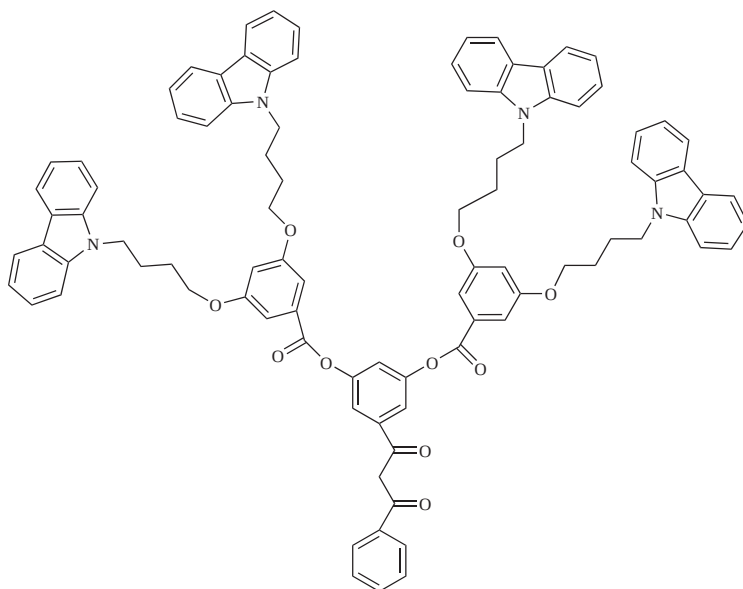


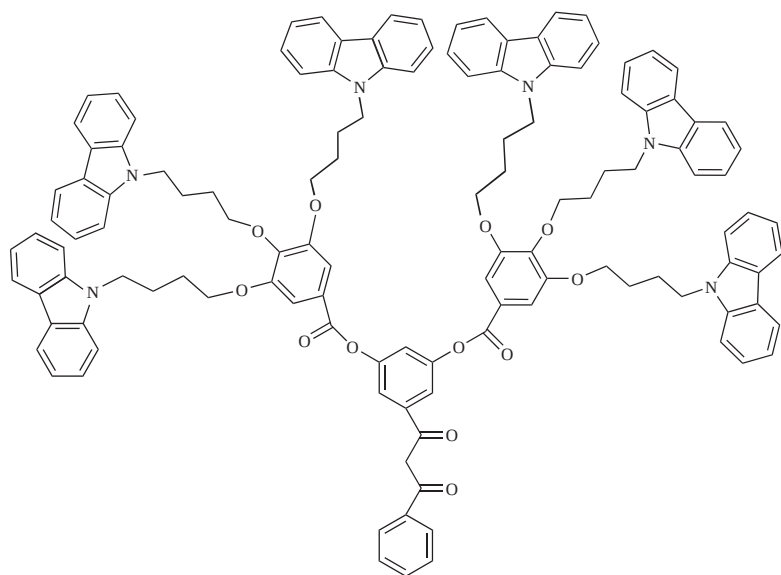
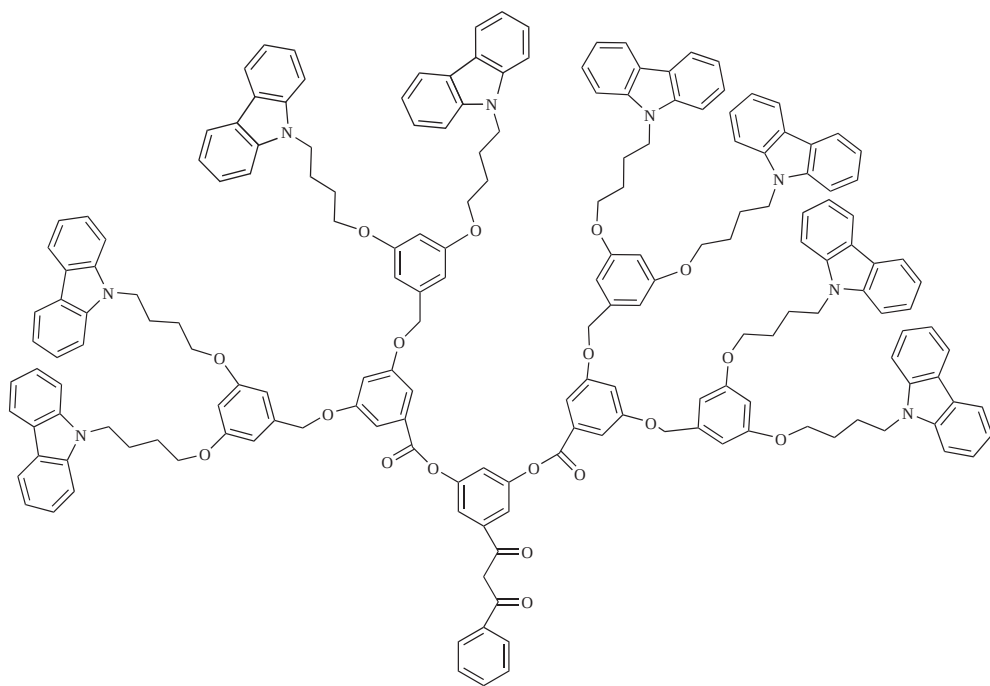
Figure 2.9 (Continued)

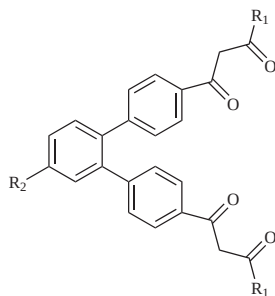
for $[\text{Eu}(\text{L}^{46})_3]$ and 20% for $[\text{Tb}(\text{L}^{46})_3]$. It was also shown that L^{46} and L^{47} are suitable for sensitizing luminescence for *all* the lanthanides that emit in the visible range, namely, Sm(III), Eu(III), Tb(III), and Dy(III). In dry CH_3CN , the lifetimes of the Eu^{3+} ($^5\text{D}_0$) level in $[\text{Eu}(\text{L}^{47})_3]$ and the Tb^{3+} ($^5\text{D}_4$) level in $[\text{Tb}(\text{L}^{47})_3]$ attained were 1.33 and 1.89 ms, respectively.

In order to eliminate potentially quenching oscillators of N–H and C–H in the imidodiphosphate binding unit, HL ⁴⁸ and its lanthanide complexes $[\text{Ln}(\text{L}^{48})_3]$, in which $\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}$,

HL⁶⁹HL⁷⁰**Figure 2.9** (Continued)

Gd, Tb, Dy, Er, Yb, Y, or Gd, were later synthesized [52c], and structurally characterized. The crystal structure of $[\text{Nd}(\text{L}^{48})_3]$ is shown in Figure 2.11. The photophysical studies showed that fluorination of the alkyl chains results in more emissive lanthanide complexes for both visible and NIR emission with the luminescence lifetimes for $[\text{Nd}(\text{L}^{48})_3]$, $[\text{Er}(\text{L}^{48})_3]$, and $[\text{Yb}(\text{L}^{48})_3]$ in deuterated acetonitrile being found to be 0.044, 0.741, and 1.111 ms, respectively.

HL⁷¹HL⁷²**Figure 2.9** (Continued)



$R_1 = CF_3$, $R_2 = SO_2Cl H_2L$ ⁷³
 CF_3 , $R_2 = H H_2L$ ⁷⁴
 C_3F_3 , $R_2 = SO_2Cl H_2L$ ⁷⁵
 C_3F_3 , $R_2 = H H_2L$ ⁷⁶

Figure 2.9 (Continued)

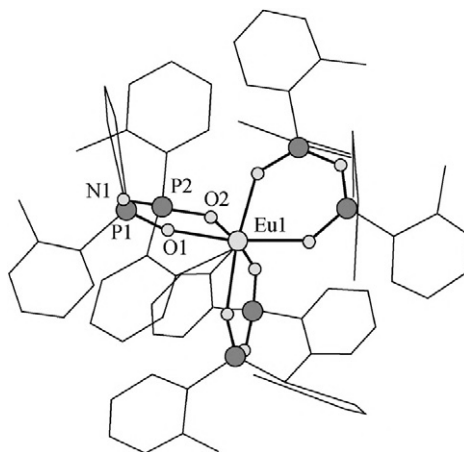


Figure 2.10 X-ray crystal structure of $[Eu(L^{47})_3]$ [52b]. (Reproduced with permission from S.W. Magennis, S. Parsons and Z. Pikramenou, "Assembly of hydrophobic shells and shields around lanthanides," *Chemistry – A European Journal*, 2002, **8**, 5761–5771. © Wiley-VCH Verlag GmbH & Co. KGaA.)

2.3.1.2 Seven-Coordinated Lanthanide Complexes with β -Diketones

He *et al.* recently structurally characterized two seven-coordinate β -diketonate monoporphyrinate ytterbium(III) complexes of $[Yb(TFPP)(L^1)(H_2O)]$ (see Figure 2.12) and $[Yb(TCNPP)(L^1)(CH_3OH)](CH_3COCH_3)$ (see Figure 2.13), where H_2TFPP = 5,10,15,20-tetra(4-fluorophenyl)porphyrin and H_2TCNPP = 5,10,15,20-tetra(4-cyanophenyl)porphyrin [69]. The results revealed that there is only one solvent water or methanol coordinating to ytterbium(III) in the complexes. Photoluminescence spectroscopy of the complexes in solution showed that the water and methanol that bind to the ytterbium(III) ion quench the NIR emission of the lanthanide, resulting in a shorter lifetime of $\sim 2.4 \mu s$.

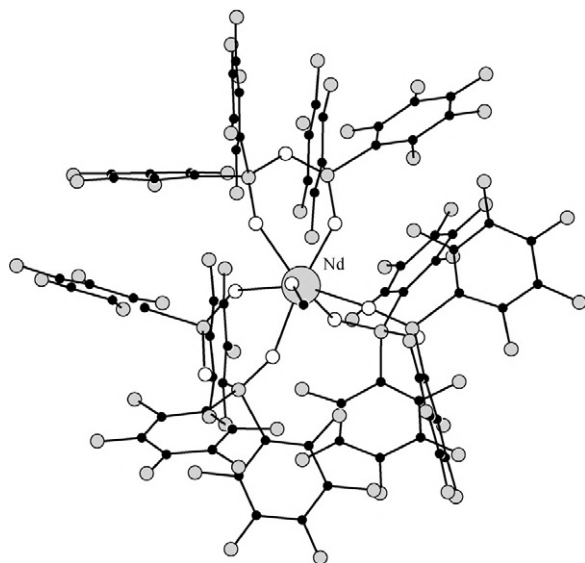


Figure 2.11 X-ray crystal structure of $[\text{Nd}(\text{L}^{48})_3]$ [52c]. (Reproduced with permission from P.B. Glover, A.P. Bassett, P. Nockemann, B.M. Kariuki, R. Van Deun and Z. Pikramenou, “Fully fluorinated imidodiphosphate shells for visible- and near IR-emitting lanthanides: hitherto unexpected effects of sensitizer fluorination on lanthanide emission properties,” *Chemistry – A European Journal*, 2007, **13**, 6308–6320. © Wiley-VCH Verlag GmbH & Co. KGaA.)

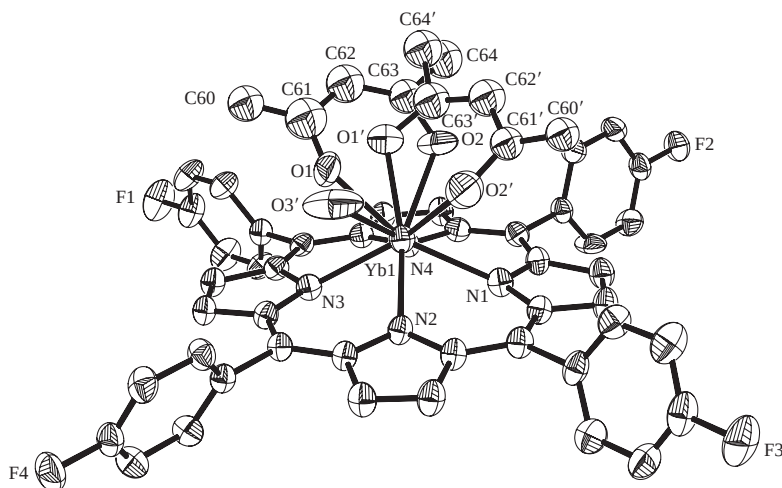


Figure 2.12 The ORTEP diagram of $[\text{Yb}(\text{TFPP})(\text{L}^1)(\text{H}_2\text{O})]$ with 40% thermal ellipsoid probability. All hydrogen atoms are omitted for clarity [69]. (Reprinted from *Inorganic Chemistry Communications*, **11**, H. He, A.G. Sykes, D. Galipeau, S.W. Ng and M. Ropp, “Crystallography and photoluminescence properties of β -diketonate monophyrinate ytterbium(III) complexes,” 1051–1053, 2008, with permission from Elsevier.)

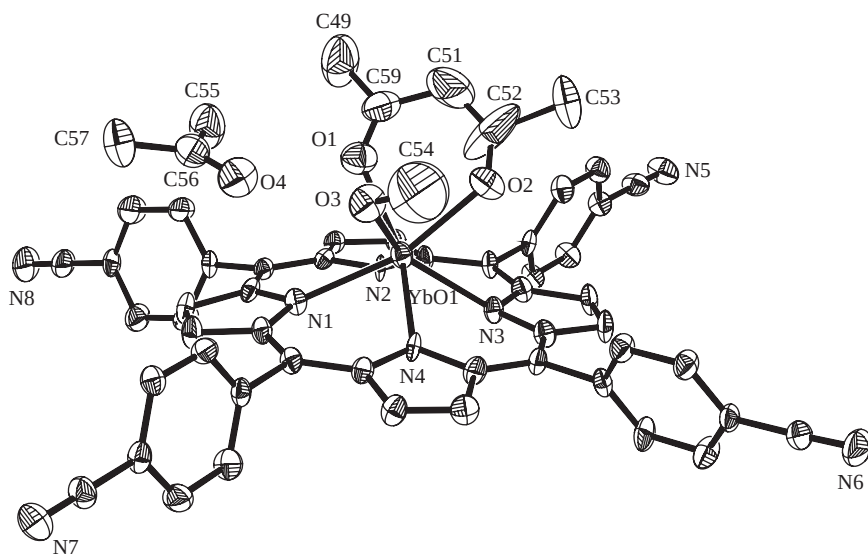


Figure 2.13 The ORTEP diagram of $[\text{Yb}(\text{TCNPP})(\text{L}^1)(\text{CH}_3\text{OH})](\text{CH}_3\text{COCH}_3)$ with 50% thermal ellipsoid probability [69]. (Reprinted from *Inorganic Chemistry Communications*, **11**, H. He, A.G. Sykes, D. Galipeau, S.W. Ng and M. Ropp, "Crystallography and photoluminescence properties of β -diketonate monoporphyryne ytterbium(III) complexes," 1051–1053, 2008, with permission from Elsevier.)

2.3.1.3 Eight-Coordinated Lanthanide Complexes with β -Diketones

The family of eight-coordinate β -diketonate lanthanides are the most widely studied, as the complexes are coordinately saturated, or almost coordinately saturated, with the emissive properties being optimized if the appropriate ligands are chosen. Li and Huang *et al.* [48] reported the synthesis, characterization, and photophysical properties of $\text{Eu}(\text{L}^{38-40})_3(\text{H}_2\text{O})_2$ and $\text{Eu}(\text{L}^{38-40})_3(\text{TPPO})(\text{H}_2\text{O})$, where TPPO = triphenylphosphine oxide. An ORTEP molecular structure diagram determined by single-crystal X-ray diffraction for the asymmetric unit of $\text{Eu}(\text{L}^{40})_3(\text{TPPO})(\text{H}_2\text{O})$ is shown in Figure 2.14. The coordination geometry of the metal center is best described as a distorted bicapped trigonal prism with the trigonal prism being composed of six oxygen atoms (O1, O2, O3, O5, O6, O8). Of these, O1, O2 and O5, and O6 are from two β -diketones, and O3 and O8 are from the third diketone and a water molecule, respectively. Another two oxygen atoms (O4, O7) cap the two quadrilateral faces O3–O5–O8–O1 and O2–O6–O3–O1, respectively.

Wang and Huang and coworkers [70] reported the synthesis, photoluminescent, and electroluminescent properties of two Eu(III) mixed-ligand complexes, $[\text{Eu}(\text{L}^5)_3(\text{PBO})]$ and $[\text{Eu}(\text{L}^5)_3(\text{PBT})]$ [PBO = 2-(2'-pyridyl)-1,3-benzoxazole, and PBT = 2-(2'-pyridyl)-1,3-benzothiazole]. Single-crystal X-ray diffraction analysis of $[\text{Eu}(\text{L}^5)_3(\text{PBO})]$ (see Figure 2.15) showed that it is eight-coordinated by three bidentate L^5 anions and one bidentate N,O-chelated PBO molecule. This is a rare example of a preference for N–O coordination rather than N–N coordination by a lanthanide ion.

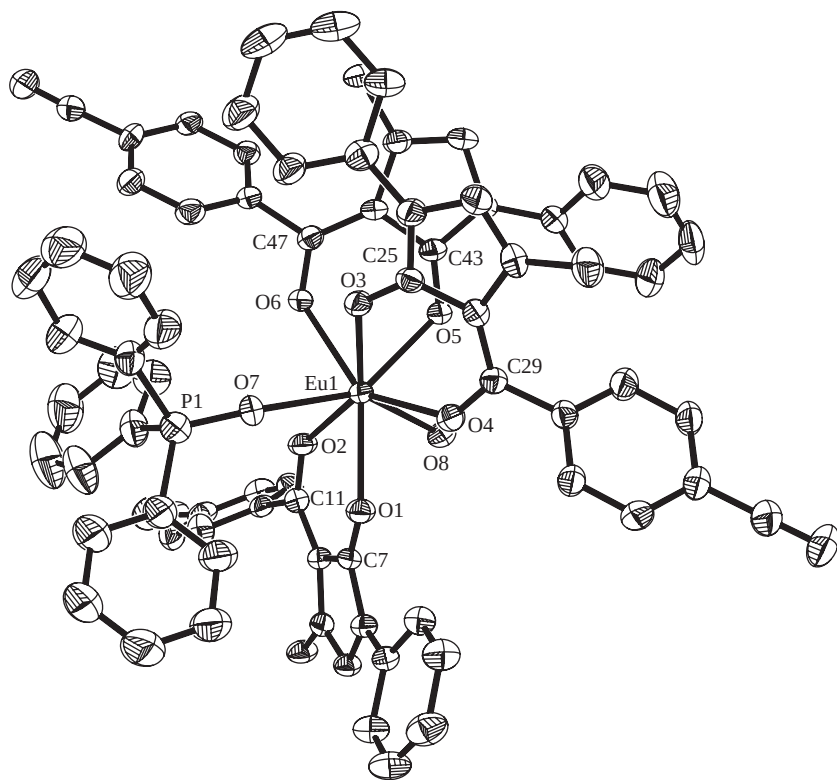


Figure 2.14 ORTEP diagram of $\text{Eu}(\text{L}^{40})_3(\text{TPPO})(\text{H}_2\text{O})$ with the thermal ellipsoids drawn at the 30% probability level and the H atoms removed for clarity [48]. (Reprinted with permission from M. Shi, F. Li, T. Yi, D. Zhang, H. Hu and C. Huang, “Tuning the triplet energy levels of pyrazolone ligands to match the $^5\text{D}_0$ level of europium(III),” *Inorganic Chemistry*, **44**, 8929–8936, 2005. © 2005 American Chemical Society.)

Tanase *et al.* [40] reported mononuclear lanthanoid complexes with the general formula of $[\text{Ln}(\text{HL}^{27})_3(\text{CH}_3\text{OH})_2] \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ ($\text{Ln}^{3+} = \text{Pr}, \text{Nd}, \text{Eu}, \text{Gd}$) by using a new β -diketone H_2L^{27} . As shown in Figure 2.16, the single-crystal X-ray structure studies on $[\text{Eu}(\text{HL}^{27})_3(\text{CH}_3\text{OH})_2] \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ indicate that the Eu(III) ion is eight-coordinated by six oxygen atoms from three monodeprotonated HL^{27} and by two oxygen atoms from two coordinated methanol molecules, and that the coordination geometry is based on a distorted square-antiprism. A three-dimensional network is formed by the intramolecular hydrogen bonding ($\text{OH} \cdots \text{O}$), intermolecular hydrogen-bonding interactions between the coordinated methanol molecule and the non-coordinated methanol molecule.

By using polyfluorinated β -diketones of HL^3 and HL^4 , and the polyfluorinated phosphine oxide of tris(pentafluorophenyl)phosphine oxide $[\text{OP}(\text{C}_6\text{F}_5)_3]$ as ligands, Monguzzi *et al.* [23c] synthesized and structurally characterized the NIR emissive Er^{3+} complexes, $[\text{Er}(\text{L}^3)_3(\text{OP}(\text{C}_6\text{F}_5)_3)_2]$, and $[\text{Er}(\text{L}^4)_3(\text{OP}(\text{C}_6\text{F}_5)_3)_2]$ (see Figures 2.17 and 2.18). Very recently, by using perfluorinated nitrosopyrazolone 3-trifluoromethyl-4-hydroxyimino-1-perfluorophenyl-1*H*-pyrazol-5-one and $\text{OP}(\text{C}_6\text{F}_5)_3$ as ligands, they have reported new types

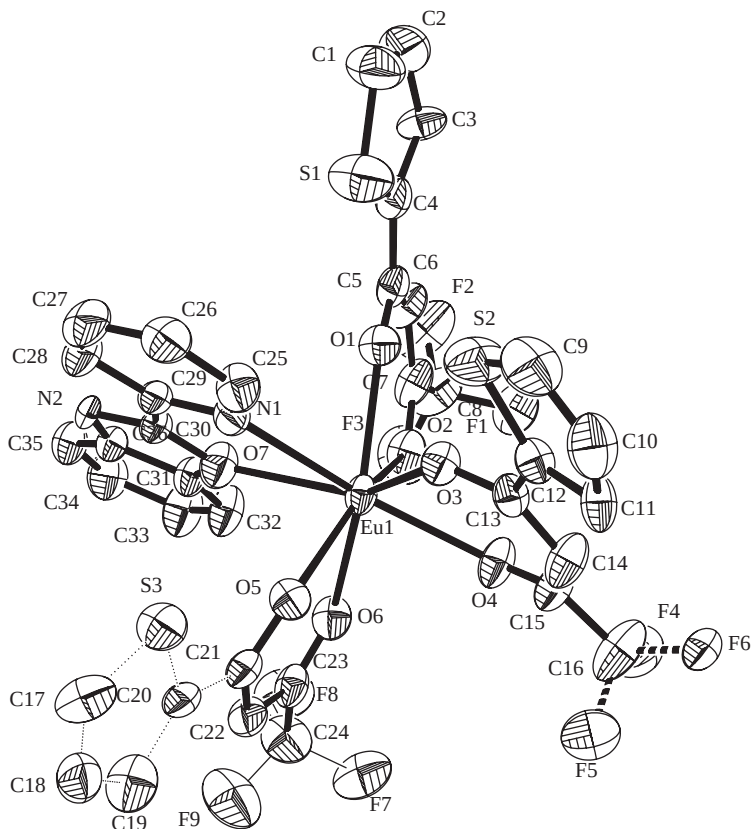


Figure 2.15 Asymmetric unit of $[\text{Eu}(\text{L}^5)_3(\text{PBO})]$ with atom numbering scheme and thermal ellipsoids (30%) [70]. (Reproduced with permission from L.H. Gao, M. Guan, K.Z. Wang, L.P. Jin and C.H. Huang, “A comparative study of the optical and electroluminescent properties of Eu^{III} complexes with TTA and 2-(2'-pyridyl)azoles: the crystal structure of $[\text{Eu}(\text{TTA})_3(\text{PBO})]$,” *European Journal of Inorganic Chemistry*, 2006, **2006**, 3731–3737. © Wiley-VCH Verlag GmbH & Co. KGaA.)

of NIR emissive Er^{3+} complexes that possess an NIR emission with lifetimes as long as 16 μs . [71]. These chelates have the advantageous characteristics of nonhygroscopic, solution processable, high solubility providing processability, low optical gap enabling visible region pumping by commercially available LEDs, and the long NIR emission lifetimes.

Zhang *et al.* have recently xerogel-bonded Ln complex ($\text{Ln} = \text{Er}, \text{Nd}, \text{Yb}, \text{Sm}$) materials and structurally characterized the NIR luminescent model complexes $\text{Ln}(\text{L}^8)_3\text{phen}$ ($\text{Ln} = \text{Er}, \text{Nd}, \text{Yb}, \text{Sm}$, and $\text{phen} = 1,10\text{-phenanthroline}$) (see Figure 2.19 for the molecular structure of the Nd complex) [35].

2-Phenyl-4-aryl-5-isoxazolones are an interesting family of β -diketone ligands for preparing promising Eu(III) and Tb(III) complex-based light-conversion molecular devices [51a,b]. Reddy *et al.* [51a,b] reported crystal structures for such types of ligand HL^{42} based lanthanide complexes $\text{Tb}(\text{L}^{42})_3(\text{H}_2\text{O})_2$ (Figure 2.20) and $\text{Eu}(\text{L}^{42})_3\cdot\text{phen}$ (Figure 2.21).

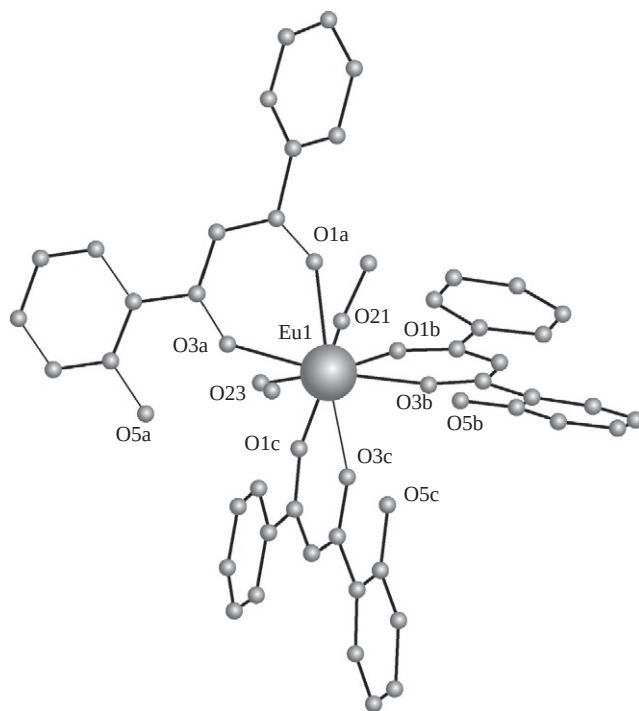


Figure 2.16 View of the molecular structure of $[\text{Eu}(\text{HL}^{27})_3(\text{CH}_3\text{OH})_2] \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$. The non-coordinated methanol molecule and hydrogen atoms were omitted for clarity [40]. (Reprinted from *Polyhedron*, **28**, S. Tanase, M. Viciano-Chumillas, J.M.M. Smits, R. de Gelder and J. Reedijk, “Copper(II) and lanthanoid(III) complexes of a new β -diketonate ligand with an appended non-coordinating phenol group,” 457–460, 2009, with permission from Elsevier.)

This group have also recently reported the crystal structure of $\text{Ln}(\text{L}^{42})_3(\text{DPEPO})$ [$\text{Ln} = \text{Eu}$, Tb; DPEPO = bis(2-(diphenylphosphino)phenyl) ether oxide] [51c]. As shown in the crystal structure of $\text{Eu}(\text{L}^{42})_3(\text{DPEPO})$ in Figure 2.22, the central Eu^{3+} ion is coordinated by six oxygen atoms furnished by three bidentate β -diketonate ligands and two oxygen atoms from the bidentate DPEPO ligand. The overall molecular geometry is distorted square prismatic. Interestingly, there are molecular ladder structures that are held together by $\pi \cdots \pi$ and intermolecular hydrogen-bonding interactions (see Figure 2.23). The replacement of the solvent molecules in $\text{Eu}(\text{L}^{42})_3(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})$ by a chelating phosphine oxide leads to an impressive enhancement in both the overall quantum yield (from 2 to 30%) and the $^5\text{D}_0$ lifetime (from 250 to 1060 μs). Furthermore, the substantial contribution of the ancillary ligand to the overall sensitization process for Eu^{3+} -centered luminescence in $\text{Eu}(\text{L}^{42})_3(\text{DPEPO})$ is confirmed by an increase in the intrinsic quantum yield from 26 to 59% and the substantial enhancement of sensitization yield (Φ_{sen}) from 8 to 45%.

By using a polyfluorinated alkyl group containing β -diketone HL^{17} as the ligands, and chelate phosphine oxide ligands of 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene oxide (DDXPO) and bis(2-(diphenylphosphino)phenyl) ether oxide (DPEPO) as co-ligands,

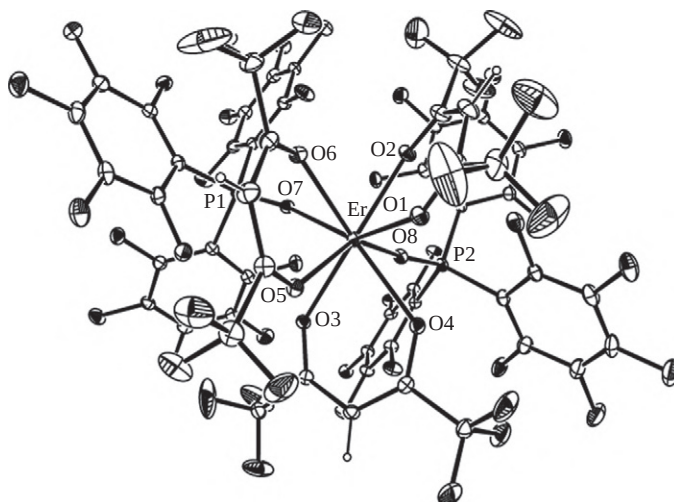


Figure 2.17 ORTEP view of the $[\text{Er}(\text{L}^3)_3(\text{OP}(\text{C}_6\text{F}_5)_3)_2]$ molecule [23c]. (Reprinted with permission from A. Monguzzi, R. Tubino, F. Meinardi *et al.*, “Novel Er^{3+} perfluorinated complexes for broad-band sensitized near infrared emission,” *Chemistry of Materials*, **21**, 128–135, 2009. © 2009 American Chemical Society.)

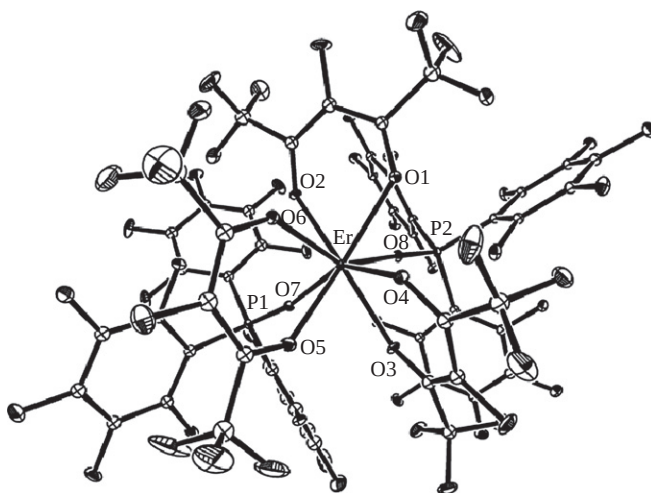


Figure 2.18 ORTEP view of the $[\text{Er}(\text{L}^4)_3(\text{OP}(\text{C}_6\text{F}_5)_3)_2]$ molecule [23c]. (Reprinted with permission from A. Monguzzi, R. Tubino, F. Meinardi *et al.*, “Novel Er^{3+} perfluorinated complexes for broad-band sensitized near infrared emission,” *Chemistry of Materials*, **21**, 128–135, 2009. © 2009 American Chemical Society.)

$\text{Eu}(\text{L}^{17})_3(\text{DDXPO})$ and $\text{Eu}(\text{L}^{17})_3(\text{DPEPO})$ were recently synthesized and structurally characterized (see Figures 2.24 and 2.25), with the coordination polyhedra being a distorted square antiprism [34]. The former complex has a solid-state photoluminescence quantum yield of 48%, about two times higher than that of the latter (28%).

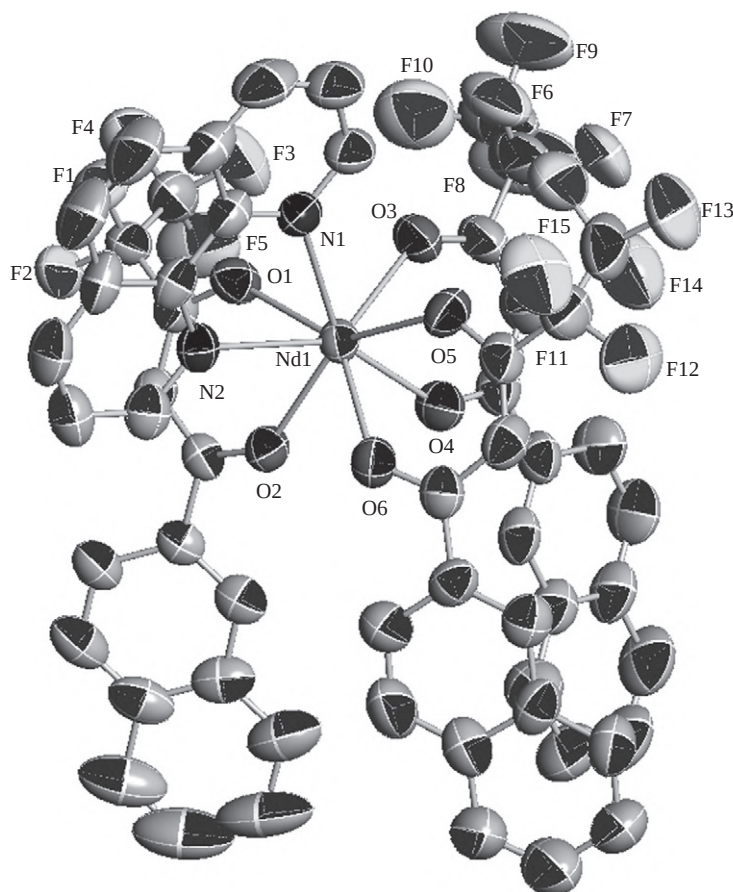


Figure 2.19 ORTEP plot for $\text{Nd}(\text{L}^8)_3\text{phen}$ with ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity [35]. (Reproduced from J. Feng, J.B. Yu, S.Y. Song, L.N. Sun, W.Q. Fan, X.M. Guo, S. Dang and H.J. Zhang, “Near-infrared luminescent xerogel materials covalently bonded with ternary lanthanide [Er(III), Nd(III), Yb(III), Sm(III)] complexes,” *Dalton Transactions*, **13**, 2406–2414, 2009, by permission of the Royal Society of Chemistry.)

Bunzli *et al.* reported the crystal structure of $\text{Nd}(\text{L}^{34})_3(\text{phen})$ (see Figure 2.26), which is eight-coordinated with a square antiprism coordination polyhedron [44]. They demonstrated that the 1,3-diketone ligands HL^{34} containing push–pull chromophores are suitable for visible light excitation of NIR emitting lanthanide ions. The main advantage of their reported ligand is its lowest-energy absorption transition, which extends into the visible range and allows excitation of lanthanide luminescence with wavelengths up to 550 nm.

Pettinari *et al.* [49] reported a Zundel ion H_5O_2^+ stabilized tetrakis(β -diketonate) europium complex, $\text{H}_5\text{O}_2^+[\text{Eu}(\text{L}^{41})_4]$. The complex anion in this ion-pair complex is charge balanced by the Zundel cations H_5O_2^+ , which is stabilized by strong H bonding with the N atoms of the anionic heterocyclic ligand L^{41} . The crystal structure study revealed that different $[\text{Eu}(\text{L}^{41})_4]^-$

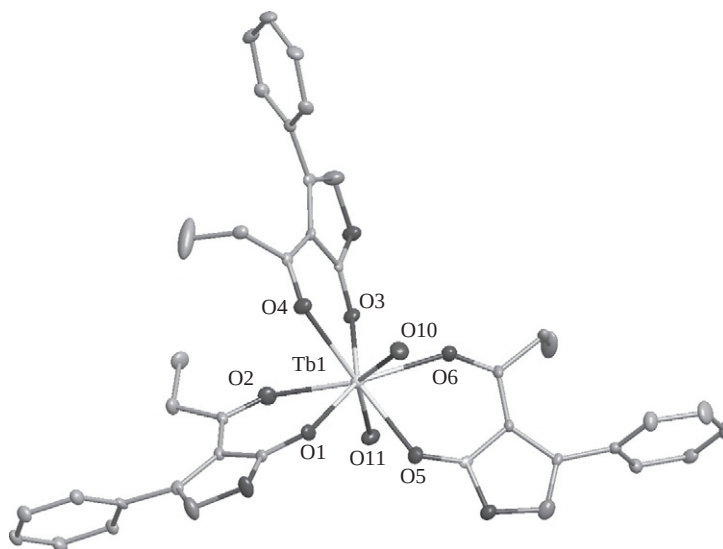


Figure 2.20 Asymmetric unit of complexes Tb(L⁴²)₃(H₂O)₂, thermal ellipsoids drawn with 30% probability and hydrogen atoms omitted for clarity [51a]. (Reproduced from S. Iju, M.L.P. Reddy, A.H. Cowley and K.V. Vasudevan, “3-Phenyl-4-acyl-5-isoxazolonate complex of Tb³⁺ doped into poly- β -hydroxybutyrate matrix as a promising light-conversion molecular device,” *Journal of Materials Chemistry*, **19**, 5179–5187, 2009, by permission of the Royal Society of Chemistry.)

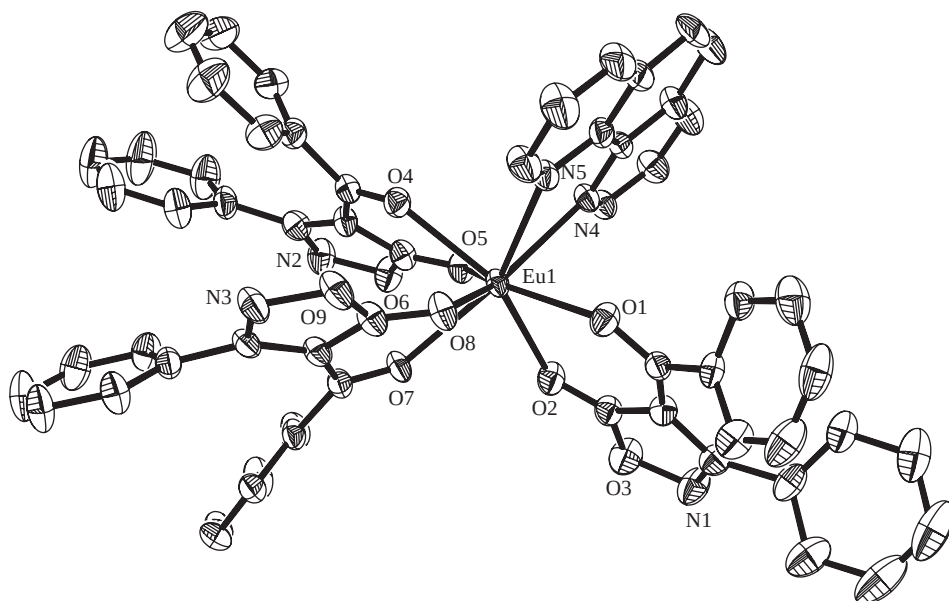


Figure 2.21 Asymmetric unit of complex Eu(L⁴²)₃·phen [51b]. (Reprinted with permission from S. Biju, D.B.A. Raj, M.L.P. Reddy and B.M. Kariuki, “Synthesis, crystal structure, and luminescent properties of novel Eu³⁺ heterocyclic β -diketonate complexes with bidentate nitrogen donors,” *Inorganic Chemistry*, **45**, 10651–10660, 2006. © 2006 American Chemical Society.)

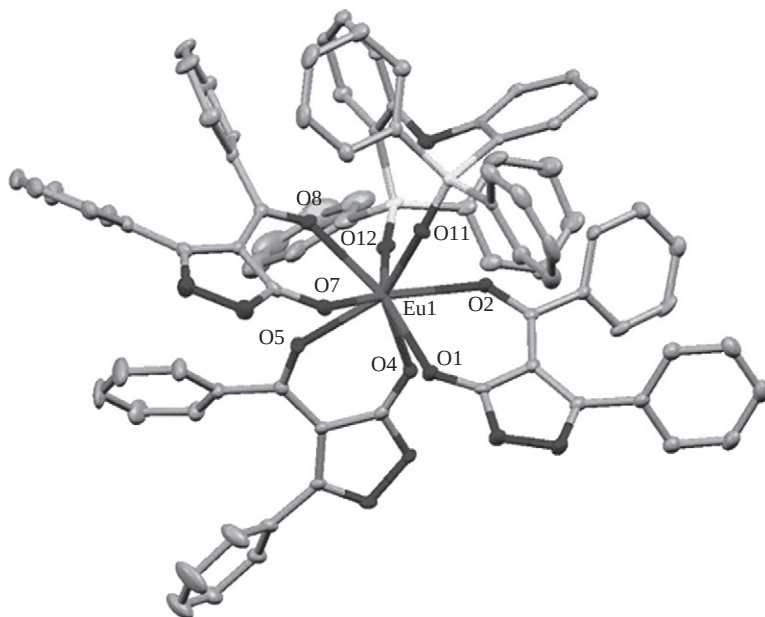


Figure 2.22 Asymmetric unit of complex $\text{Eu}(\text{L}^{42})_3(\text{DPEPO})$. Thermal ellipsoids are shown at the 30% probability level and all hydrogen atoms have been omitted for clarity [51c]. (Reprinted with permission from S. Biju, M.L.P. Reddy, A.H. Cowley and K.V. Vasudevan, "Molecular ladders of lanthanide-3-phenyl-4-benzoyl-5-isoxazolonate and bis(2-(diphenylphosphino)phenyl) ether oxide complexes: the role of the ancillary ligand in the sensitization of Eu^{3+} and Tb^{3+} luminescence," *Crystal Growth and Design*, **9**, 3562–3569, 2009. © 2009 American Chemical Society.)

anions in the crystal are connected by $[\text{H}_5\text{O}_2]^+$ bridges. In $[\text{Eu}(\text{L}^{41})_4]^-$, the Eu is eight-coordinated by four bidentate acylpyrazolonate moieties, the metal center geometry being well described as a square antiprism with square planes. This family of complexes may have both luminescent and proton conductive properties.

By using a bis(β -diketone) of 4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolone (H_2L^{58}) as a ligand, and sodium dibenzo-18-crown-6 [$\text{Na}(\text{DB18C6})$] as the counter cation, Remya *et al.* synthesized and structurally characterized $[\text{Tb}(\text{L}^{58})_2][\text{Na}(\text{DB18C6})\text{H}_2\text{O}]$ (see Figure 2.27) [59]. The crystal structure of $[\text{Tb}(\text{L}^{58})_2][\text{Na}(\text{DB18C6})\text{H}_2\text{O}]$ is a one-dimensional molecular ladder structure based on C–H/ π , intra- and intermolecular hydrogen-bonding interactions featuring a Tb^{3+} center surrounded by two tetradentate bis-pyrazolone L^{58} in a somewhat distorted square-antiprismatic geometry. The Na^+ coordination environment is distorted hexagonal pyramidal and involves six oxygen atoms furnished by DB18C6 and one oxygen atom from a water molecule. The quantum yields and $^5\text{D}_4$ lifetimes for $[\text{Tb}(\text{L}^{58})_2][\text{Na}(\text{DB18C6})\text{H}_2\text{O}]$ in the solid state were found to be 18.13% and 2.82°ms, respectively.

Li and Huang *et al.* reported a series of dendrimer β -diketonate lanthanide complexes and structurally characterized $\text{Tb}(\text{L}^{59})_3(\text{H}_2\text{O})_2$ [62]. They confirmed that dendrimer β -diketonate lanthanide complexes exhibited enhanced emission due to the light-harvesting antenna and shell effects.

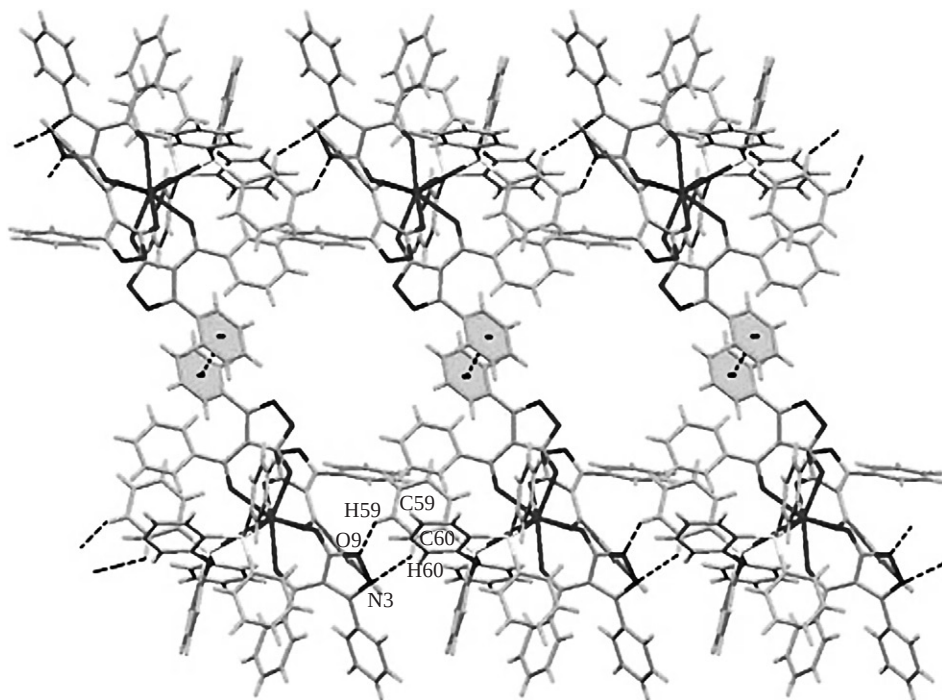


Figure 2.23 Molecular ladder of complex $\text{Eu}(\text{L}^{42})_3(\text{DPEPO})$ involving $\pi \cdots \pi$ interactions (C4-C9) and intermolecular hydrogen bonding interactions (C59-H59 $\cdots$ O9, C60-H60 $\cdots$ N3), when viewed along the direction of the c -axis [51c]. (Reprinted with permission from S. Biju, M.L.P. Reddy, A.H. Cowley and K.V. Vasudevan, "Molecular ladders of lanthanide-3-phenyl-4-benzoyl-5-isoxazolonate and bis(2-(diphenylphosphino)phenyl) ether oxide complexes: the role of the ancillary ligand in the sensitization of Eu^{3+} and Tb^{3+} luminescence," *Crystal Growth and Design*, **9**, 3562–3569, 2009. © 2009 American Chemical Society.)

2.3.1.4 Nine-Coordinated Lanthanide Complexes with β -Diketones

Zheng and coworkers structurally characterized [25] a series of nine-coordinate adducts of lanthanide β -diketonates of the general formula $\text{Ln}(\beta\text{-diketonate})_3(\text{TPTZ})$ by single-crystal X-ray diffraction [TPTZ = 2,4,6-tri(2-pyridyl)-1,3,5-triazine, a rigid Lewis base with a large π system]. The molecular structure of $\text{Eu}(\text{L}^5)_3(\text{TPTZ})$ is shown in Figure 2.28. The TPTZ ligands stack to form a centrosymmetric "dimer" in the crystals, as shown in Figure 2.29. The lanthanide ion in each of these complexes is coordinated with six β -diketonate oxygen atoms and three TPTZ nitrogen atoms, forming a monocapped square antiprism coordination polyhedron. All complexes showed significantly enhanced luminescence quantum yields when compared with the corresponding aqua analogs, with one of the Eu^{3+} complexes displaying a quantum yield of 69.7% in chloroform.

By reacting redox active 4-(2-tetrathiafulvalenyl-ethenyl)pyridine ($\text{TTF}-\text{CH}=\text{CH}-\text{Py}$) with $\text{Nd}(\text{L}^3)_3$, Pointillart *et al.* synthesized a structurally characterized nine-coordinate complex $\{[\text{Nd}(\text{L}^3)_4(\text{H}_2\text{O})][(\text{TTF}-\text{CH}=\text{CH}-\text{Py}^+)]\}_2$ [23d], which consists of two monoanionic

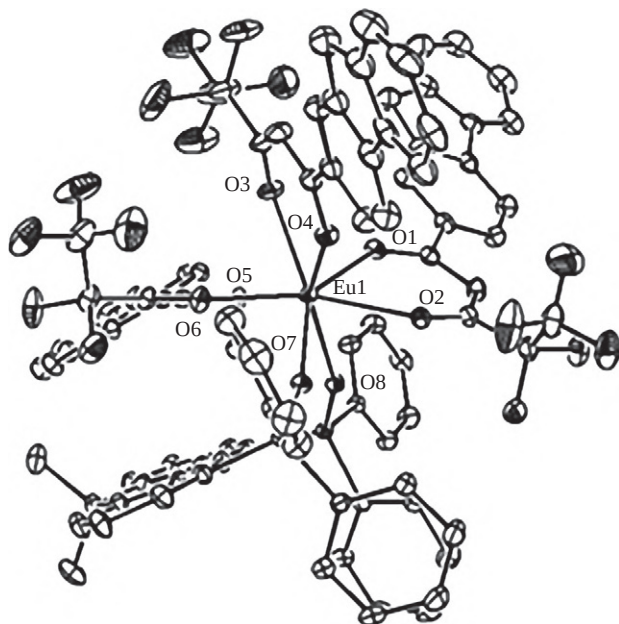


Figure 2.24 Asymmetric unit of $\text{Eu}(\text{L}^{17})_3(\text{DDXPO})$: thermal ellipsoids drawn with 30% probability, H atoms, and non-coordinated solvent molecules omitted for clarity [34]. (Reproduced from D.B.A. Raj, S. Biju and M.L.P. Reddy, “4,4,5,5,5-Pentafluoro-1-(9H-fluoren-2-yl)-1,3-pentanedione complex of Eu^{3+} with 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene oxide as a promising light-conversion molecular device,” *Dalton Transactions*, **36**, 7519–7528, 2009, by permission of the Royal Society of Chemistry.)

$[\text{Nd}(\text{L}^3)_4(\text{H}_2\text{O})]^-$ complexes (see Figure 2.30) and two $\text{TTF}-\text{CH}=\text{CH}-\text{Py}^+$ radical cations (drawn as balls and sticks in Figure 2.30). Each Nd(III) ion is surrounded by nine oxygen atoms from four bis-chelating L^3 ligands and one water molecule. The coordination geometry of the Nd(III) ions is a distorted capped square antiprism. The $[\text{Nd}(\text{L}^3)_4(\text{H}_2\text{O})]^-$ complex, related through the inversion center, forms pseudo-dimeric units with strong hydrogen bonds between the water molecules and oxygen atoms of the L^3 anions.

Among the fluorinated β -diketones reported, the hexafluorinated 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (HL^3) ligand was found to have a tendency to form a nine-coordinated metal center with distorted monocapped square antiprism coordination polyhedra, while other fluorinated β -diketones tend to form ten-coordinated complexes with distorted square antiprism coordination polyhedra. The reasons are twofold. Firstly, owing to the presence of the stronger electron-withdrawing hexafluoroacetyl group on L^3 , interactions between the central Eu(III) ion with the oxygen atom of the nearby hexafluoroacetyl group become weaker than those occurring in the complexes of thenoyltrifluoroacetate (HL^5) and 4,4,4-trifluoro-1-phenyl-1,3-butanedionate (HL^6), leading to longer Eu–O bonds, as observed. Secondly, a larger ligand–metal separation (the longer Eu–O bonds) reduces steric hindrance around the lanthanide ion as compared with the complexes with other fluorinated β -diketones, making the accommodation of additional solvent molecules of water and ethanol facile. De Silva *et al.* [26b] reported

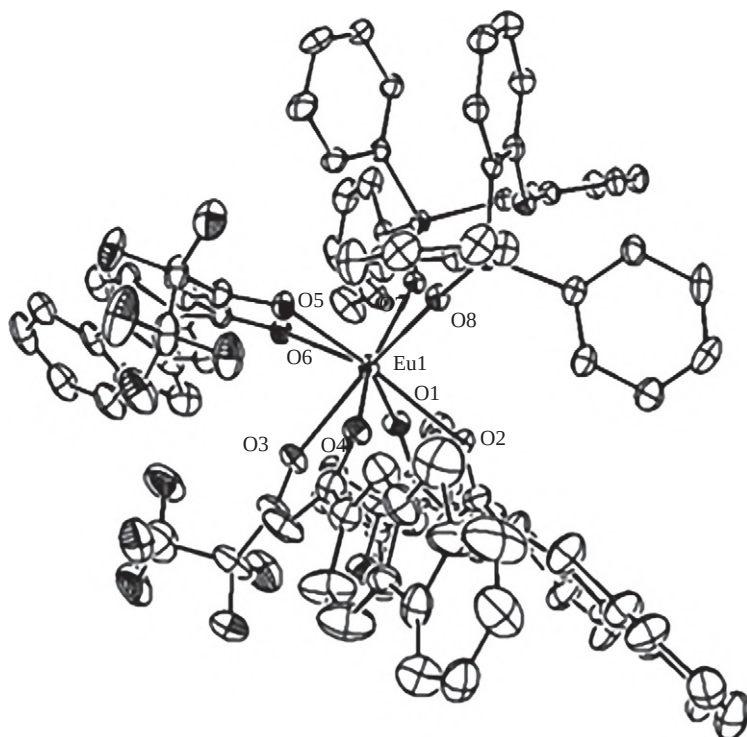


Figure 2.25 Asymmetric unit of $\text{Eu}(\text{L}^{17})_3(\text{DPEPO})$: thermal ellipsoids drawn with 30% probability, H atoms, and non-coordinated solvent molecules omitted for clarity [34]. (Reproduced from D.B.A. Raj, S. Biju and M.L.P. Reddy, “4,4,5,5,5-Pentafluoro-1-(9H-fluoren-2-yl)-1,3-pentanedione complex of Eu^{3+} with 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene oxide as a promising light-conversion molecular device,” *Dalton Transactions*, **36**, 7519–7528, 2009, by permission of the Royal Society of Chemistry.)

the crystal structure of nine-coordinated $[\text{Eu}(\text{L}^3)_3(\text{dmphen})(\text{EtOH})]$ (dmphen = 2,9-dimethyl-1,10-phenanthroline) (Figure 2.31), which is in contrast with the structure of eight-coordinated $\text{Eu}(\text{L}^5)_3(\text{dmphen})$ (see Figure 2.32). It is interesting to note that a molecule of non-coordinating dmphen is found in the solid state, and is involved in π – π interactions with the coordinated neutral ligand. The aromatic interplanar separation is 3.301–3.429 Å.

Malandrino *et al.* [72] recently reported two new neodymium metal organic chemical vapor deposition precursors, the $\text{Nd}(\text{L}^3)_3 \cdot \text{monoglyme} \cdot \text{H}_2\text{O}$ and the $\text{Nd}(\text{L}^3)_3 \cdot \text{diglyme}$ [monoglyme = (dimethoxyethane) and diglyme = (bis(2-methoxyethyl)ether)] with the crystal structures of the former being shown in Figure 2.33. The two complexes are both nine-coordinated by six oxygen atoms of three L^3 anions and by three oxygen atoms of a diglyme molecule or a monoglyme and a water, with the former complex having two coordination geometries of a distorted capped square antiprism and a distorted tricapped trigonal prism, and the latter complex being a monocapped square antiprism. They have applied $\text{Nd}(\text{L}^3)_3 \cdot \text{diglyme}$ for the MOCVD (metal organic chemical vapor deposition) fabrication of $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films on MgO substrates.

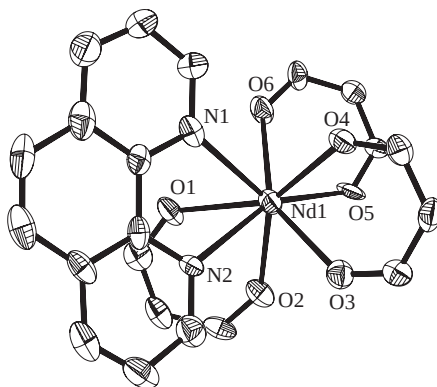


Figure 2.26 Structure of the complex $\text{Nd}(\text{L}^{34})_3(\text{phen})$ as viewed down the square face of a square-antiprismatic coordination polyhedron of $\text{Nd}(\text{III})$ center (50% probability ellipsoids, H atoms, co-crystallized solvent molecules, and phenyl groups of the 1,3-diketonato ligands omitted) [44]. (Reproduced with permission from N.M. Shavaleev, R. Scopelliti, F. Gumy and J.C.G. Bunzli, “Visible-light excitation of infrared lanthanide luminescence via intra-ligand charge-transfer state in 1,3-diketonates containing push-pull chromophores,” *European Journal of Inorganic Chemistry*, 2008, **9**, 1523–1529. © Wiley-VCH Verlag GmbH & Co. KGaA.)

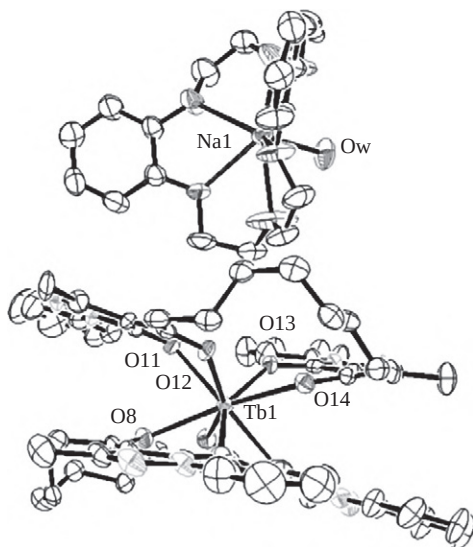


Figure 2.27 ORTEP diagram of $[\text{Na}(\text{DB18C6})\text{H}_2\text{O}][\text{Tb}(\text{L}^{58})_2]$ with the thermal ellipsoids drawn at the 30% probability level and the hydrogen atoms removed for clarity [59]. (Reprinted with permission from P.N. Remya, S. Biju, M.L.P. Reddy, A.H. Cowley and M. Findlater, “1D Molecular ladder of the ionic complex of terbium-4-sebacoylbis(1-phenyl-3-methyl-5-pyrazolonate) and sodium dibenzo-18-crown-6: synthesis, crystal structure, and photophysical properties,” *Inorganic Chemistry*, **47**, 7396–7404, 2008. © 2008 American Chemical Society.)

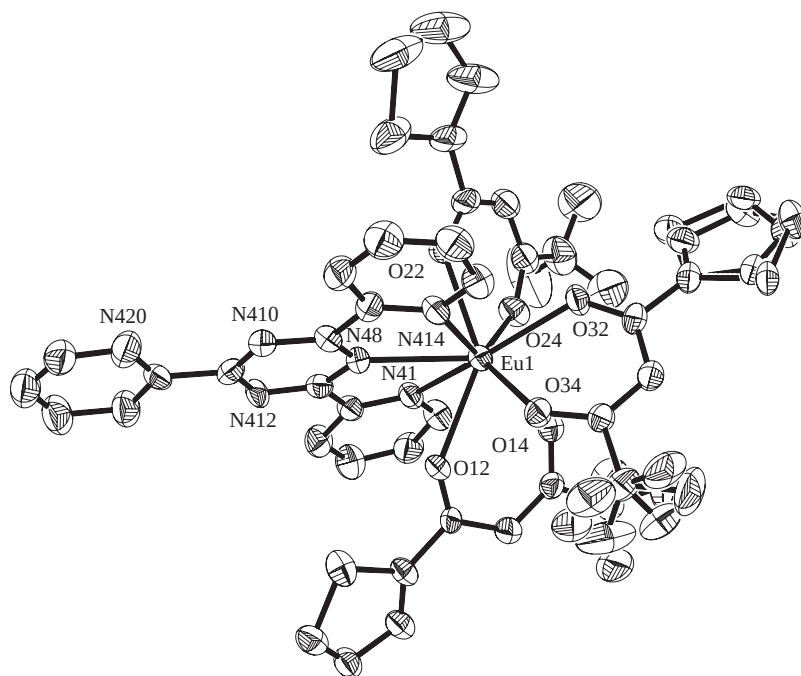


Figure 2.28 An ORTEP view of the crystal structure of $\text{Eu}(\text{L}^5)_3(\text{TPTZ})$ with partial atomic labeling. Thermal ellipsoids are drawn at the 50% probability level [25]. (Reprinted from *Polyhedron*, **26**, C.R. De Silva, J.R. Maeyera, A. Dawson and Z. Zheng, “Adducts of lanthanide β -diketonates with 2,4,6-tri(2-pyridyl)-1,3,5-triazine: synthesis, structural characterization, and photoluminescence studies,” 1229–1238, 2007, with permission from Elsevier.)

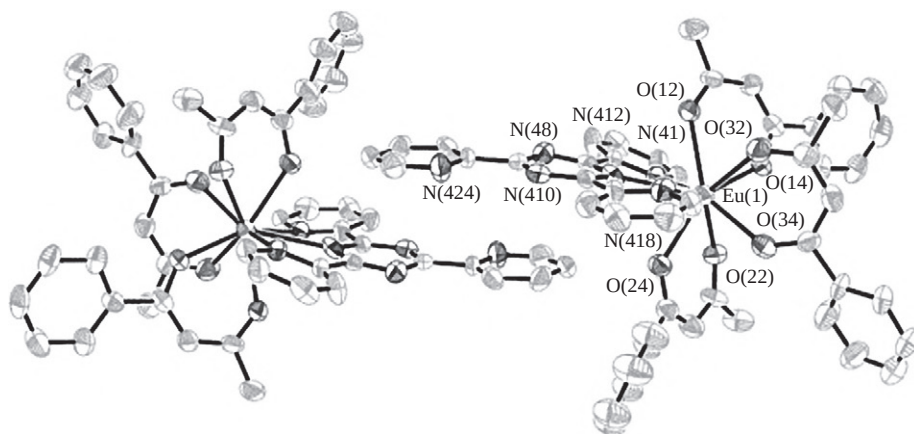


Figure 2.29 The TPTZ ligands stack to form a centrosymmetric “dimer” in the crystal structure of $\text{Eu}(\text{L}^5)_3\text{TPTZ}$. [25]. (Reprinted from *Polyhedron*, **26**, C.R. De Silva, J.R. Maeyera, A. Dawson and Z. Zheng, “Adducts of lanthanide β -diketonates with 2,4,6-tri(2-pyridyl)-1,3,5-triazine: synthesis, structural characterization, and photoluminescence studies,” 1229–1238, 2007, with permission from Elsevier.)

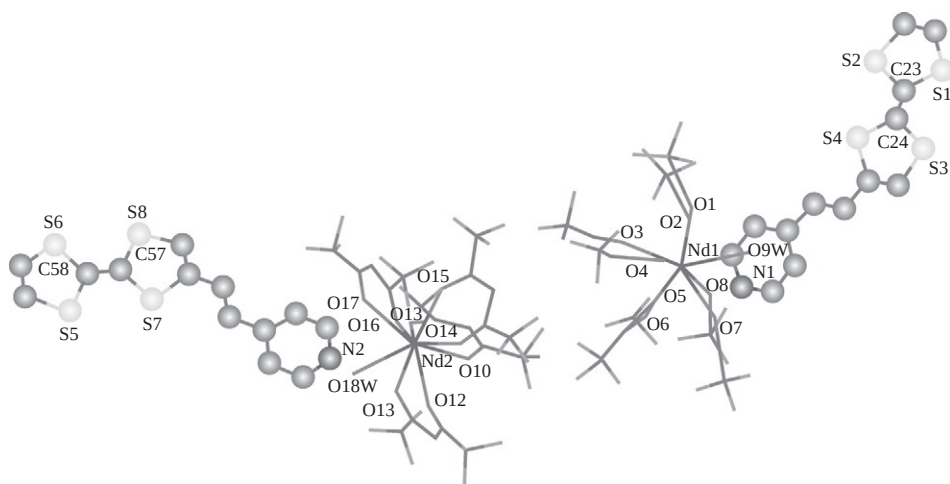


Figure 2.30 Representation of the asymmetric unit of $\{[\text{Nd}(\text{L}^3)_4(\text{H}_2\text{O})][(\text{TTF}-\text{CH}=\text{CH}-\text{Py}^+)]\}_2$. The radical cation donors are drawn as balls and sticks; the paramagnetic anionic coordination complexes of Nd(III) are drawn as capped sticks [23d]. (Reprinted with permission from F. Pointillart, O. Maury, Y. Le Gal, S. Golhen, O. Cador and L. Ouahab, “4-(2-Tetrathiafulvalenyl-ethenyl)pyridine (TTF-CH=CH-py) radical cation salts containing poly(β -diketonate) rare earth complexes: synthesis, crystal structure, photoluminescent and magnetic properties,” *Inorganic Chemistry*, **48**, 7421–7429, 2009. © 2009 American Chemical Society.)

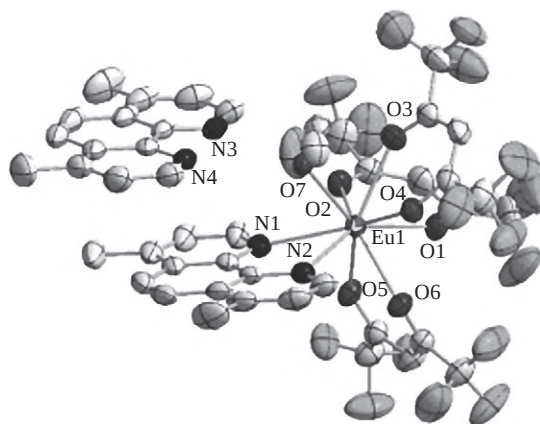


Figure 2.31 Molecular structure of $\text{Eu}(\text{L}^3)_3(\text{dmphen})(\text{EtOH})\text{dmphen}$. (Displacement ellipsoids for non-H atoms are shown at the 50% probability level and H atoms are represented by circles of arbitrary size) [26b]. (Reprinted from *Inorganica Chimica Acta*, **360**, C.R. De Silva, J.R. Maeyer, R. Wang, G.S. Nichol, Z. Zheng, “Adducts of europium β -diketonates with nitrogen p,p’-disubstituted bipyridine and phenanthroline ligands: Synthesis, structural characterization, and luminescence studies,” 3543–3552, 2007, with permission from Elsevier.)

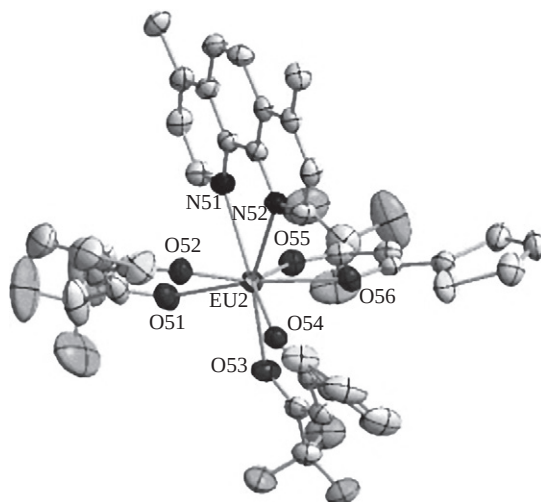


Figure 2.32 An ORTEP view of the crystal structure of $\text{Eu}(\text{L}^5)_3(\text{dmphen})$ with partial atomic labeling. Thermal ellipsoids are drawn at the 50% probability level [26b]. (Reprinted from *Inorganica Chimica Acta*, **360**, C.R. De Silva, J.R. Maeyer, R. Wang, G.S. Nichol, Z. Zheng, “Adducts of europium β -diketonates with nitrogen *p,p'*-disubstituted bipyridine and phenanthroline ligands: Synthesis, structural characterization, and luminescence studies,” 3543–3552, 2007, with permission from Elsevier.)

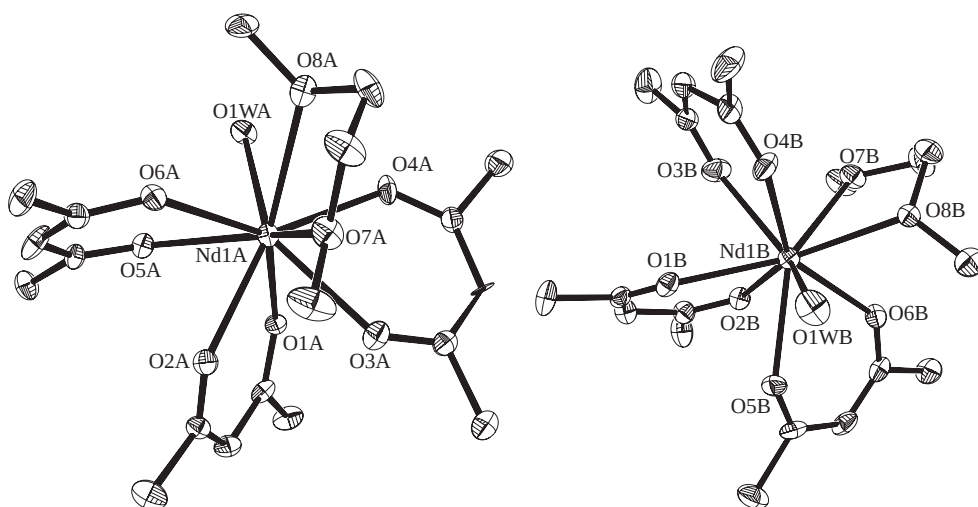


Figure 2.33 ORTEP view of the two independent molecules in the asymmetric unit of $\text{Nd}(\text{L}^3)_3 \cdot \text{monoglyme} \cdot \text{H}_2\text{O}$ (ellipsoid probability 30%). Fluorine and hydrogen atoms have been omitted for clarity [72]. (Reprinted from *Inorganica Chimica Acta*, **362**, R.L. Nigro, R.G. Toro, M.E. Fragalà, P. Rossi, P. Dapporto and G. Malandrino, “Neodymium β -diketonate glyme complexes: Synthesis and characterization of volatile precursors for MOCVD applications,” 4623–4629, 2009, with permission from Elsevier.)

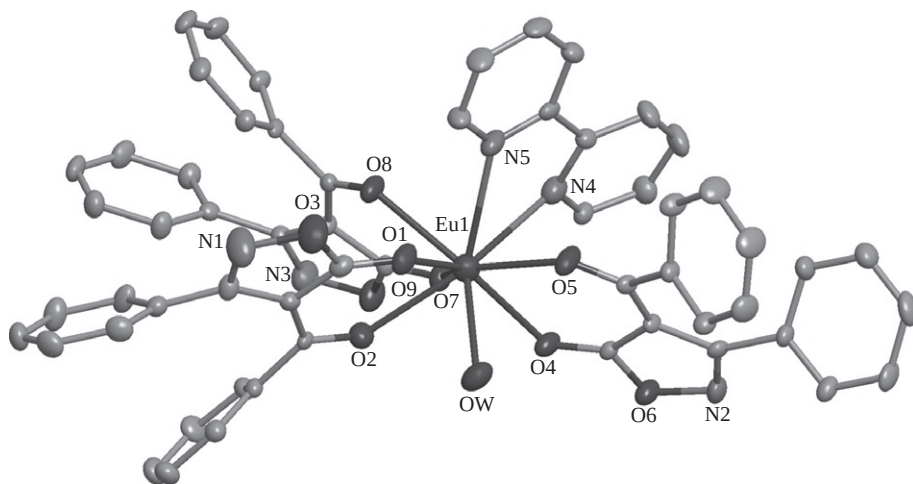


Figure 2.34 ORTEP diagram of the asymmetric unit of compound $\text{Eu}(\text{L}^{42})_3 \cdot \text{bpy} \cdot \text{H}_2\text{O}$ with thermal ellipsoids drawn at the 50% probability. Hydrogen atoms omitted for clarity [73]. (Reproduced from S. Biju, D.B.A. Raj, M.L.P. Reddy, C.K. Jayasankar, A.H. Cowley and M. Findlater, “Dual emission from stoichiometrically mixed lanthanide complexes of 3-phenyl-4-benzoyl-5-isoxazolonate and 2,2'-bipyridine,” *Journal of Materials Chemistry*, **19**, 1425–1432, 2009, by permission of the Royal Society of Chemistry.)

As the very similar coordination ability of lanthanide ions provides a good opportunity for accurately mixing two types of lanthanide ions to make one complex, accordingly resulting in dual emissions, Reddy and coworkers [73] prepared three new stoichiometrically mixed lanthanide complexes of $\text{Sm}_{1/2}\text{Eu}_{1/2}(\text{L}^{42})_3 \cdot \text{bpy} \cdot \text{H}_2\text{O}$, $\text{Sm}_{1/2}\text{Tb}_{1/2}(\text{L}^{42})_3 \cdot \text{bpy} \cdot \text{H}_2\text{O}$, and $\text{Eu}_{1/2}\text{Tb}_{1/2}(\text{L}^{42})_3 \cdot \text{bpy} \cdot \text{H}_2\text{O}$ (bpy = 2,2'-bipyridine). The crystal structure studies showed that $\text{Eu}(\text{L}^{42})_3 \cdot \text{bpy} \cdot \text{H}_2\text{O}$ (see Figure 2.34) is a nine-coordinated mononuclear complex with the coordination polyhedron of a distorted monocapped trigonal prism, in which six coordination atoms come from three bidentate L^{42} ligands, two from a bidentate bpy ligand, and one from a water molecule. There are many interesting π – π , interplanar, and intermolecular hydrogen-bonding interactions in the crystal. Their results indicated that the luminescent intensity can be enhanced and better quantum yields obtained by addition of a controlled amount of a second, carefully selected lanthanide. The dual emissions observed, particularly those of the mixed lanthanide systems, should find applications in the field of organic light emitting diodes (OLEDs).

2.3.1.5 Ten-Coordinated Lanthanide Complexes with β -Diketones

Fratini *et al.* [74] structurally characterized $\text{Ln}(\text{L}^3)_3\text{bpm}$ ($\text{Ln} = \text{Nd}(\text{III})$, $\text{Gd}(\text{III})$, or $\text{Tb}(\text{III})$; bpm = 2,2'-bipyrimidine). The Nd and Gd complexes are ten-coordinate with repeating Ln –bpm units, forming one-dimensional arrays. However, in contrast, the Tb complex does not form a one-dimensional array with its structure being nine-coordinate, where the ninth position is occupied by a covalently bonded H_2O molecule, which is H-bonded to the bpm group from another complex in the solution.

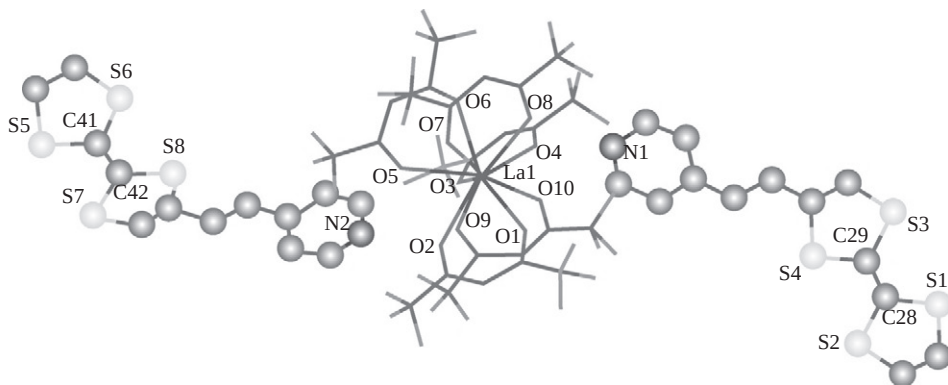


Figure 2.35 The asymmetric unit of $\{[La(L^3)_5][(TTF-CH=CH-Py^+)]_2\}$. The radical cation donors are drawn as balls and sticks; the anionic coordination complex of La(III) is drawn as capped sticks [23d]. (Reprinted with permission from F. Pointillart, O. Maury, Y. Le Gal, S. Golhen, O. Cador and L. Ouahab, “4-(2-Tetrathiafulvalenyl-ethenyl)pyridine (TTF-CH=CH-py) radical cation salts containing poly(β -diketonate) rare earth complexes: synthesis, crystal structure, photoluminescent and magnetic properties,” *Inorganic Chemistry*, **48**, 7421–7429, 2009. © 2009 American Chemical Society.)

L^3 has an ability to form even higher coordination number complexes with big lanthanide ions. Very recently, Pointillart *et al.* [23d] reported a ten-coordinate La(III) complex $\{[La(L^3)_5][(TTF-CH=CH-Py^+)]_2\}$ (Figure 2.35). The La(III) ion is coordinated by ten oxygen atoms from five bis-chelating L^3 ligands. The arrangement of the ten coordinated oxygen atoms leads to a tetradecahedral polyhedron around the lanthanum.

2.3.2 Polynuclear β -Diketonate Lanthanide Complexes

2.3.2.1 f-f Polynuclear β -Diketonate Lanthanide Complexes

Junk *et al.* [43] reported that reaction of $GdCl_3(H_2O)_6$ and 1,3-bis(pyridin-4-yl)propane-1,3-dione (HL^{31}) in methanol with an excess of triethylamine produced a monodimensional polymeric chain $\{[Gd(L^{31})_3(H_2O)] \cdot 4H_2O\}_\infty$, whereas treatment of $HoCl_3(H_2O)_6$ with 1,3-bis(pyridin-2-yl)propane-1,3-dione (HL^{32}) yielded a trinuclear cluster $[Ho_3(L^{32})_3(\mu_3-OH)_2(H_2O)_4Cl_2]Cl_2$. The molecular structures of these two complexes are shown in Figures 2.36 and 2.37.

Bis- β -diketonates have been demonstrated to be powerful ligands in the engineering of supramolecular architectures. Pikramenou and coworkers [53a] used two bis- β -diketonates of 1,3-bis(3-phenyl-3-oxopropanoyl)benzene (H_2L^{49}) and 1,3-bis(3-phenyl-3-oxopropanoyl) 5-ethoxy-benzene (H_2L^{52}) to synthesize neutral homodimetallic complexes $[Ln_2(L^{49})_3]$ ($Ln = Eu, Nd, Sm, Y, Gd$) and $[Ln_2(L^{52})_3]$ ($Ln = Eu, Nd$) and also an anionic dinuclear lanthanide complex $[Eu_2(L^{49})_4]^{2-}$. The detailed studies by NMR, electrospray, and MALDI (matrix assisted laser desorption ionization) mass spectrometry, by addition of chiral Pirkle's reagent, revealed that $[Ln_2(L^{49})_3]$ and $[Eu_2(L^{49})_4]^{2-}$ (see Figure 2.38) are chiral, and have triple- and quadruple-stranded supramolecular structures, respectively, with the latter being more strongly emissive than the former.

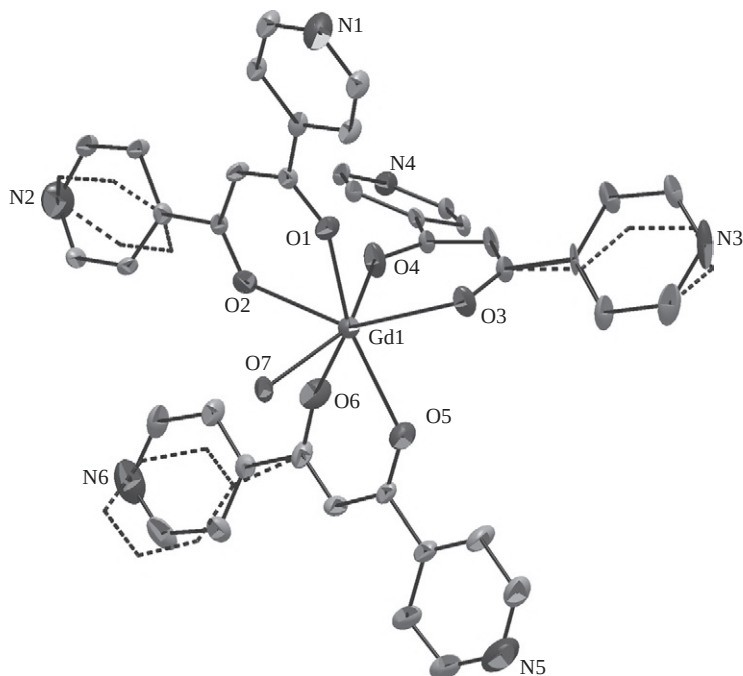


Figure 2.36 Molecular structure of $[\{\text{Gd}(\text{L}^{31})_3(\text{H}_2\text{O})\} \cdot 4\text{H}_2\text{O}]_\infty$ showing 30% ellipsoids with all H atoms and lattice solvent molecules removed [43]. (Reproduced with permission from P.C. Andrews, G.B. Deacon, R. Frank, B.H. Fraser, P.C. Junk, *et al.*, “Formation of Ho^{III} trinuclear clusters and Gd^{III} monodimensional polymers induced by ortho and para regioisomers of pyridyl-functionalised β -diketones: synthesis, structure, and magnetic properties,” *European Journal of Inorganic Chemistry*, 2009, **6**, 744–751. © Wiley-VCH Verlag GmbH & Co. KGaA.)

Semenov *et al.* [53b] used a bis-acylpyrazolone ligand H_2L^{57} to preform triple-stranded helical complexes $\text{Tb}_2(\text{L}^{57})_3(\text{H}_2\text{O})_2$ and $\text{Tb}_2(\text{L}^{57})_3(\text{DMF})_2$, which were then reacted with the bridging ligand diphenylphosphinethane dioxide (dppeO_2) affording the final polymeric product $[\text{Tb}_2(\text{L}^{57})_3(\text{dppeO}_2)]_n$. The crystal structure of $[\text{Tb}_2(\text{L}^{57})_3(\text{dppeO}_2)]_n$ consists of infinite parallel chains formed by the helical units $\{\text{Tb}_2(\text{L}^{57})_3\}$ with dppeO_2 ligands (Figure 2.39).

By using an α -NH substituted β -diketone ligand carrying two carboxylic acid groups, H_3L^{35} , Zebret *et al.* prepared a trinuclear discrete complex $[\text{Eu}_3(\text{L}^{35})_3(\text{H}_2\text{O})_6]$ [45], in which nine-coordinate cations are linked by ligands to provide a triangular complex, as revealed by X-ray crystallography (see Figure 2.40). Each europium cation in the crystal structure is nine-coordinated by five donor atoms from one L^{35} , two oxygen atoms from the amidic carbonyl groups of the neighboring L^{35} , and the two remaining oxygens coming from two water molecules. The coordination sphere of $\text{Eu}(\text{III})$ is a distorted mono-capped square antiprism, in which one water molecule caps the rectangular face formed by two carbonyl and two carboxylate oxygens. The final edifice is electroneutral due to the europium positive charges being fully compensated by the two carboxylates and the deprotonated amide nitrogen.

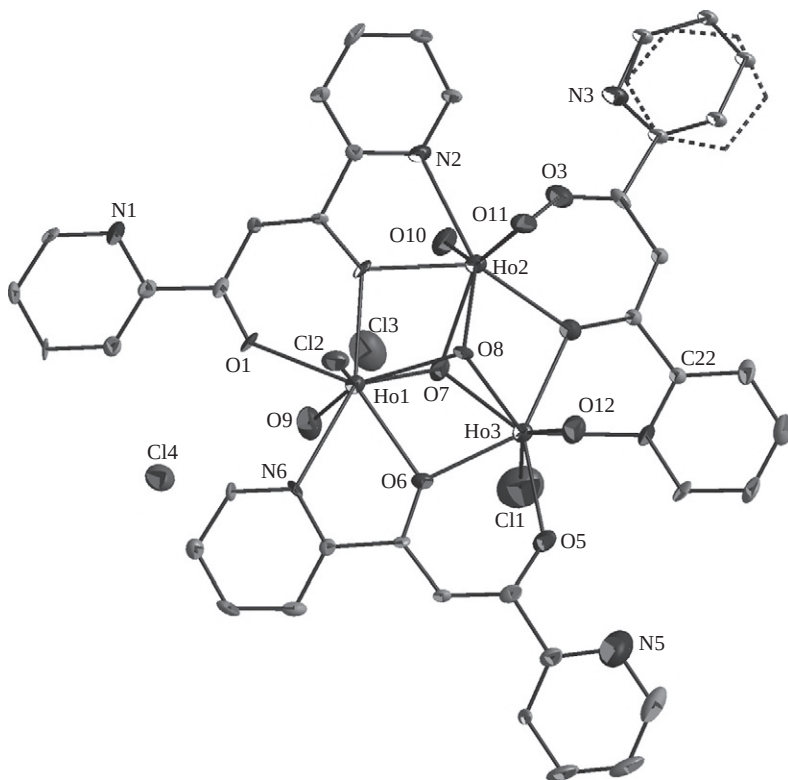


Figure 2.37 Molecular structure of $[\text{Ho}_3(\text{L}^{32})_3(\mu_3\text{-OH})_2(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}_2$ showing 30% ellipsoids with all H atoms and lattice solvent molecules removed [43]. (Reproduced with permission from P.C. Andrews, G.B. Deacon, R. Frank, B.H. Fraser, P.C. Junk, *et al.*, “Formation of Ho^{III} trinuclear clusters and Gd^{III} monodimensional polymers induced by ortho and para regioisomers of pyridyl-functionalised β -diketonates: synthesis, structure, and magnetic properties,” *European Journal of Inorganic Chemistry*, 2009, **6**, 744–751. © Wiley-VCH Verlag GmbH & Co. KGaA.)

The reaction of lanthanide with β -diketonates in a basic media often gives interesting polynuclear oxo-hydroxo clusters. By reacting $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ with ortho-hydroxydibenzoylmethane (H_2L^{27}) in a 1:2 molar ratio in methanol and in the presence of an excess of triethylamine as a base, Jami *et al.* [75] prepared an interesting hexanuclear yttrium oxo-hydroxo cluster $[\text{Y}_6(\text{L}^{27})_6(\text{HL}^{27})_4(\mu_3\text{-OH})_2(\text{MeOH})_4]$ (see Figure 2.41), in which phenolic β -diketonate ligands coordinate to the central Y(III) in chelating and chelating–bridging fashions. The yttrium atoms that make up the butterfly core are eight-coordinate and the peripheral yttriums are seven-coordinate.

Souz *et al.* synthesized and structurally characterized a tetramer complex $[\text{Eu}_4(\text{ETA})_9(\text{OH})_3(\text{H}_2\text{O})_3]$ (see Figure 2.42 [76], where ETA = ethyl 4,4,4-trifluoroacetoacetate. From these structural data, they calculated the ground-state geometry of the tetramer by using the Sparkle/AM1 model. The emission spectrum shows that the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transitions in the emission spectrum are consistent with the Eu^{3+} ion occupying four different sites in chemical environments of low symmetries.

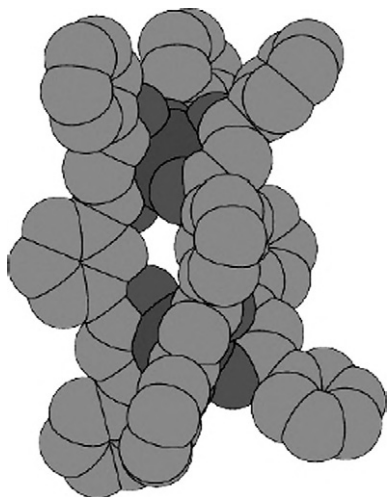


Figure 2.38 Molecular model of the $[\text{Eu}_2(\text{L}^{49})_3]$ complex [53a]. (Reprinted with permission from A.P. Bassett, S.W. Magennis, P.B. Glover *et al.*, “Highly luminescent, triple- and quadruple-stranded, dinuclear Eu, Nd, and Sm(III) lanthanide complexes based on bis-diketonate ligands,” *Journal of the American Chemical Society*, **126**, 9413–9424, 2004. © 2004 American Chemical Society.)

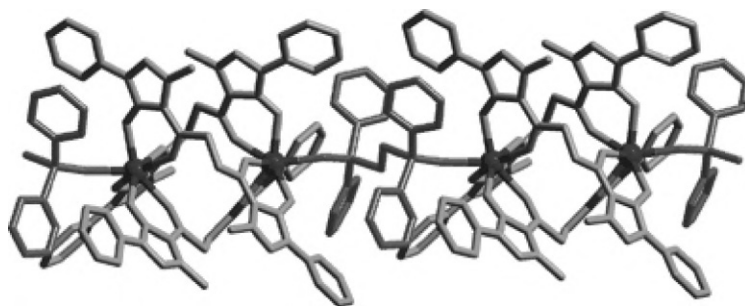


Figure 2.39 Fragment of the polymeric chain in $[\text{Tb}_2(\text{L}^{57})_3(\text{dppeO}_2)]_n$. [53b]. (Reproduced from S.N. Semenov, A.Y. Rogachev, S.V. Eliseeva, C. Pettinari, F. Marchetti, A.A. Drozdov and S.I. Troyanov, “First direct assembly of molecular helical complexes into a coordination polymer,” *Chemical Communications*, **17**, 1992–1994, 2008, by permission of the Royal Society of Chemistry.)

Petit *et al.* [77] recently reported a series of Y(III), Eu(III), and Tb(III) clusters with β -diketonates of HL^1 , HL^{20} , and 2,2,6,6-tetramethylheptane-3,5-dione (Hthd), showing increasing nuclearities of 5, 8, and 9 with decreasing steric hindrance of the ligand. These clusters include $[\text{Ln}(\text{III})_5(\text{L}^{20})_{10}(\mu_3\text{-OH})_4(\mu_4\text{-OH})]$ ($[\text{Ln}_5]$) ($\text{Ln} = \text{Eu}, \text{Tb}$), $[\text{Ln}(\text{III})_8(\text{thd})_{10}(\mu_4\text{-O})_1(\mu_3\text{-OH})_{12}]$ ($\text{Ln} = \text{Eu}$ and Y), $[\text{Ln}(\text{III})_9(\text{L}^1)_{16}(\mu_3\text{-OH})_8(\mu_4\text{-O})(\mu_4\text{-OH})] \cdot \text{H}_2\text{O}$ ($[\text{Ln}_9]$). ($\text{Ln} = \text{Eu}, \text{Tb}$, and Y), and their crystal and molecular structures are shown in Figures 2.43–2.45, respectively.

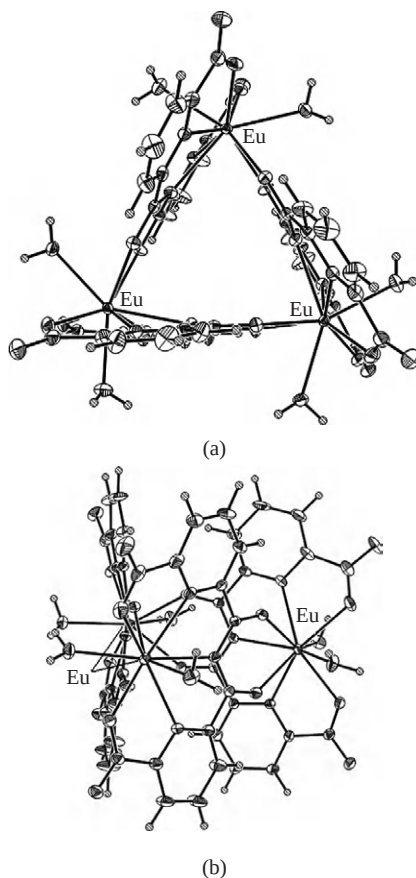


Figure 2.40 Crystal structure of $[\text{Eu}_3(\text{L}^{35})_3(\text{H}_2\text{O})_6]$. View of the trinuclear complex (a) along and (b) perpendicular to the threefold axis [45]. (Reproduced with permission from S. Zebret, N. Dupont, G. Bernardinelli and J. Hamacek, “Self-assembly of a trinuclear luminescent europium complex,” *Chemistry – A European Journal*, 2009, **15**, 3355–3358. © Wiley-VCH Verlag GmbH & Co. KGaA.)

The position of the lanthanides within the pentanuclear cluster forms a square pyramid. Each triangular face of this pyramid is capped by $\mu^3\text{-OH}$ groups while the four metal atoms of the square plane are connected by one $\mu_4\text{-OH}$ ligand. The local symmetry of the Ln(III) cations in the square plane (Ln1, Ln2, Ln3, and Ln4) is a bi-capped trigonal prism where the metal is surrounded by three hydroxyl oxygens and five β -diketone oxygens. The lanthanide at the top of the pyramid (Eu5) is surrounded by four hydroxyl oxygens and four β -diketone oxygens, creating a slightly distorted square antiprismatic local symmetry. The molecular structure of octanuclear clusters consists of a discrete and neutral $[\text{Ln}_8]$ aggregate (Figure 2.44) in which four Eu(III) ions are eight coordinate (Eu1 and Eu2) and four others are seven coordinate. The cluster arrangement can be viewed as two symmetrical $[\text{Eu}_4]$ tetrahedra (both built from Eu1, Eu2, Eu3, and Eu4) tilted by an angle close to 90° . These tetrahedra are connected via two types of bridges: eight $\mu_3\text{-OH}$ bridges (O21, O22, O23, and O26) and one $\mu_4\text{-O}$ bridge (O11). The nonanuclear

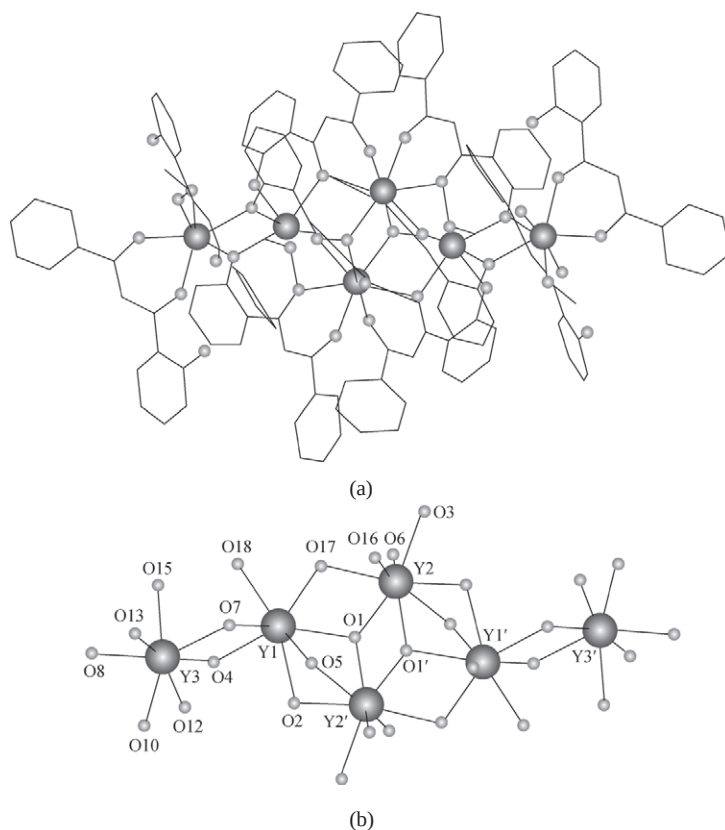


Figure 2.41 (a) Solid state structure of $[Y_6(L^{27})_6(HL^{27})_4(\mu_3-OH)_2(MeOH)_4]$, hydrogen atoms and solvents of crystallization are omitted for clarity; (b) the yttrium oxo core of the cluster $[Y_6(L^{27})_6(HL^{27})_4(\mu_3-OH)_2(MeOH)_4]$ omitting carbon and hydrogen atoms [75]. (Reprinted from *Polyhedron*, **28**, A.K. Jami, P.V.V.N. Kishore and V. Baskar, "Functionalised β -diketone assisted self-assembly of a hexanuclear yttrium oxo-hydroxo cluster," 2284–2286, 2009, with permission from Elsevier.)

clusters (Figure 2.45) can be considered to be two $[Eu_5]$ clusters (described above) condensed by the lanthanide atom located on the top of the square pyramid forming a square antiprism.

The reaction products of 2,2'-bipyrimidine (bpm), β -diketones, and lanthanide ions demonstrated the diverse nuclearity and dimensionality. As stated in the last section, dinuclear eight-coordinate $[Ln_2(\beta\text{-diketonate})_6(bpm)]$ could be formed [78, 79]. Zucchi *et al.* [26a] reacted $Nd(NO_3)_3$ with bpm to afford the mononuclear nine-coordinate adduct $[Nd(NO_3)_3(bpm)(MeOH)_2]$, while reactions of hydrated $NdCl_3$ and various β -diketonates in the presence of bpm gave the binuclear nine-coordinate compounds $[\{Nd(L^{20})_3(THF)\}_2(\mu\text{-bpm})]$ (see Figure 2.46) and $[\{Nd(L^6)_3(MeOH)\}_2(\mu\text{-bpm})]\cdot bpm$ (see Figure 2.47) and the one-dimensional coordination polymer $[Nd(L^5)_3(\mu\text{-bpm})\cdot MeOH]_\infty (4\cdot MeOH)$ (see Figures 2.48 and 2.49). Other groups have also reported the one-dimensional arrays $[Ln(L^3)_3(\mu\text{-bpm})]_\infty$ ($Ln = Eu$ [80], Gd, and Nd [75]).

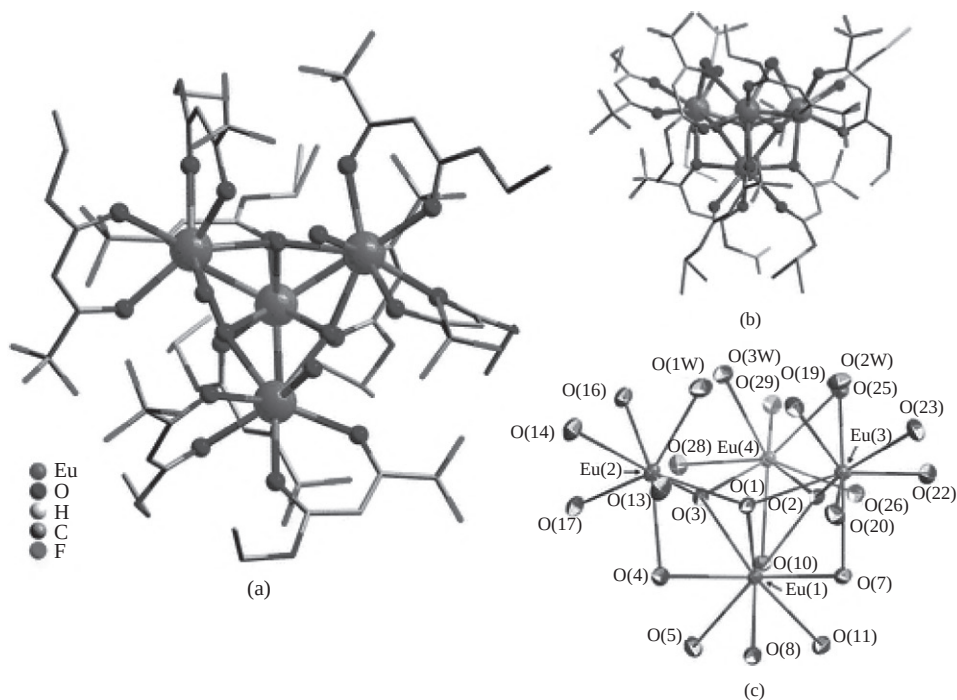


Figure 2.42 (a and b) Top and side views of the $[\text{Eu}_4(\eta^3\text{-ETA})_3(\eta^2\text{-ETA})_6(\mu^3\text{-OH})_3(\text{H}_2\text{O})_3]$ complex, emphasizing the inner tetrametallic core surrounded by the ETA-residues (represented as thin sticks). (c) Inner $\{\text{Eu}_4\text{O}_{18}(\text{OH})_3(\text{H}_2\text{O})_3\}$ core of the $[\text{Eu}_4(\eta^3\text{-ETA})_3(\eta^2\text{-ETA})_6(\mu^3\text{-OH})_3(\text{H}_2\text{O})_3]$ complex showing the labeling scheme for all non-hydrogen atoms. Hydrogen atoms have been omitted for clarity purposes, and thermal ellipsoids are drawn at the 50% probability level [76]. (Reprinted with permission from A.P. Souza, F.A.A. Paz *et al.*, “Synthesis, crystal structure, and modelling of a new tetramer complex of europium,” *The Journal of Physical Chemistry B*, **111**, 9228–9238, 2007. © 2007 American Chemical Society.)

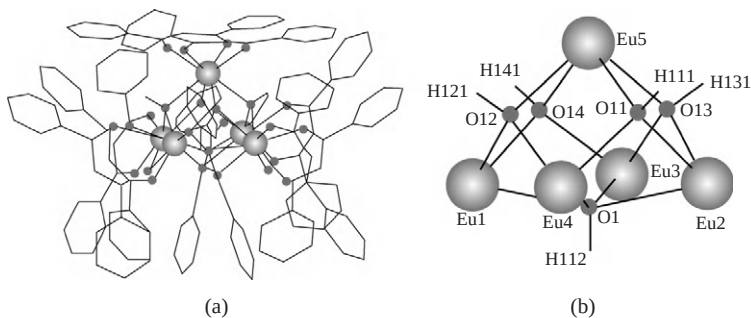


Figure 2.43 (a) $[\text{Ln}_5]$ clusters, hydrogen atoms have been removed for clarity; (b) view of the cluster where ligands have been removed for clarity [77]. (Reproduced from S. Petit, F. Baril-Robert, G. Pilet, C. Reber and D. Luneau, “Luminescence spectroscopy of europium(III) and terbium(III) penta-, octa- and nonanuclear clusters with β-diketonate ligands,” *Dalton Transactions*, **34**, 6809–6815, 2009, by permission of the Royal Society of Chemistry.)

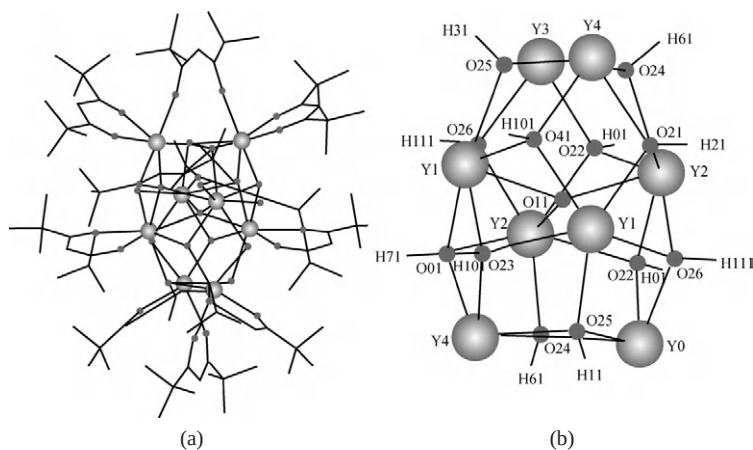


Figure 2.44 (a) [Ln₈] clusters, hydrogen atoms have been removed for clarity; (b) view of the cluster where ligands have been removed for clarity [77]. (Reproduced from S. Petit, F. Baril-Robert, G. Pilet, C. Reber and D. Luneau, "Luminescence spectroscopy of europium(III) and terbium(III) penta-, octa- and nonanuclear clusters with β -diketonate ligands," *Dalton Transactions*, **34**, 6809–6815, 2009, by permission of the Royal Society of Chemistry.)

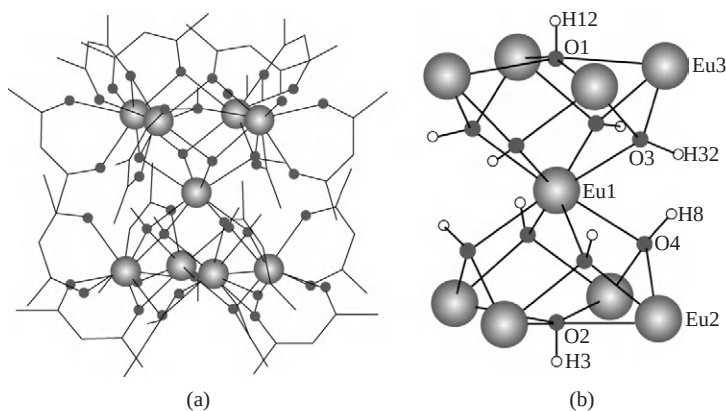


Figure 2.45 (a) [Ln₉] clusters, hydrogen atoms have been removed for clarity; (b) view of the cluster where ligands have been removed for clarity [77]. (Reproduced from S. Petit, F. Baril-Robert, G. Pilet, C. Reber and D. Luneau, "Luminescence spectroscopy of europium(III) and terbium(III) penta-, octa- and nonanuclear clusters with β -diketonate ligands," *Dalton Transactions*, **34**, 6809–6815, 2009, by permission of the Royal Society of Chemistry.)

Eliseeva and coworkers [81] reported two types of dimeric complexes [Ln₂(L³)₆(μ -2-O(CH₂)₂NHMe₂)₂] and [Ln(thd)₂(μ -2, η ²-O(CH₂)₂NMe₂)₂] [Ln = Y(III), Eu(III), Gd(III), Tb(III), Tm(III), Lu(III)], which were obtained by reacting [Ln(L³)₃(H₂O)₂] and [Ln(thd)₃], respectively, with *N,N*-dimethylaminoethanol in toluene. The Tb(III) compounds have been structurally characterized. The coordination mode of *N,N*-dimethylaminoethanol was

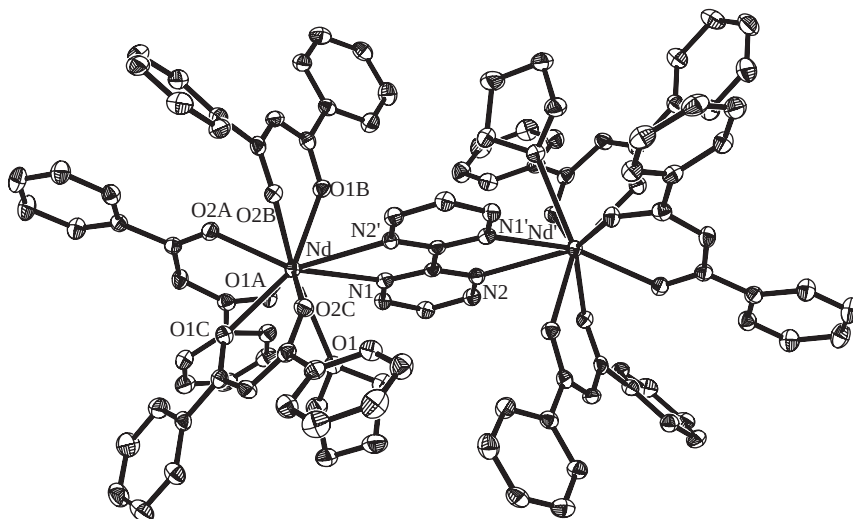


Figure 2.46 Molecular structure of $[\{\text{Nd}(\text{L}^{20})_3(\text{THF})\}_2(\mu\text{-bpm})]$, hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 50% probability level [26a]. (Reprinted with permission from G. Zucchi, O. Maury, P. Thuery and M. Ephritikhine, “Structural diversity in neodymium bipyrimidine compounds with near infrared luminescence: from mono- and binuclear complexes to metal-organic frameworks,” *Inorganic Chemistry*, **47**, 10398–10406, 2008. © 2008 American Chemical Society.)

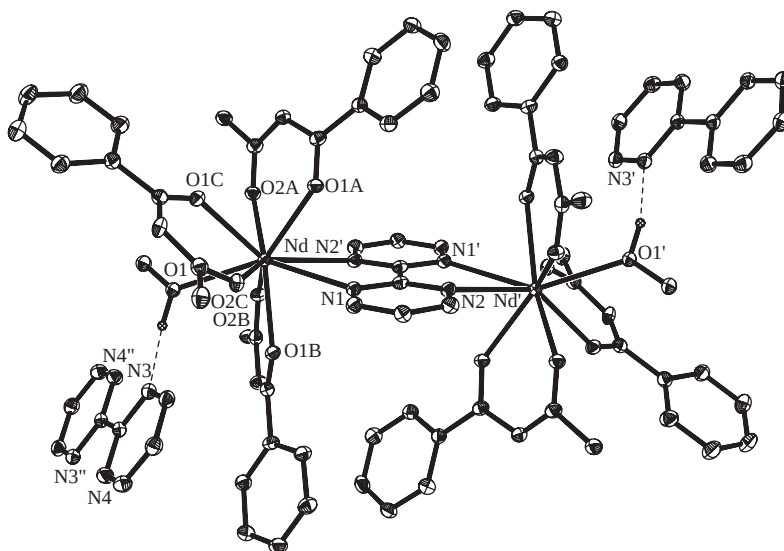


Figure 2.47 Molecular structure of $[\{\text{Nd}(\text{L}^6)_3(\text{MeOH})\}_2(\mu\text{-bpm})]$. Fluorine atoms and carbon-bound hydrogen atoms are omitted. Hydrogen bonds are shown as dashed lines [26a]. (Reprinted with permission from G. Zucchi, O. Maury, P. Thuery and M. Ephritikhine, “Structural diversity in neodymium bipyrimidine compounds with near infrared luminescence: from mono- and binuclear complexes to metal-organic frameworks,” *Inorganic Chemistry*, **47**, 10398–10406, 2008. © 2008 American Chemical Society.)

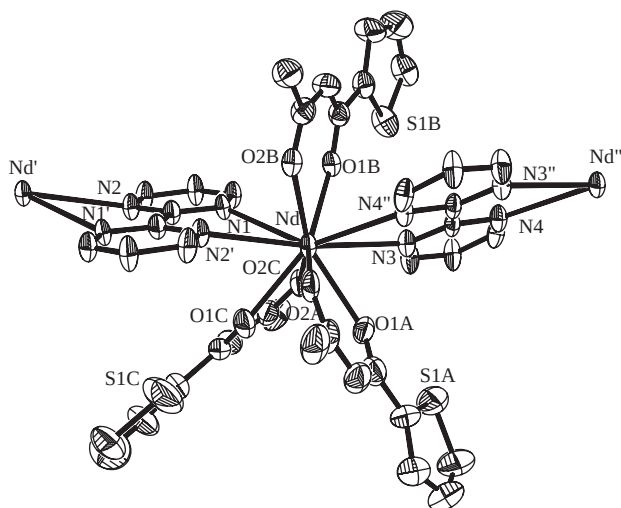


Figure 2.48 Partial view of $[\text{Nd}(\text{L}^5)_3(\mu\text{-bpm})]_\infty$. Fluorine and hydrogen atoms are omitted [26a]. (Reprinted with permission from G. Zucchi, O. Maury, P. Thuery and M. Ephritikhine, "Structural diversity in neodymium bipyrimidine compounds with near infrared luminescence: from mono- and binuclear complexes to metal-organic frameworks," *Inorganic Chemistry*, **47**, 10398–10406, 2008. © 2008 American Chemical Society.)

found to depend on the nature of the β -diketonate. In $[\text{Tb}_2(\text{L}^3)_6(\mu_2\text{-O}(\text{CH}_2)_2\text{NHMe}_2)_2]$ (see Figure 2.50), eight-coordinate Tb(III) ions adopt distorted square antiprismatic coordination environments and are O-bridged by two zwitterionic *N,N*-dimethylaminoethanol ligands with a $\text{Tb1} \cdots \text{Tb2}$ separation of 3.684(1) Å. In $[\text{Tb}(\text{thd})_2(\mu_2, \eta^2\text{-O}(\text{CH}_2)_2\text{NMe}_2)]_2$ (see Figure 2.51), the *N,N*-dimethylaminoethanol acts as a chelating-bridging O,N-donor anion and the Tb(III) ions are seven coordinate with the $\text{Tb1} \cdots \text{Tb1A}$ separation being as large as 3.735(2) Å. Thin films of the most luminescent compound $[\text{Eu}_2(\text{L}^3)_6(\text{O}(\text{CH}_2)_2\text{NHMe}_2)_2]$ obtained by vacuum sublimation display photophysical properties analogous with those of the solid-state sample, thus opening up opportunities for applications in electroluminescent devices.

While Eliseeva *et al.* [82] used HL^3 and 4-cyanopyridine-*N*-oxide (4-cpyNO) to synthesize dimeric lanthanide complexes with compositions of $[\text{Ln}_2(\text{L}^3)_6(4\text{-cpyNO})_3]$ [$\text{Ln} = \text{Sm(III)}\text{--Dy(III)}$, Tm(III)], and structurally characterized $[\text{Tb}_2(\text{L}^3)_6(4\text{-cpyNO})_3] \cdot \text{CHCl}_3$ (see Figure 2.52), in which Tb ions are nine coordinated by six O atoms from three L^3 ligands and three O atoms from three bridging 4-cpyNO molecules.

2.3.2.2 d-f Polynuclear β -Diketonate Lanthanide Complexes

Many efforts have been made to use ferrocene derivatives, optically active transition metal Re(I), Au(I), Ru(II), Pt(II), and Os(III) complexes, as the energy donors, in order to shift the excitation wavelength of lanthanide β -diketonate complexes to the visible light region and to enhance luminescent efficiencies by efficient energy transfers. As elegant reviews on the sensitized lanthanide luminescence have been given by the groups of Ward, Chen and Faulkner [9, 12, 13] and also by Chen in Chapter 12 of this book, we will focus our attention on the recent developments of the sensitized visible luminescence of β -diketonate lanthanide complexes.

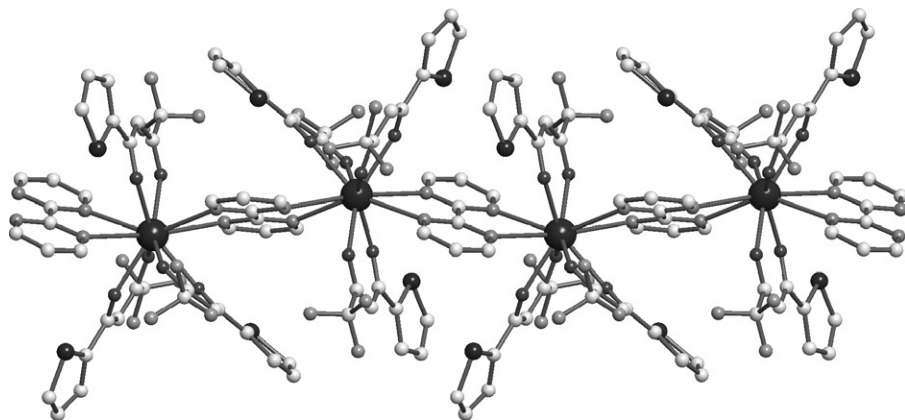


Figure 2.49 View of the polymeric arrangement in $[\text{Nd}(\text{L}^5)_3(\mu\text{-bpm})]_\infty$. Hydrogen atoms are omitted. [26a]. (Reprinted with permission from G. Zucchi, O. Maury, P. Thuery and M. Ephritikhine, "Structural diversity in neodymium bipyrimidine compounds with near infrared luminescence: from mono- and binuclear complexes to metal-organic frameworks," *Inorganic Chemistry*, **47**, 10398–10406, 2008. © 2008 American Chemical Society.)

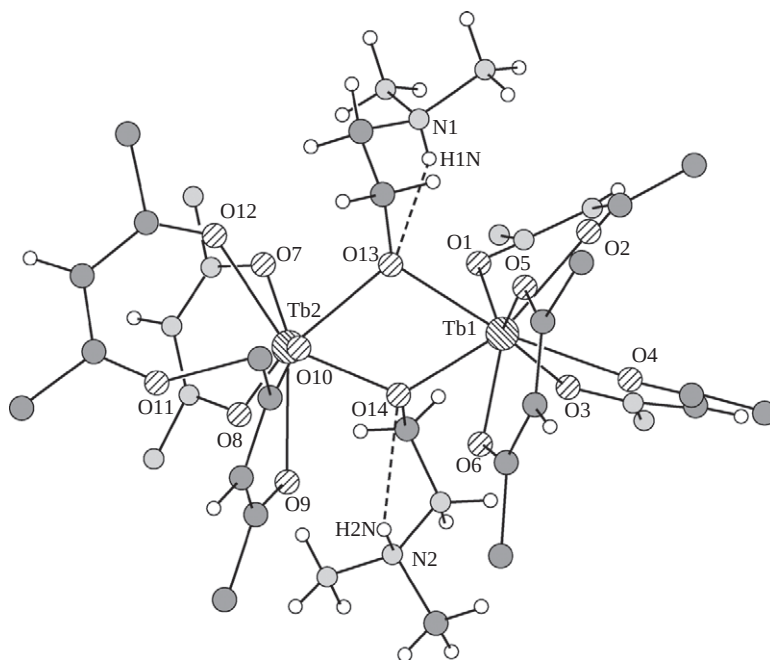


Figure 2.50 Molecular structure of $[\text{Tb}_2(\text{L}^3)_6(\mu^2\text{-O}(\text{CH}_2)_2\text{NHMe}_2)_2] \cdot \text{C}_7\text{H}_8$. Fluorine atoms and solvate toluene molecule are omitted for clarity [81]. (Reprinted with permission from S.V. Eliseeva, O.V. Kotova *et al.*, "Role of the ancillary ligand *N,N*-dimethylaminoethanol in the sensitization of Eu^{III} and Tb^{III} luminescence in dimeric β -diketonates," *The Journal of Physical Chemistry A*, **112**, 3614–3626, 2008. © 2008 American Chemical Society.)

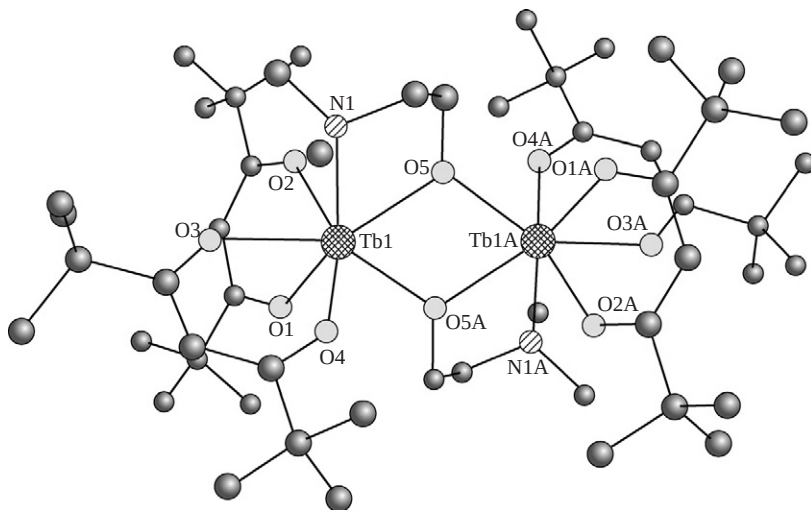


Figure 2.51 Molecular structure of $[\text{Tb}(\text{thd})_2(\mu^2, \eta^2\text{-O}(\text{CH}_2)_2\text{NMe}_2)]_2$. Hydrogen atoms are omitted for clarity [81]. (Reprinted with permission from S.V. Eliseeva, O.V. Kotova *et al.*, “Role of the ancillary ligand *N,N*-dimethylaminoethanol in the sensitization of Eu^{III} and Tb^{III} luminescence in dimeric β -diketonates,” *The Journal of Physical Chemistry A*, **112**, 3614–3626, 2008. © 2008 American Chemical Society.)

Nockemann and coworkers [33] prepared the ferrocene derivatives bis(ferrocenyl-ethynyl)-1,10-phenanthroline (Fc_2phen) and ferrocenoyltrifluoroacetone (HL^{15}) and their rare earth β -diketonate complexes of $[\text{Eu}(\text{L}^5)_3(\text{Fc}_2\text{phen})]$ and $[\text{Eu}(\text{L}^{15})_3(\text{phen})]$ (where $\text{Ln} = \text{La}, \text{Nd}, \text{Eu}, \text{Yb}$). The molecular structure of $[\text{Nd}(\text{L}^5)_3(\text{Fc}_2\text{phen})]$ is shown in Figure 2.53. The visible light with a wavelength up to 420 nm (blue light) could be used for excitation of $\text{Eu}(\text{III})$ to observe the red emission of the $\text{Eu}(\text{III})$ complex.

The majority of effort has been devoted to sensitized near-infrared lanthanide luminescence using d-block transition metal complexes as energy donors [9, 12, 13], while studies on sensitized visible lanthanide luminescence are relatively rare. By using a 1,10-phenanthroline-substituted β -diketone of HL^{15} as the ligand, Bian, and Huang *et al.* [32] prepared an intermediate $\text{Ir}(\text{III})$ complex substituted β -diketone of $\text{Ir}(\text{dfppy})_2(\text{L}^{16})$ [$\text{dfppy} = 2\text{-(4',6'-difluorophenyl)-pyridinato-N,C}^2$]. Using this $\text{Ir}(\text{III})$ complex as a ligand, they synthesized two novel iridium-europium bimetallic complexes of $\{[(\text{dfppy})_2\text{Ir}(\mu\text{-L}^{16})]_3\text{EuCl}\}\text{Cl}_2$ and $(\text{dfppy})_2\text{Ir}(\mu\text{-L}^{16})\text{Eu}(\text{L}^2)_3$ [32]. The molecular and crystal structure of $\{[(\text{dfppy})_2\text{Ir}(\mu\text{-L}^{16})]_3\text{EuCl}\}\text{Cl}_2$ is shown in Figure 2.54. In $\{[(\text{dfppy})_2\text{Ir}(\mu\text{-L}^{16})]_3\text{EuCl}\}\text{Cl}_2$, the $\text{Eu}(\text{III})$ ion is seven coordinated by six oxygen atoms from the three β -diketonates and one chloride ion from the starting material $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$. The nonbonding distances for $\text{Eu} \cdots \text{Ir}$ are 6.028, 5.907, and 6.100 Å, ensuring effective energy transfer from the $\text{Ir}(\text{III})$ center to the $\text{Eu}(\text{III})$ emissive states, as the effective energy transfer distances were reported to be around 6 Å (< 10 Å). The highly efficient pure red luminescence from the $\text{Eu}(\text{III})$ ion sensitized by the $^3\text{MLCT}$ energy of the $\text{Ir}(\text{III})$ complex-ligand was observed. Remarkably, the excitation window for the bimetallic complexes $\{[(\text{dfppy})_2\text{Ir}(\mu\text{-L}^{16})]_3\text{EuCl}\}\text{Cl}_2$ (1×10^{-3} M in EtOH) extended up to 530 nm.

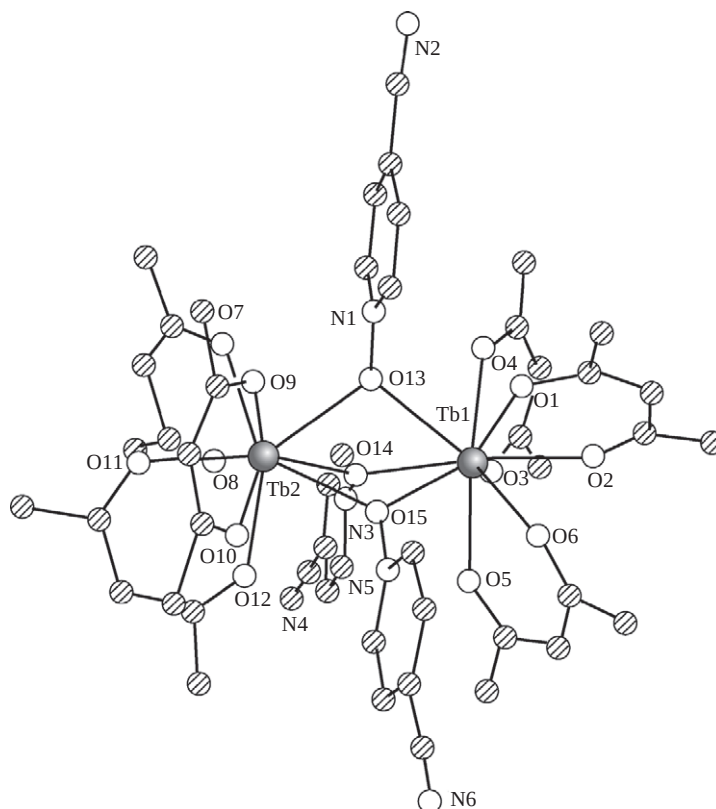


Figure 2.52 Molecular structure of $[\text{Tb}_2(\text{L}^3)_6(4\text{-cpyNO})_3]\cdot\text{CHCl}_3$ (all fluorine and hydrogen atoms, and also CHCl_3 , are omitted for clarity [82]. (Reprinted from *Journal of Alloys and Compounds*, **451**, S.V. Eliseeva, O.V. Kotova, V.G. Kessler, F. Gumi, J.C.G. Bünzli and N.P. Kuzmina, “Dimeric lanthanide hexafluoroacetylacetonate adducts with 4-cyanopyridine-n-oxide,” 414–417, 2008, with permission from Elsevier.)

Ziessel and coworkers reported a bimetallic nine-coordinate Pt–Eu complex ($^t\text{Buterpy}$) $\text{Pt}(\text{C}\equiv\text{Ctpy})\text{Eu}(\text{L}^3)_3$ ($^t\text{Buterpy}$ = 4, 4', 4'-*tert*-butyl-2,2':6',2'-terpyridine, $\text{C}\equiv\text{Ctpy}$ = 4'-ethynyl-2,2':6',2'-terpyridine) and its crystal structure (see Figure 2.55) [83]. They interestingly found that a strong Eu(III) luminescence with a lifetime of 868 μs and a luminescence quantum yield of 38%, independent of the presence of oxygen, was generated from a quantitative energy transfer from the visible-light irradiation up to 460 nm.

2.4 Summary and Outlook

The synthetic flexibility of β -diketonates has led to an explosion in the developments of related lanthanide complexes and their coordination chemistry. The β -diketonate lanthanide complexes have been demonstrated to have variable coordination numbers ranging from six to ten, and diverse structural motifs. This family of complexes, having desirable luminescent properties

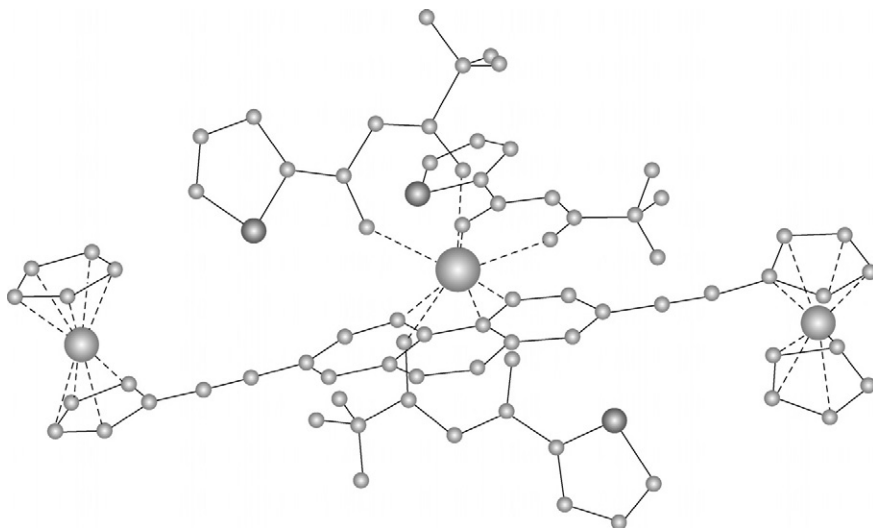


Figure 2.53 Molecular structure of $[\text{Nd}(\text{L}^5)_3(\text{Fc}_2\text{phen})]$ [33]. (Reprinted with permission from Y.F. Yuan, T. Cardinaels, K. Lunnstroot *et al.*, “Rare-earth complexes of ferrocene-containing ligands: visible-light excitable luminescent materials,” *Inorganic Chemistry*, **46**, 5302–5309, 2007. © 2007 American Chemical Society.)

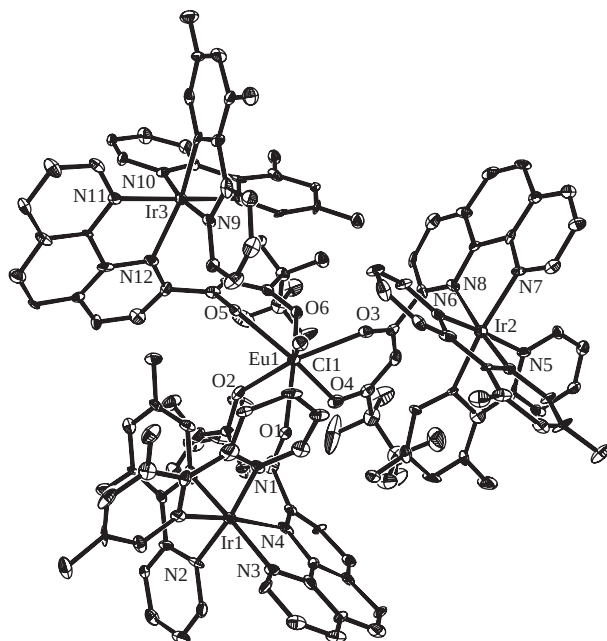


Figure 2.54 ORTEP diagrams of complexes $\{[(\text{dfppy})_2\text{Ir}(\mu\text{-L}^{16})]_3\text{EuCl}\}\text{Cl}_2$, thermal ellipsoids shown at the 20% probability level. The hydrogen atoms, counterions, and solvent molecules are omitted for clarity [32]. (Reprinted with permission from F.F. Chen, Z.Q. Bian, Z.W. Liu *et al.*, “Highly efficient sensitized red emission from europium(III) in Ir–Eu bimetallic complexes by $^3\text{MLCT}$ energy transfer,” *Inorganic Chemistry*, **47**, 2507–2513, 2008. © 2008 American Chemical Society.)

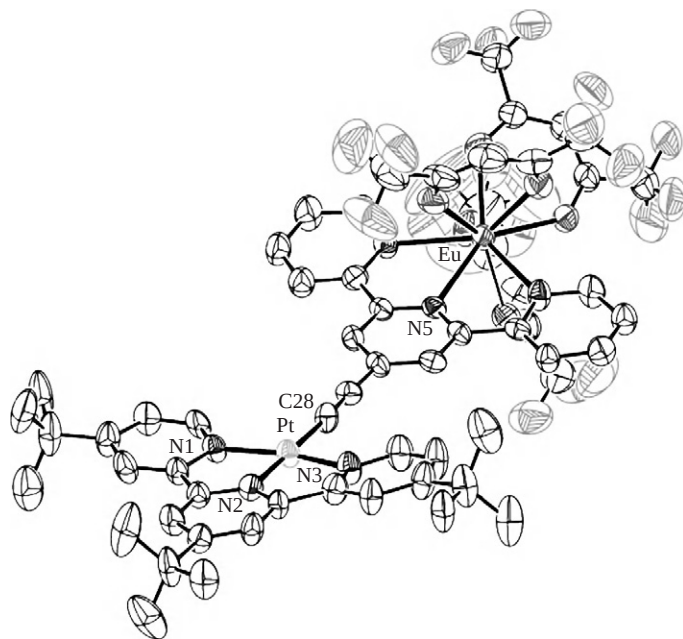


Figure 2.55 ORTEP view of $(^4\text{Buterpy})\text{Pt}(\text{C}\equiv\text{Ctpy})\text{Eu}(\text{L}^3)_3$ (ellipsoids at 50% probability), with hydrogen atoms omitted for clarity [83]. (Reproduced with permission from R. Ziessel, S. Diring, P. Kadjane, L. Charbonniere, P. Retailleau and C. Philouze, “Highly efficient blue photoexcitation of europium in a bimetallic Pt-Eu complex,” *Chemistry – An Asian Journal*, 2007, 2, 975–982. © Wiley-VCH Verlag GmbH & Co. KGaA.)

in the visible and near-infrared regions, holds great potential for widespread practical applications. The prospects for poly- β -diketonates in supramolecular chemistry have been bright in recent years, although they have been relatively ill-explored and are in their infancy. Current challenges are the synthesis and structural characterization of the β -diketonate lanthanides through tailoring their properties not only at the molecular level but also at the nanometer dimensional level, such as the supramolecular assemblies in nanomaterials or other underlying levels, fulfilling smart, and controllable functionalities for high-technological applications on the borders of chemistry, materials chemistry, chemistry biology, and medicine.

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3

Rare Earth Complexes with Carboxylic Acids, Polyaminopolycarboxylic Acids, and Amino Acids¹

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3.1 Introduction

The coordination chemistry of rare earth elements (RE) had a late start when compared with that of the transition metals. However, the research activities in this area have been intense in the past three decades, driven by their rich chemistry, unique physical properties, and their diverse and important applications. Owing to their hard Lewis acid character and large ionic radii, RE(III) ions prefer bonding with hard Lewis base donors, such as F, O, and N, and to have high coordination numbers (CN). Carboxylic acids, polyaminopolycarboxylic acids, which have O and N as coordinating atoms and versatile structures to satisfy the high CN requirement, are among the most suitable ligands for the coordination of RE(III) ions. In fact, interest in the coordination chemistry of rare earths with carboxylic acids and polyaminopolycarboxylic acids has been increasing with the development of rare earth chemistry since the very beginning, when citrate and polyaminopolycarboxylates were used as the initial eluents for separating rare earths using cation-exchange resins [1, 2]. Nowadays, rare earth complexes

¹All structures in this chapter were created using the data available at the Cambridge Structure Database: Allen, F.H., "The Cambridge Structural Database: a quarter of a million crystal structures and rising," *Acta Crystallographica Section B: Structural Science*, **B58**, 380–388, 2002.

with carboxylic acids, polyaminopolycarboxylic acids, and amino acids have found a great variety of binding modes, extensive applications in biology, clinical areas, and advanced function materials, such as NLO (nonlinear optical), OLED (organic light emitting diode), MOF (metal–organic framework), and so on [3–5], and even as corrosion inhibitors as a replacement for the traditional and toxic chromate-based compounds [6].

On the other hand, the use of the rare earths in various materials, especially the increasing use of rare earth compounds in clinical treatments and medications, can cause concerns over the long- and short-term effects of rare earths to human beings and animals. Indeed, some unique biological effects associated with rare earths have been confirmed, and the primary site for rare earths to interact with living cells is at the external surface; one of the major physiological effects of the RE(III) is to block both voltage operated and receptor operated calcium channels [7–9]. Amino acids play critical roles in life, and are the building blocks of proteins. Study of the interactions between rare earths and amino acids is of significant importance to understand the chemistry behind these effects. So far, a lot of work has been done with the solution chemistry of rare earth–amino acid complexes, and around 100 complexes obtained at pH 1–4 or pH 6–7 have been structurally characterized by X-ray single crystal analysis [9, 10]. At pH 6–7, the RE(III) ions start to hydrolyze and the $-\text{NH}_3^+$ groups begin to deprotonate, thus the complexes obtained under the high-pH conditions are all characterized by the presence of the cluster-type $[\text{RE}_4(\mu_3\text{-OH})_4]^{8+}$ motif. This particular aspect of the rare earth–amino acid coordination will be discussed in Chapter 4. The present chapter only deals with the complexes synthesized at pH 1–4.

This chapter will cover the synthetic, structural, and solution chemistry of rare earth complexes with carboxylic acids, polyaminopolycarboxylic acids, and amino acids, with an emphasis on their structural chemistry. As the carboxylate groups play the key roles in the metal–ligand coordination bonding in these complexes, we will start the chapter with the coordination chemistry of rare earth–carboxylic acid complexes, followed by rare earth–polyaminopolycarboxylic acid and rare earth–amino acid coordination chemistry. Owing to length limitations, an exhaustive citation of the large amount of research activities on the subjects is not possible. Instead, only selected examples are detailed to highlight the key features of this chemistry.

3.2 Rare Earth Complexes with Carboxylic Acids

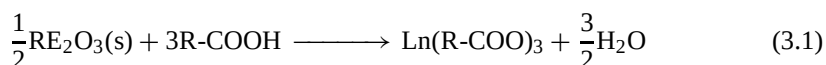
Rare earth–carboxylic acid complexes are sometimes called rare earth carboxylates. This section will focus on the synthetic methods, structural modes and connectivity, and solution chemistry. Distinct structural features and the general trends in structural change with various RE or ligands will be emphasized.

3.2.1 Preparation of Rare Earth Complexes with Carboxylic Acids

Many synthetic methods have been developed to prepare pure rare earth–carboxylic acid complexes with high yields. Based on the starting materials, the methods can be put into two categories: (i) rare earth oxides and (ii) rare earth salts. The synthesis can be done in aqueous solutions, organic media, or mixtures of the two, depending on the solubility and the nature of the ligands and the complexes, under ambient conditions, by hydro(solvo)thermal synthesis, or by gel synthesis. Under hydro(solvo)thermal conditions (in aqueous or non-aqueous media

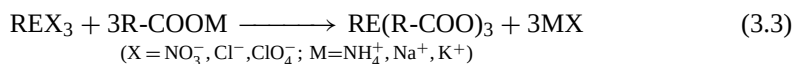
with temperatures above boiling point and pressures higher than 1 bar; 1 bar = 10^5 Pa), the solvents and the reactants can behave very differently from the same reaction carried out under ambient conditions [11]. This is very useful for the reactions where the reactants or products have low solubility under ambient conditions. Alternatively, gel synthesis or crystal growth in gel is a unique way of obtaining high quality single crystals. It was introduced by Liesegang more than a century ago [12], and, today it still proves to be a very powerful and inexpensive method to prepare single crystals. In fact, both hydro(solvo)thermal synthesis and gel synthesis have been successfully applied in the preparation of rare earth–polycarboxylic acid complexes.

3.2.1.1 Synthesis Starting with Rare Earth Oxides



The synthesis is normally done under atmospheric pressure. By heating and/or refluxing the mixture of RE_2O_3 with a stoichiometric amount of R-COOH in water or an organic solvent, such as MeOH, EtOH, DMF or DMSO, a clear solution of the complex can be obtained. The product can be harvested by filtration followed by evaporation of the solvents, or by adding a less-polar solvent to the solution. About 5% in excess of RE_2O_3 is typically used to avoid the possible contamination from the un-reacted R-COOH , and the unused RE_2O_3 can then be removed by filtration after the reaction is completed.

3.2.1.2 Synthesis Starting with Rare Earth Salts



The synthesis is in two steps: (i) the neutralization of R-COOH with a base, such as ammonia, NaOH, or KOH (Equation 3.2) and (ii) the reaction of the resulting solution with the rare earth salts (Equation 3.3). The most commonly used salts are rare earth nitrates, chlorides, and perchlorates, largely because of their good solubility in water or in the polar solvents (THF, MeOH, EtOH, MeCN, DMF, and DMSO). The synthesis can be accomplished under either ambient conditions or by solvothermal synthesis.

3.2.1.3 Hydro(solvo)thermal Synthesis

Hydro(solvo)thermal synthesis is a heterogeneous reaction in aqueous or non-aqueous media with temperatures above the boiling point of the solvent and pressures higher than 1 bar. Hydrothermal synthesis is believed to have been first introduced by Schafhautl in 1845 with water as the reacting media, and the device in the modern form of hydro(solvo)thermal synthesis, a sealed glass ampoule in an autoclave, was developed by de Senarmont in 1851 [11].

Hydro(solvo)synthesis has many advantages over conventional synthesis, and one of them is the single crystal growth of low solubility compounds, such as rare earth–polycarboxylic acid complexes. The starting materials can be polycarboxylic acids and rare earth oxides or salts (nitrates, chlorides or perchlorates) with or without a base. The medium can be water or organic solvents, such as methanol, ethanol, THF, or mixtures of different solvents. Many MOF materials have been synthesized through hydro(solvo)synthesis. However, for different systems, the reaction conditions, including the choice of the solvents, the concentrations of the starting materials, the reaction temperature, the controls of the heating and cooling, and so on, may vary greatly, and the same system could result in different products if any of these conditions are changed. In addition, the products and/or their structures are generally not predictable a priori [13].

3.2.1.4 Gel Synthesis – Crystal Growth in Gel

Rare earth–polycarboxylic acid complexes generally display high thermal stability and are considered to be very promising candidates as MOF materials. However, their limited solubility in water or organic solvents makes growing single crystals a big obstacle for their detailed structural characterization. Single crystals are generally not obtainable by routine operations. Hydro(solvo)thermal synthesis has been proved to be a very effective means of solving this problem, but the inherently demanding experimental requirements (100°C or higher) and the unpredictability prevents this method from being generally useful. Gel synthesis, operating under ambient conditions, is a good alternative to hydro(solvo)thermal synthesis [14–16].

A gel is a two-component system that is semi-solid that is particularly rich in liquid and has fine pores in it. Several gels, such as silica gels, oleates, gelatin, poly(vinyl alcohol), and agar, have been used for crystal growth, with silica gels, derived from water glass or sodium metasilicate, being the most widely used. When acids, such as HCl, HNO₃ or CH₃COOH, are added to a silicate solution, the silicate ion reacts with itself to produce Si–O–Si bonds and forms a cross-linked 3D-framework with the channels or pockets filled by water molecules, the channels being very important for the formation of crystals in the gel. To prepare single crystals of rare earth–polycarboxylic acid complexes in a gel, a common practice is to first dissolve a polycarboxylic acid in the gel, which is then allowed to set in a test-tube or beaker, and finally a solution of the rare earth salt, usually, chloride, nitrate or perchlorate, is added to the top of the gel. The solution slowly diffuses through the pockets in the gel enabling the reaction to take place between the rare earth ions and the polycarboxylic acid. After allowing a certain period of time for diffusion (days to months), well-shaped crystals may be seen in the gel. Single crystals obtained by gel synthesis usually contain more lattice water, and rare earth–polycarboxylic acid complexes with larger channels have been prepared efficiently by this method. Readers are referred to pertinent references for more details [17].

3.2.2 Structural Chemistry of Rare Earth Complexes with Carboxylic Acids

Owing to the high positive charge, large ionic radii, hard Lewis acid character of RE(III), and the ionic nature of the RE(III)–ligand bonds, RE(III) ions tend to form complexes with high coordination numbers and flexible coordination geometries. A wide range of interesting structures and distinct connectivities have been observed. For RE(III)–carboxylic acid complexes, the coordination numbers for the RE(III) are known to be between six and ten, achieved by the

formation of dimeric or polymeric structures and/or with a high degree of solvation, although mononuclear complexes do exist. The most frequently observed coordination numbers (CN) are eight and nine, with square antiprism and tricapped trigonal-prism coordination geometry, respectively. The light and mid-lanthanide ions (La^{3+} – Tb^{3+}) prefer $\text{CN} = 9$, while the heavy lanthanide ions (Dy^{3+} – Lu^{3+}) prefer $\text{CN} = 8$. For the Y(III) complexes, they usually fall into the heavy lanthanide group with $\text{CN} = 8$, while a few Sc(III) complexes stand out with $\text{CN} = 6$ and an octahedral coordination geometry [18].

3.2.2.1 Coordination Modes and Types of Connectivity

Compared with 3d metal–carboxylic acid complexes, where the carboxylate groups are usually unidentate, the coordination modes in rare earth–carboxylic acid complexes are far more diverse. This is because: (i) as hard large Lewis acids, RE(III) ions are oxophilic and require high coordination numbers and (ii) owing to the ionic nature of RE(III)–ligand bonds, RE(III) ions have no coordination geometry preference. In rare earth–carboxylic acid complexes, RE(III) ions tend to maximize their coordination numbers by coordinating to up to eight carboxylate groups, and solvent molecules, in particular those containing O atoms, such as water, DMF, DMSO, EtOH, MeOH, THF, and so on, with irregular coordination geometries. Because there is no geometry requirement, the coordination atoms can approach the RE(III) ions from any direction, which makes bidentate, tridentate or chelating coordination modes possible. Also, the large size of the RE(III) makes the four-member chelating ring (Figure 3.1b, g, and i) more stable than those in 3d metal complexes. Carboxylates have been found to adopt several coordination modes in the complexes (Figure 3.1). However, as indicated by Ouchi *et al.* [19], these modes are the only typical forms. It is not uncommon to see an intermediate mode between the two distinct types. For example, a chelating tridentate mode $\mu_2\text{-}\eta^2\eta^1$ (Figure 3.1g), when the RE–O' distance is much longer than those of the RE–O and RE'–O' bonds, is regarded as the intermediate between the chelating tridentate ($\mu_2\text{-}\eta^2\eta^1$) and the bidentate mode ($\mu_2\text{-}\eta^1\eta^1$ ZE) (Figure 3.1f). The most common coordination modes for carboxylates are unidentate η^1 , simple chelating η^2 , bridging bidentates $\mu_2\text{-}\eta^1\eta^1$ ZZ, $\mu_2\text{-}\eta^1\eta^1$ EE, and $\mu_2\text{-}\eta^1\eta^1$ ZE, and the chelating tridentate $\mu_2\text{-}\eta^2\eta^1$. In mononuclear complexes, carboxylates usually adopt unidentate (a) and the simple chelating (b), while in dimeric or polymeric complexes, the most popular coordination modes for carboxylate are bridging bidentate $\mu_2\text{-}\eta^1\eta^1$ ZZ, chelating tridentate $\mu_2\text{-}\eta^2\eta^1$, and the simple chelating η^2 .

In addition to the variety of coordination modes, a wide range of fascinating bridging modes are also observed in the dimeric and polymeric complexes (Figure 3.2). In the dimeric complexes, the two RE(III) ions can be held together by either two or four bridging carboxylates with the same or different coordination modes, while up to four bridging interactions can occur in one structure for polymeric complexes. Amongst the different bridging modes, the $\mu_2\text{-}\eta^2\eta^1$ bridging mode makes the shortest RE···RE distances while $\mu_2\text{-}\eta^1\eta^1$ EE makes the longest, and with the same bridging mode, the more bridges there are, the shorter the RE···RE distances [20, 21].

3.2.2.2 Control of the Polymerization of the Complexes

Owing to the high positive charge, large ionic radii of RE(III) ions and the ionic nature of the RE(III)–oxygen bonds, RE(III) ions tend to share the carboxylato-groups to form polymeric

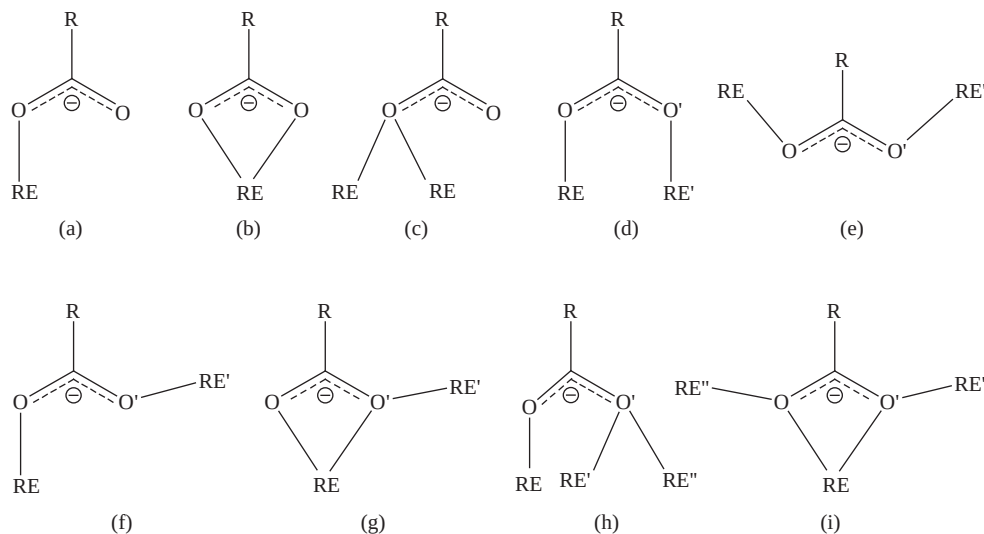


Figure 3.1 Coordination modes observed for rare earth-carboxylic acid complexes: (a) η^1 ; (b) η^2 ; (c) $\mu_2\text{-}\eta^1\eta^1$ (O, O); (d) $\mu_2\text{-}\eta^1\eta^1$ ZZ; (e) $\mu_2\text{-}\eta^1\eta^1$ EE; (f) $\mu_2\text{-}\eta^1\eta^1$ ZE; (g) $\mu_2\text{-}\eta^2\eta^1$; (h) $\mu_3\text{-}\eta^2\eta^1$; and (i) $\mu_3\text{-}\eta^2\eta^2$.

complexes. In theory, this tendency can be prevented either by supplying “extra” donor atoms or by increasing the steric hindrance of the ligands. In fact, monomeric or dimeric RE(III) complexes are obtainable by using bulky ligands, raising the molar ratio of carboxylate to RE(III), or introducing auxiliary ligands, such as phen, bipy or terp, to the complexes.

Steric Hindrance of the Ligand

When a carboxylate is bulky enough relative to the sizes of the RE(III) ions, the carboxylate itself can prevent the complex from polymerizing. As such, dimeric or monomeric complexes can be obtained. Formate has the smallest steric hindrance. Its complexes with RE(III) are not surprisingly all polymeric. At least two series of formate-RE(III) complexes have been reported, one with the general formula $[\text{REL}_3]_n$ (RE = La, Ce, Gd, Tb, Tm, and Gd) [22] and the other $[\text{REL}_3(\text{H}_2\text{O})_2]_n$ (RE = Gd, Tb, Dy, Ho, Er, Tm, and Y) [23, 24]. For acetic acid, its complexes with large RE(III) ions (RE = La–Nd) are polymeric, but the complexes with smaller RE(III) ions (RE = Gd–Lu) are dimeric, and its mid-rare earth ions (RE = Sm and Eu) complexes are either dimeric [25] or polymeric dimeric [26]. Only a handful of propionic acid complexes with RE(III) have been structurally characterized, but the trend is very similar to the complexes with acetic acid, that is, small RE(III) ions form dimers while the large ones form polymers [27–29]. Similar trends are also found for benzoic acid complexes: polymeric structures for the complexes of large RE(III) ions [RE(III) = La–Tb], and dimeric structures for the complexes of small RE(III) ions, for example, Y(III) and Yb(III).

Figure 3.3 shows several bulky carboxylic acid ligands. Pivalic acid forms monomeric complexes with small RE(III) ions. Its complex with Dy(III), $[\text{DyL}_3(\text{H}_2\text{O})_3] \cdot (\text{HL})$ is a monomer with Dy(III) coordinated by three chelating pivalates [30], while its complexes with large RE(III) (RE = La–Eu) are dimeric: $[\text{RE}_2\text{L}_6(\text{HL})_6]$ (HL = pivalic acid), where the two RE(III)

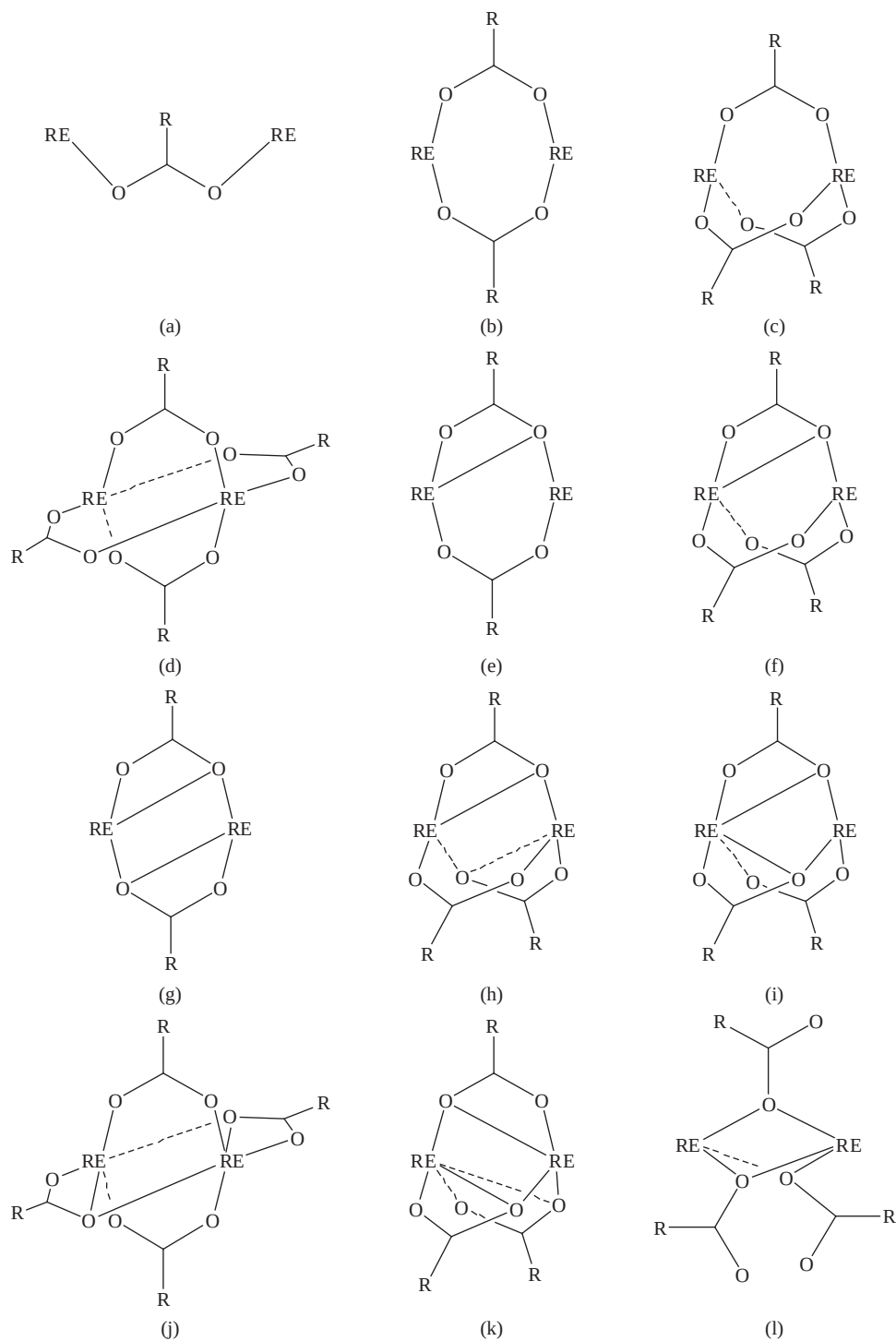


Figure 3.2 Bridging connectivities observed in dimeric and polymeric rare earth complexes with carboxylic acids.

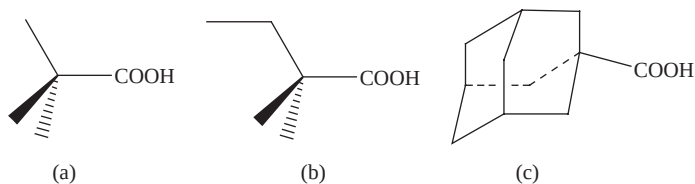


Figure 3.3 Structures of (a) pivalic acid; (b) 2,2-dimethylbutyric acid; and (c) 1-adamantane carboxylic acid.

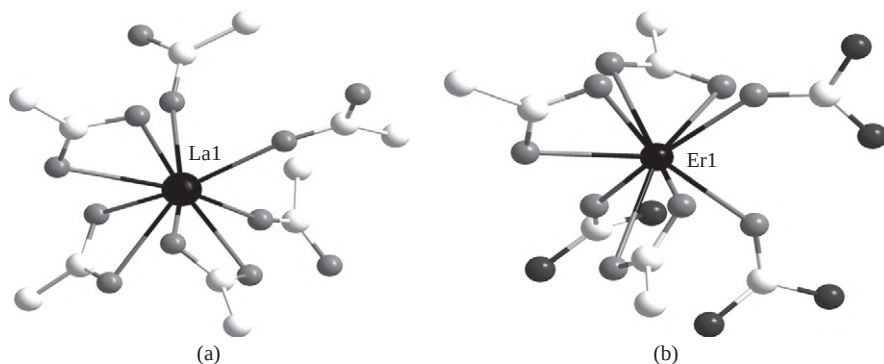


Figure 3.4 Structures of (a) [LaL₆]³⁺ and (b) [ErL₃L'₃] (HL = acetic acid, L' = urea) [RE, black (large balls); O, grey; N, black (small balls); C, white; H, omitted]. (Redrawn from the CIF files of G. Meyer and D. Gieseke-Vollmer, “Anhydrous lanthanum acetate, La(CH₃COO)₃, and its precursor, ammonium hexaacetatolanthanate hemihydrate (NH₄)₃[La(CH₃COO)₆]·1/2H₂O: synthesis, structures, thermal behaviour,” *Zeitschrift für Anorganische und Allgemeine Chemie*, **619**, 1603–1608, 1993 [35]; and G.V. Romanenko *et al.*, “Crystal structure of tris(acetato)tris(urea)erbium(III) monourea,” *Zhurnal Strukturnoi Khimii*, **26** (5), 103–108, 1985 [36].)

ions are bridged by four bidentate (μ_2 - $\eta^1\eta^1$ ZZ) pivalates. Each of the two RE(III) ions are coordinated by one unidentate pivalate and three unidentate pivalic acid molecules with CN = 8 [31]. The complexes of two bulkier monocarboxylates (Figure 3.3b and c) with large RE(III) (RE = La, Nd) ions have also been found to be dimeric [32, 33]. So far, no structural data are available for their complexes with smaller RE(III) ions.

Molar Ratio of Coordinating Carboxylate to RE(III)

The molar ratio of coordinating carboxylate to RE(III) is usually noted as “carboxylate/RE.” From the discussion above, we have seen that formic acid forms coordination polymers with the whole series of RE(III) when the carboxylate/RE = 3. However, when carboxylate/RE = 6 or 8, the complexes become monomeric, where the metal centers are eight-coordinated either by four unidentate (η^1) and two bidentate (η^2) formates, or by eight unidentate (η^1) formates [34]. Similarly, the acetate complexes, (NH₄)₂[LaL₆]·0.5H₂O, are also of monomeric structure, where the carboxylate/RE ratio is 6, with the RE(III) being coordinated by three unidentate (η^1) acetates and three chelating (η^2) acetates with CN = 9 [35] (Figure 3.4a). Complex [ErL₃L'₃]·L' (HL = acetic acid; L' = urea) stands out as a unique example of this category (Figure 3.4b).

The carboxylate/RE ratio of the complex is 3, but the structure of $[\text{ErL}_3\text{L}'_3]$ is very much the same as $[\text{LaL}_6]^{3-}$ (HL = acetic acid). The three acetates coordinate to the Er(III) ion in a chelating mode (η^2), while the three urea molecules act as another three unidentate acetates [36]. So far, this type of monomeric complex has only been found in the formate and acetate complexes.

Use of Auxiliary Ligands

Some chelating ligands, for example, 1,10-phenanthroline (phen), 2,2'-bipyridine (bipy) or 2,2':6',2''-terpyridine (terp), can prevent the complexes from polymerizing. It has been found that ternary complexes, $[\text{RE}_2\text{L}_6(\text{phen})_2]$ (HL = acetic acid; RE = Ce, Ho, and Lu) is dimeric [37–39], where the two RE(III) ions are bridged by four acetates, and each of the two RE(III) is chelated by an acetate and a phen. With 4-aminobenzonic acid, a bulkier ligand, three types of ternary complexes with monomeric structures are isolated: (I) $[\text{LaL}_3(\text{HL})(\text{phen})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ [40], (II) $[\text{REL}_3(\text{phen})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (RE = Eu, Tb) [40], and (III) $[\text{TbL}_2(\text{phen})_2(\text{H}_2\text{O})_2] \cdot (\text{L})(\text{phen}) \cdot 4\text{H}_2\text{O}$ [41]. In type I complexes, the metal center is coordinated by three carboxylates [(two unidentate (η^1) and one chelating (η^2)), one protonated carboxylate [unidentate (η^1)], and two chelating phen, with its coordination number as ten (Figure 3.5a). In type II complexes, however, the RE(III) ions are coordinated by three chelating (η^2) carboxylates, one chelating phen, and one water with CN = 9 (Figure 3.5b). Type III complexes were obtained when the molar ratio of phen in the structure is high (RE : L : phen = 1 : 3 : 2). One of the 4-aminobenzoates is pushed out of the coordination sphere by the second phen. The Tb(III) center is coordinated by two unidentate (η^1) carboxylates, two chelating phen, and two water molecules, and the coordination number is thus eight, which shows the strong coordination ability of phen to RE(III).

The use of bipy or terp as the auxiliary ligand can also lead to the formation of the monomeric or dimeric structures. In $[\text{PrL}_3(\text{bipy})_2]$ (HL = trichloroacetic acid) [42], the three carboxylates chelate (η^2) to Pr(III), whereas the two bipy coordinate to the metal center with their two nitrogen atoms. $[\text{TbL}_3(\text{terp})(\text{H}_2\text{O})]_2$ (L = 4-aminobenzonic acid) is a dimer, where the

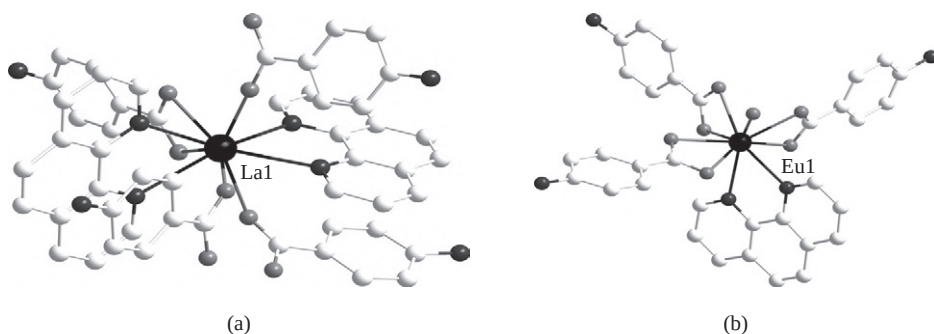


Figure 3.5 Structures of (a) $[\text{LaL}_3(\text{HL})(\text{phen})_2(\text{H}_2\text{O})]$ and (b) $[\text{EuL}_3(\text{phen})(\text{H}_2\text{O})]$ (HL = 4-aminobenzonic acid) [RE, black (large balls); O, grey; N, black (small balls); C, white; H, omitted]. (Redrawn from the CIF files of T. Fiedler *et al.*, “Synthesis, structural and spectroscopic studies on the lanthanoid p-aminobenzoates and derived optically functional polyurethane composites,” *European Journal of Inorganic Chemistry*, **2007**, 291–301, 2006 [40].)

two Tb(III) are joined together by two ($\mu_2\text{-}\eta^1\eta^1$) and each of the two Tb(III) ions is coordinated further by a terp, one unidentate (η^1) and one chelating (η^2) ligand in addition to two water molecules, resulting in a CN = 9 [40].

3.2.2.3 Structures of the Rare Earth Complexes with Monocarboxylic Acids

While most of the RE(III)–monocarboxylic acid complexes are polymeric, some of them are monomeric, dimeric, and tetrameric. For dimeric and tetrameric complexes, their structures are pretty simple: there are four types (two with double bridging and two with quadruple bridging) of dimers and only two types of tetramers. However, the structures of the polymeric complexes are much more complicated: the bridging modes between two neighboring metals can be single, double, triple, or quadruple bridging, and up to three different bridging modes can be present in one structure. However, owing to the limited size of this chapter, only polymers with one and two bridging modes in the structures will be discussed here.

Monomeric Complexes

When the ligand is bulkier and the RE(III) ion is smaller, the complex is more likely to be monomeric. Most of the monomeric complexes have the formula $[\text{REL}_3(\text{sol})_n]$, where sol is a coordinating solvent, such as H_2O , EtOH, MeOH, DMF or DMSO, and so on. In most cases, the three carboxylates are in a chelating (η^2) mode, and n is 2 or 3, CN = 8 or 9. However, when the ligand is too bulky, there would not be enough room for all of the three carboxylates to be in the chelating mode, and one or two of them have to be in a monodentate (η^1) mode, and the number of solvent molecules (n) becomes three or four. In $[\text{DyL}_3(\text{H}_2\text{O})_3]\cdot(\text{HL})_2$ (HL = pivalic acid) [30], Dy(III) is coordinated by three chelating (η^2) pivalates and three water, CN = 9 (Figure 3.6a). In the complex $[\text{TbL}_3(\text{H}_2\text{O})_4]$, where HL is 2,6-dihydroxybenzoic acid, only one ligand is chelating, and the other two are unidentate (Figure 3.6b) [43].

As discussed in Section 3.2.2.2, when the carboxylate/RE ratio is high (≥ 4), anionic monomeric complexes are possible. For example, the acetate complex, $(\text{NH}_4)_2[\text{LaL}_6]\cdot 0.5\text{H}_2\text{O}$,

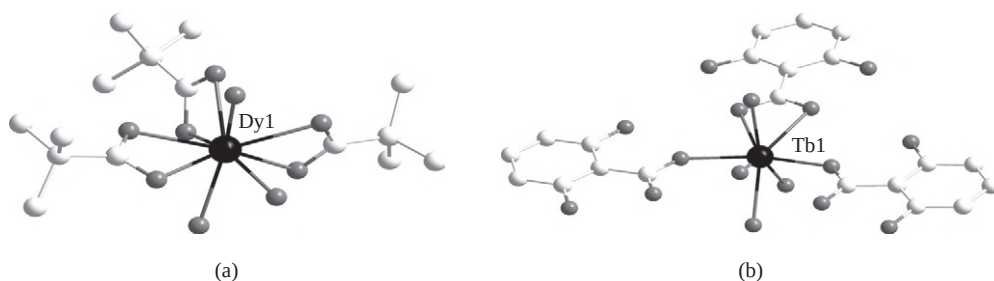


Figure 3.6 Structures of (a) $[\text{DyL}_3(\text{H}_2\text{O})_3]$ and (b) $[\text{TbL}'_3(\text{H}_2\text{O})_4]$ (HL = pivalic acid and HL' = 2, 6-dihydroxybenzoic acid) [RE, black; O, grey; C, white; H, omitted]. (Redrawn from the CIF files of M.L. Huang *et al.*, “Study on the synthesis and the structures of rare earth complexes with 4-aminobenzoic acid,” *Huaxue Yanjiu Yu Yingyong* (Chinese) (Chemical Research Applications), **18**, 245–251, 2006 [30]; and T. Glowiak *et al.*, “Crystal structure of the isomorphous complexes tetraaquabis(2,6-dihydroxybenzoato-O)(2,6-dihydroxybenzoato-O, O)terbium(III) and holmium(III)dihydrate,” *Journal of Coordination Chemistry*, **48** (4), 477–486, 1999 [43].)

is monomeric, where the carboxylate/RE ratio is six, the RE(III) is coordinated by three unidentate (η^1) acetates and three chelating (η^2) acetates with CN = 9 [35].

With phen as the auxiliary ligand, monomeric complexes with the formula $[\text{REL}_3(\text{phen})_2(\text{sol})_n]$ (sol = solvent molecule) can be obtained. When the three carboxylates are all in the chelating modes (η^2), there is no coordination solvent in the structure, and the CN = 10. When one or two of the coordination carboxylates are unidentate, there will be one coordinating solvent. Examples can be found in Section 3.2.2.2.

Dimeric Complexes

The structures of dimeric complexes are characterized by the number of carboxylate bridges between the two metal centers and also the ways of bridging. So far, the bridge numbers found for such complexes are either two or four, and single- or triple-bridged dimers have not been reported, although bridge numbers from one to four are common for polymeric structures. Most of the dimeric structures are centrosymmetric. Thus, only a half of the dimer is unique crystallographically, meaning that the two RE(III) ions have exactly the same coordination environment. Based on the bridging type, the dimeric complexes can be grouped into four types: (I) double bidentate bridging ($(\mu_2-\eta^1\eta^1)_2$); (II) double tridentate bridging ($(\mu_2-\eta^2\eta^1)_2$); (III) quadruple bidentate bridging ($(\mu_2-\eta^1\eta^1)_4$), and (IV) quadruple mixed bridging (= “double bidentate bridging + double tridentate bridging”) “ $(\mu_2-\eta^2\eta^1)_2 + (\mu_2-\eta^1\eta^1)_2$.”

Only a small number of ligands have been found to form dimers with double-bridging (acetic acid, propionic acid, benzoic acid and some *para*-substituted derivatives of benzoic acid ($p\text{-RC}_6\text{H}_4\text{COOH}$) (R = $-\text{NH}_2$, $-\text{OCH}_3$, $-\text{CN}$, and so on for type I and acetic acid, methacrylic acid, 3-(2-hydroxyphenyl) acrylic acid, 2-thiophene carboxylic acid, 2-methoxybenzoic acid, 3-hydroxybenzoic acid, 4-hydroxy-3-methoxybenzoic acid, and 2,6-dichlorobenzoic acid for type II), but most of the monocarboxylic acid can form quadruply bridged dimers, that is, types III and IV. The structure of $[\text{TbL}_3(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$ (HL = *p*-aminobenzoic acid) is shown in Figure 3.7a, the two Tb(III) are bridged by two bidentate ($\mu_2-\eta^1\eta^1$) carboxylates, and each of them is coordinated further by two chelating (η^2) carboxylates and two water, CN = 8 [44]. In complexes $[\text{RE}_2\text{L}_6(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ (RE = Sm–Lu; HL = acetic acid) [45], the two RE(III) centers are bridged by two tridentate ($\mu_2-\eta^2\eta^1$) carboxylates. Each of the RE(III) ions is further coordinated by two chelating (η^2) carboxylates and four terminal water, CN = 9 (Figure 3.7b).

Only trifluoroacetic acid is found to form quadruple simple bridging $[(\mu_2-\eta^1\eta^1)_4]$ dimers without any auxiliary ligands: $[\text{RE}_2\text{L}_6(\text{H}_2\text{O})_6]$ (HL = trifluoroacetic acid; RE = Pr, Gd, and Lu) [25, 46]. Other carboxylic acids can only form this type of complex with the help of auxiliary ligands, such as phen, terp, bipy, DMSO (dimethyl sulfoxide), DMF (*N,N'*-dimethylformamide), ethanol, methanol, NO_3^- , and even the carboxylate (L^-) or the carboxylic acid (HL). The structures of $[\text{GdL}_3(\text{H}_2\text{O})_3]_2$ (HL = trifluoroacetic acid) and $[\text{EuL}_3(\text{phen})(\text{H}_2\text{O})]_2$ (HL = *p*-cynobenzoic acid) [47] are shown in Figure 3.8.

More than one third of the reported dimeric complexes are with quadruple chelating bridging interactions, and almost all of the monocarboxylic acids can form dimers with this type 2 of connectivity with or without auxiliary ligands. In a typical structure, the two RE(III) ions are bridged by two tridentate bridging $[(\mu_2-\eta^2\eta^1)_2]$ carboxylates and two bidentate bridging $[(\mu_2-\eta^1\eta^1)_2]$ carboxylates. Each of the two metal ions is further coordinated by one chelating (η^2) and one auxiliary ligand. The structures of $[\text{CeL}_3(\text{phen})]_2$ (HL = acetic acid) [37] and $[\text{EuL}_3(\text{phen})]_2$ (HL = 2-furancarboxylic acid) [48] are shown in Figure 3.9.

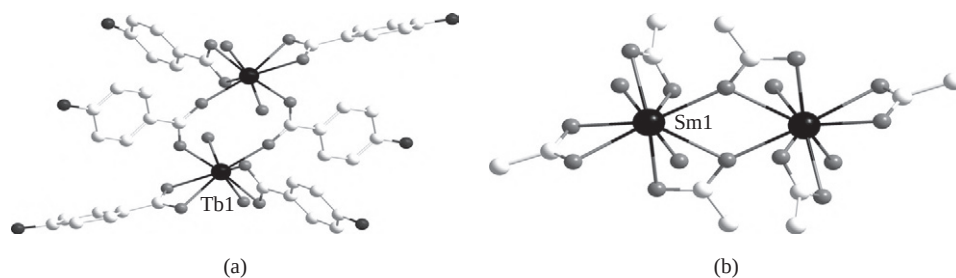


Figure 3.7 Structures of (a) $[\text{TbL}_3(\text{H}_2\text{O})_2]_2$ (HL = *p*-aminobenzoic acid) and (b) $[\text{SmL}_3(\text{H}_2\text{O})_2]_2$ (HL = acetic acid) [RE, black (large balls); O, grey; N, black (small balls); C, white; H, omitted]. (Redrawn from the CIF files of L. Oyang *et al.*, “Crystal structure and luminescence property of ternary terbium *p*-aminobenzoic acid complexes with different second ligands,” *Journal of Molecular Structure*, **740**, 175–180, 2005 [44]; and R. Vadura and J. Kvapil, “Growth and lattice parameters of the lanthanide carboxylates I. Tetrahydrated lanthanide acetates,” *Materials Research Bulletin*, **6**, 865–873, 1971 [45].)

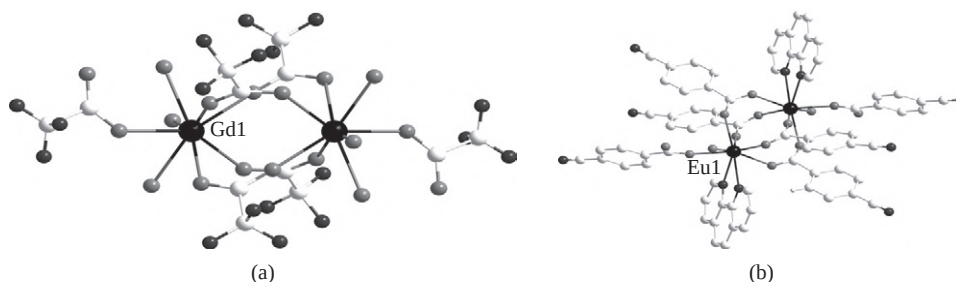


Figure 3.8 Structures of (a) $[\text{GdL}_3(\text{H}_2\text{O})_3]_2$ (HL = trifluoroacetic acid) and (b) $[\text{EuL}_3(\text{phen})(\text{H}_2\text{O})]_2$ (HL = *p*-cyanobenzoic acid) [RE, black (large balls); O, grey; N and F, black (small balls); C, white; H, omitted]. (Redrawn from the CIF files of D. John, A. Rohde and W. Urland, “Synthesis, crystal structure and magnetic behaviour of dimeric and polymeric gadolinium trifluoroacetate complexes,” *Zeitschrift für Naturforschung, B: Chemical Sciences*, **61** (6), 699–707, 2006 [46]; and Y. Li *et al.*, “Crystal structures and magnetic and luminescent properties of a series of homodinuclear lanthanide complexes with 4-cyanobenzoic ligand,” *Inorganic Chemistry*, **45** (16), 6308–6316, 2006 [47].)

By comparing the structures of the four types of dimeric complexes, we can see some trends: (i) large RE(III) ions prefer to form type II and IV complexes, while smaller RE(III) ions prefer type I and III; (ii) without any auxiliary ligands, RE(III) ions tend to form double-bridged complexes, that is, type I and type II, whereas with an auxiliary ligand, such as phen, bipy, and even carboxylate anions, the complexes will adopt the modes of type III or IV, where the auxiliary ligands push one non-bridging carboxylate from each end to form two new bridges.

Tetrameric Complexes

Only four tetrameric complexes in two types have been reported so far, and they are all the complexes of small RE(III) (RE = Y, Dy, Tm, and Lu) ions. $[\text{YL}_3(\text{H}_2\text{O})_2]_4$ (HL = *p*-hydroxybenzoic acid) [49] is of a linear structure. Only half of the tetramer is unique. The four

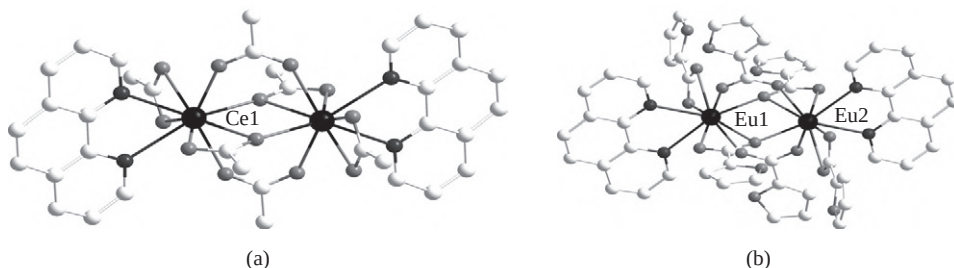


Figure 3.9 Structures of (a) $[\text{CeL}_3(\text{phen})]_2$ (HL = acetic acid) and (b) $[\text{EuL}_3(\text{phen})]_2$ (HL = 2-furancarboxylic acid) [RE, black (large balls); O, grey; N, black (small balls); C, white; H, omitted]. (Redrawn from the CIF files of A. Panagiotopoulos *et al.*, “Molecular structure and magnetic properties of acetato-bridged lanthanide(III) dimers,” *Inorganic Chemistry*, **34**, 4918–4920, 1995 [37]; and X. Li *et al.*, “Synthesis, structure and luminescence property of the ternary and quaternary europium complexes with furoic acid,” *Journal of Molecular Structure*, **604**, 65–71, 2002 [48].)

Y(III) ions are linked together by simple double bridges $[(\mu_2-\eta^1\eta^1)_2]$. Each of the two terminal Y(III) are then coordinated by two chelating (η^2) ligands and two water, and each of the two internal Y(III) are coordinated by one chelating (η^2) ligand and two water, CN = 8 (Figure 3.10a). Similar structures are found for three *p*-nitrobenzoic acid complexes, $[\text{REL}_3(\text{H}_2\text{O})_2]_4$ (RE = Dy [50], Tm, and Y [51]; L = *p*-nitrobenzoic acid).

There is only one example for the second type of tetramer. $\text{Cs}_4[\text{LuL}_4]_4$ (HL = acetic acid), is a closed square, and only half of the structure is unique [52]. Lu1 and Lu2 or Lu1a and Lu2a are linked together by a mixed triple bridge $[(\mu_2-\eta^2\eta^1)_2 + (\mu_2-\eta^1\eta^1)]$, while Lu1 and Lu2a or Lu2 and Lu1a, on the other hand, are bridged by a bidentate bridging ligand, resulting a square with four Lu(III) at the corners. Lu1 is then coordinated by two chelating (η^2) carboxylates, CN = 9. Lu2 has very a similar coordination environment, except that only one carboxylate is in the chelating (η^2) mode, and the other one is unidentate (η^1), CN = 8 (Figure 3.10b). The formation mechanism of the tetramers is still not clear, although the sizes of the metals may play important roles here.

Polymeric Complexes with One Bridging Mode

In these complexes, the same bridging modes repeat in between the two neighboring metal ions. So far, seven bridging modes have been observed in the complexes: (i) single bidentate bridging $\mu_2-\eta^1\eta^1$; (ii) double bidentate bridging $(\mu_2-\eta^1\eta^1)_2$; (iii) double tridentate bridging $(\mu_2-\eta^2\eta^1)_2$; (iv) triple bidentate bridging $(\mu_2-\eta^1\eta^1)_3$; (v) triple mixed bridging A $[(\mu_2-\eta^1\eta^1)_2 + (\mu_2-\eta^2\eta^1)]$; (vi) triple mixed bridging B $[(\mu_2-\eta^1\eta^1) + (\mu_2-\eta^2\eta^1)_2]$; and (vii) triple tridentate bridging, $(\mu_2-\eta^2\eta^1)_3$ [53].

In $[\text{YbL}_3(\text{H}_2\text{O})_2]_n$ (HL = formic acid), the two neighboring Yb(III) ions are linked together by a single bidentate bridging $(\mu_2-\eta^1\eta^1)$ formate, and each of the Yb(III) ions are then coordinated by two chelating (η^2) formates and two aqua ligands, CN = 8 [54]. The same connections are also observed in $[\text{YbL}_3(\text{H}_2\text{O})_2]_n$ (HL = methylthioacetic acid) [55].

There are two double bridging modes, $(\mu_2-\eta^1\eta^1)_2$ and $(\mu_2-\eta^2\eta^1)_2$. Of these, $(\mu_2-\eta^1\eta^1)_2$ is only found in the complexes of benzoic acid and some of its derivatives, while $(\mu_2-\eta^2\eta^1)_2$ is popular in the complexes with aliphatic acids, such as acetates and propionates. This is because

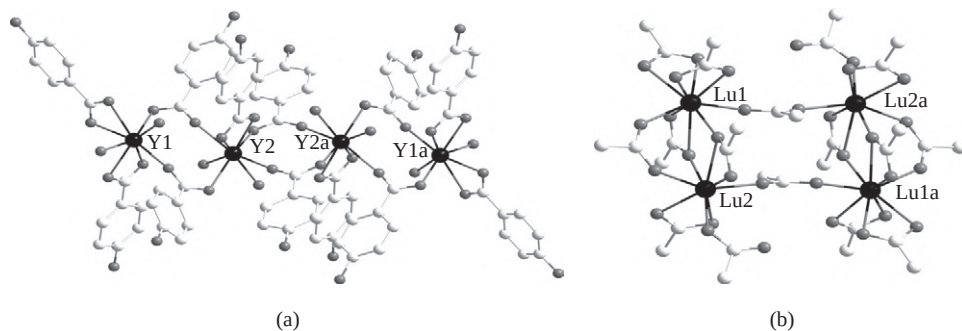


Figure 3.10 Structures of (a) $[\text{YL}_3(\text{H}_2\text{O})_2]_4$ (HL = *p*-hydroxybenzoic acid) and (b) $[\text{LuL}_4]_4^{4-}$ (HL = acetic acid) [RE, black; O, grey; C, white; H, omitted]. (Redrawn from the CIF files of M.S. Khiyalov *et al.*, “Crystalline and molecular structure of (*p*-hydroxybenzoato)yttrium(III),” *Koordinatsionnaya Khimiya* (Coordination Chemistry) (in Russian), 7 (8), 1255–1261, 1981 [49]; and A. Lossin and G. Meyer, “Ternary acetates of the lanthanides with cesium: dimers in $\text{CsLu}(\text{CH}_3\text{COO})_4$ and trimers in $\text{Cs}_2[\text{Lu}_3(\text{CH}_3\text{COO})_{10}(\text{OH})(\text{H}_2\text{O})]$. Synthesis, crystal structures, thermolysis,” *Zeitschrift für Anorganische und Allgemeine Chemie*, 619 (8), 1465–1473, 1993 [52].)

aliphates, with smaller steric hindrance than aromates, can approach RE(III) centers more facilely to accommodate tridentate chelating. In $[\text{REL}_3(\text{MeOH})_2]_n$ (RE = Sm [56], Eu, Gd, and Tb [20]; HL = benzoic acid), the two adjacent RE(III) ions are joined together by two bidentate benzoates, and each of the RE(III) centers is coordinated further by one chelating (η^2) benzoate and two methanol, CN = 8 (Figure 3.11a). In $[\text{Pr}_2\text{L}_6(\text{H}_2\text{O})_3]_n \cdot 3n\text{H}_2\text{O}$ (HL = propionic acid) [57], the adjacent Pr(III) ions are bridged together by two tridentate chelating $[(\mu_2-\eta^2\eta^1)_2]$ acetates. Each of them is then coordinated by a chelating (η^2) propionate and three water molecules, CN = 9 (Figure 3.11b).

Three of the four types of triple bridging polymeric structures are found with the RE(III) complexes with acetates. For Sc(III), the smallest RE(III), its anhydrous complex with acetic acid, $[\text{ScL}_3]_n$, has a triple bidentate bridging mode $(\mu_2-\eta^1\eta^1)_3$, where the two adjacent Sc(III) ions are bridged together through three acetates in mode $\mu_2-\eta^1\eta^1$. Each of the Sc(III) ions is thus coordinated by six oxygen atoms from six different acetates, CN = 6 [58]. The late rare earth analogs, $[\text{REL}_3]_n$ (RE = Tm–Lu), on the other hand, are in the bridging mode, $[(\mu_2-\eta^2\eta^1) + (\mu_2-\eta^1\eta^1)_2]$, with CN = 7 [59], while the triple bridging mode $[(\mu_2-\eta^1\eta^1) + (\mu_2-\eta^2\eta^1)_2]$, is found with the anhydrous complex with larger RE(III) ions, $[\text{HoL}_3]_n$, and in the hydrated complexes with early RE(III) ions, $[\text{RE}_2\text{L}_6(\text{H}_2\text{O})]_n$ (RE = Sm and Eu) [60]. A few other ligands, such as β -phenylacrylic acid [61], *p*-methylbenzoic acid [62], *m*-methylbenzoic acid [63], and *o*-aminobenzoic acid [64] are reported to form anhydrous complexes with early RE(III) ions, $[\text{REL}_3]_n$, in a triple tridentate bridging mode $(\mu_2-\eta^2\eta^1)_3$.

Polymeric Structures with Two Bridging Modes Alternated

The three most often observed structure types with two bridging modes are the alternating double bidentate bridging $(\mu_2-\eta^1\eta^1)_2$ and double tridentate bridging $(\mu_2-\eta^2\eta^1)_2$, referred to as $(\mu_2-\eta^1\eta^1)_2/(\mu_2-\eta^2\eta^1)_2$, alternating double bridging and triple bridging, referred to as

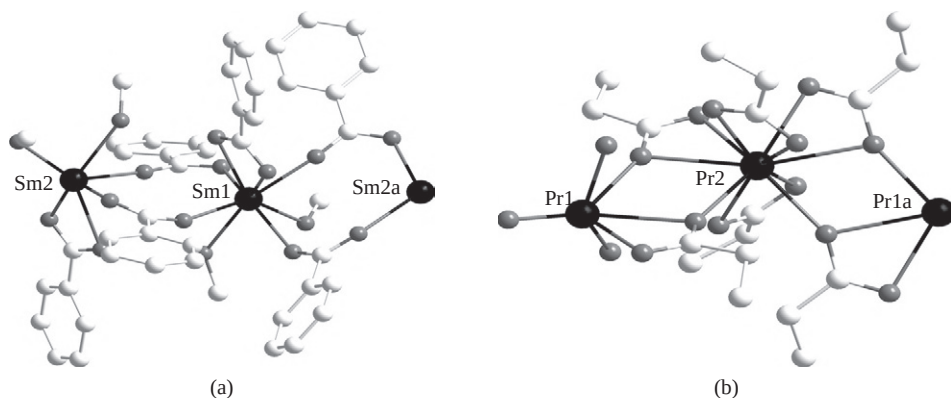


Figure 3.11 Structures of (a) $[\text{Sm}_2\text{L}_6(\text{MeOH})_4]_n$ (HL = benzoic acid) and (b) $[\text{Pr}_2\text{L}_6(\text{H}_2\text{O})_3]_n$ (HL = acetic acid) [RE, black; O, grey; C, white; H, omitted]. (Redrawn from the CIF files of U.P. Singh, R. Kumar and S. Upreti, "Synthesis, structural, photophysical and thermal studies of benzoate bridged Sm(III) complexes," *Journal of Molecular Structure*, **831** (1–3), 97–105, 2007 [56]; and D. Deiters and G. Meyer, "Synthesis and crystal structure of praseodymium propionate trihydrate, $\text{Pr}(\text{CH}_3\text{CH}_2\text{COO})_3(\text{H}_2\text{O})_3$," *Zeitschrift für Anorganische und Allgemeine Chemie*, **622** (2), 325–328, 1996 [57].)

$(\mu_2-\eta^1\eta^1)_2//(\mu_2-\eta^1\eta^1)(\mu_2-\eta^2\eta^1)_2$, and also alternating double bridging and quadruple bridging, referred to as $(\mu_2-\eta^1\eta^1)_2//(\mu_2-\eta^1\eta^1)_4$ or $(\mu_2-\eta^1\eta^1)_2//(\mu_2-\eta^1\eta^1)_2(\mu_2-\eta^2\eta^1)_2$.

The bridging mode $(\mu_2-\eta^1\eta^1)_2//(\mu_2-\eta^2\eta^1)_2$ is found in $[\text{La}(\text{L})_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})]_n \cdot n\text{CH}_3\text{OH}$ [L = *E*-3-(4-hydroxyl-phenyl)-acrylic acid] [65]. Two La(III) are linked together through the double tridentate bridging $(\mu_2-\eta^2\eta^1)_2$, and each of the two La(III) then connects to its neighboring La(III) through the double bidentate bridging. Each of the La(III) is also coordinated by a monodentate (η^1) carboxylate, two methanol molecules, and one water, CN = 10.

Three *p*-nitrobenzoic acid complexes, $[\text{RE}_2\text{L}_6(\text{H}_2\text{O})_4]_n \cdot 2n\text{H}_2\text{O}$ (RE = La [53], Eu [66], and Tb [67]; HL = *p*-nitrobenzoic acid), are found to have the alternating double bridging and triple bridging structure: $(\mu_2-\eta^1\eta^1)_2//(\mu_2-\eta^1\eta^1)(\mu_2-\eta^2\eta^1)_2$. As shown in Figure 3.12a, Eu2 and Eu1a are linked by the double bridging $(\mu_2-\eta^1\eta^1)_2$, and Eu1 and Eu2 are bridged through a triple bridging $(\mu_2-\eta^1\eta^1)(\mu_2-\eta^2\eta^1)_2$ with the two pairs of η^2 oxygen atoms coordinating to Eu1 and Eu2, respectively. Eu1 is then coordinated by three water molecules, while Eu2 is coordinated further by a ligand in the η^2 mode and a water molecule. Both Eu1 and Eu2 are nine-coordinated.

The bridging mode, $(\mu_2-\eta^1\eta^1)_2//(\mu_2-\eta^1\eta^1)_4$, is found in $[\text{RE}_2\text{L}_6(\text{H}_2\text{O})_3]_n \cdot n\text{H}_2\text{O}$ (RE = Er, Dy; HL = trichloroacetic acid) (Figure 3.12b) [68]. The two independent RE(III) ions are joined together by the quadruple bridge, that is, $(\mu_2-\eta^1\eta^1)_4$, and each of them are then linked to the neighboring RE(III) ions with a double bridge $(\mu_2-\eta^1\eta^1)_2$. In addition, the two metal ions are also bound to two and one water, CN = 8 or 7.

The second form of alternating double bridging and quadruple bridging is $(\mu_2-\eta^1\eta^1)_2//(\mu_2-\eta^1\eta^1)_2(\mu_2-\eta^2\eta^1)_2$, where the quadruple bridging consists of a double bidentate bridge and double tridentate bridge. The terbium complex with *m*-nitrobenzoic acid obtained from DMF, $[\text{Tb}_2\text{L}_6(\text{DMF})_2]_n$, exhibits this type of bridging [69], while its lanthanum analog is of a bridging mode, $(\mu_2-\eta^1\eta^1)_2//(\mu_2-\eta^1\eta^1)_4$ [70].

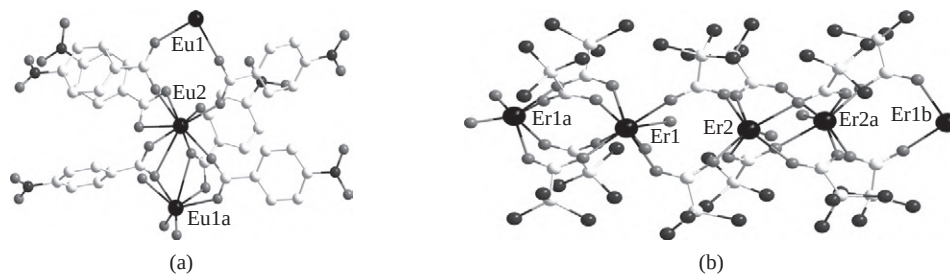


Figure 3.12 Structures of (a) $[\text{Eu}_2\text{L}_6(\text{H}_2\text{O})_4]_n$ (HL = *p*-nitrobenzoic acid) and (b) $[\text{Er}_2\text{L}_6(\text{H}_2\text{O})_3]_n$ (HL = trichloroacetic acid) [RE, black (large balls); N and Cl black (small balls); O, grey; C, white; H, omitted]. (Redrawn from the CIF files of Ad. Bettencourt-Dias and S. Viswanathan, “Nitro-functionalization and luminescence quantum yield of Eu(III) and Tb(III) benzoic acid complexes,” *Dalton Transactions*, 4093–4103, 2006 [66]; and T. Imai and A. Ouchi, “The structure of μ -aquabis(μ -trichloroacetato) bis[aquabis(trichloroacetato)erbium(III)] hydrate, $[[\text{Er}(\text{CCl}_3\text{CO}_2)_2(\text{H}_2\text{O})]_2(\text{CCl}_3\text{CO}_2)_2(\text{H}_2\text{O})]_n \cdot n\text{H}_2\text{O}$,” *Bulletin of the Chemical Society of Japan*, **60** (1), 408–410, 1987 [68].)

3.2.2.4 Structures of the Rare Earth Complexes with Polycarboxylic Acids

As we have seen from Section 3.2.2.3 carboxylate groups tend to bridge RE(III) ions through various coordination modes (Figure 3.2c–i), frequently leading to coordination polymers. These characteristics can certainly be translated into rare earth–polycarboxylic acids complexes, where two or more carboxylate groups in the same ligands are expected to bridge the RE(III) ions in a similar fashion, leading to much more complicated 2D- or 3D-polymeric structures. In fact, rare earth–polycarboxylic acid complexes are generally 2D- or 3D-polymers in nature, and are sparingly soluble in most solvents, such as water, THF (tetrahydrofuran), DMF, or DMSO, and thus are very hard to crystallize as single crystals. This may be why they have received much less attention in past decades than the rare earth monocarboxylates. However, driven by the fascinating structures and their potential applications, research activities in this area has been growing exponentially in recent years, supported by the widely applied hydro(solvo)thermal synthesis, and many fascinating 2D- and 3D-structures have been reported.

All of the coordination modes shown in Figure 3.1 have been observed in the dicarboxylic acid complexes, although far fewer RE(III) complexes with polycarboxylic acids have been structurally characterized, when compared with complexes with monocarboxylic acids. The carboxylate groups within the same ligand may display distinctly different coordination modes, and the four most frequently observed modes are tridentate bridging ($\mu_2\text{-}\eta^2\eta^1$), chelating (η^2), *ZZ*-bidentate bridging ($\mu_2\text{-}\eta^1\eta^1$ *ZZ*), and *ZE*-bidentate bridging ($\mu_2\text{-}\eta^1\eta^1$ *ZE*). The two neighboring RE(III) ions are generally bridged by up to four carboxylate groups from different ligands to form a chain of edge-sharing rare earth–oxygen polyhedra REO_m ($m = 7\text{--}10$), and the ligands then use the remaining carboxylate groups to construct more identical or similar chains and to link them together. When all the ligands stretch out in the same plane, they will hold the chains in the same plane, and the complexes are of 2D-layered structures. Thus, when the ligands stretch out in two or more different planes to join the chains of rare earth–oxygen polyhedra, the complexes will be in 3D-network structures.

Therefore, RE(III)–polycarboxylic acid complexes can be considered as polymeric structures made by edge-sharing rare earth–oxygen polyhedra REO_m ($m = 7\text{--}10$) linked together by carbon chains [71].

Nevertheless, the ionic character of the RE–O bond, the high coordination number requirement, and flexible coordination geometry of rare earth ions often makes the structures of complexes unpredictable. As a result, very few complexes obtained so far can be potentially used for gas storage, liquid absorption, magnetic materials, fluorescent probes or as Lewis acid catalysts. Among them are $[\text{Tb}_2(\text{bdc})_3(\text{H}_2\text{O})_4]_n$, $[\text{Tb}(\text{btc})(\text{H}_2\text{O})]_n \cdot 0.5n\text{H}_2\text{O} \cdot n\text{DMF}$ $[\text{Tb}(\text{btc})(\text{DMF})_2]_n \cdot n\text{H}_2\text{O}$, and $[\text{Tb}(\text{bpdc})_{1.5}(\text{H}_2\text{O})]_n \cdot 0.5n\text{DMF}$. It is worth noting that $[\text{Tb}_2(\text{bdc})_3(\text{H}_2\text{O})_4]_n$ reported by Yaghi and coworkers can be viewed as the first rare earth-based MOF material. The work was the very first attempt to seek open metal–organic framework materials beyond transition metal compounds, and it is also the first time rare earth–carboxylic acid complexes were examined as porous materials [72].

$[\text{Tb}_2(\text{bdc})_3(\text{H}_2\text{O})_4]_n$ was prepared by hydrothermal synthesis using an aqueous mixture of $\text{Tb}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, 1,4-benzodicarboxylic acid (H_2bdc), and triethylamine [72]. In the structure, each Tb(III) ion is coordinated by six oxygens of the bdc anions in a monodentate fashion and two water molecules, $\text{CN} = 8$ (Figure 3.13). The overall structure can be described as a

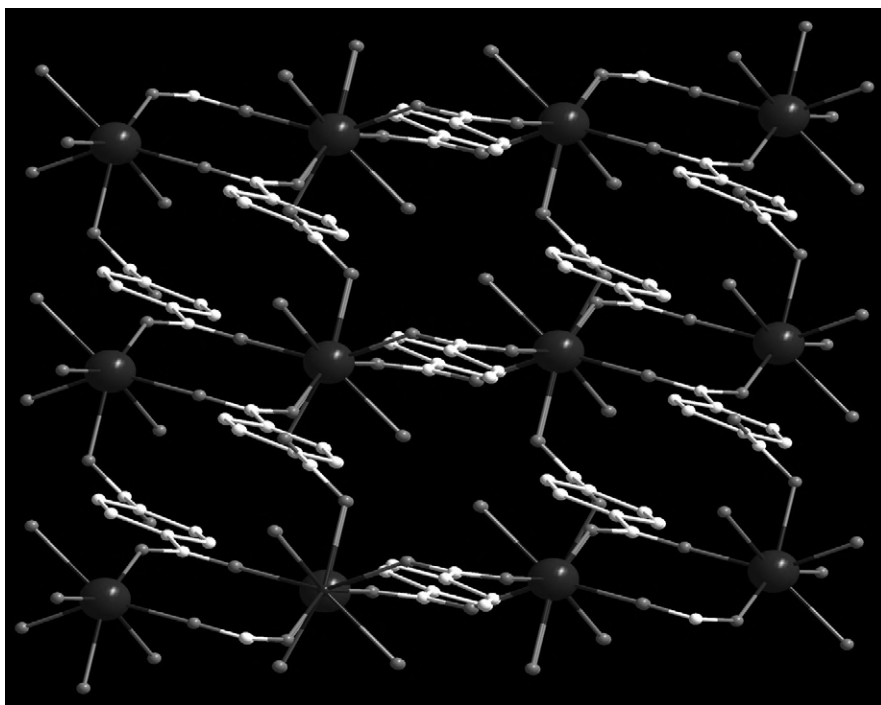


Figure 3.13 The crystal structure of $[\text{Tb}_2(\text{BDC})_3 \cdot (\text{H}_2\text{O})_4]_n$ shown approximately down the crystallographic b -axis, where aqua ligands are found to point toward the center of the 1D-channels (Tb, black; O, grey; C, white; H, omitted). (Redrawn from the CIF file of T.M. Reineke *et al.*, “From condensed lanthanide coordination solids to microporous frameworks having accessible metal sites,” *Journal of the American Chemical Society*, **121**, 1651–1657, 1999 [72].)

parallelepipedal motif with a terbium center on each of its eight corners and a bdc^{2-} on its four faces (the ab and bc crystallographic planes and their symmetry equivalent counterparts), leaving a 1D-channel ($5.1 \times 6.1 \text{ \AA}^2$) running in the b direction filled with coordination water. Experiment showed that the aqua ligands were removed at 115°C without the framework collapsing, and re-introduction of water to the dehydrated sample restored the original porous structure. The dehydrated porous solid with coordinatively unsaturated metal sites may be useful as a fluorescent probe and a Lewis acid catalyst.

$[\text{Tb}(\text{btc})(\text{H}_2\text{O})]_n \cdot 0.5n\text{H}_2\text{O} \cdot n\text{DMF}$ ($\text{H}_3\text{btc} = 1,3,5\text{-benzenetricarboxylic acid}$), dubbed as MOF-76, was obtained by solvothermal synthesis [73]. The structure is shown in Figure 3.14. Each Tb(III) ion is linked to each of its two Tb(III) neighbors through three carboxylates with the mode of $\mu_2\text{-}\eta^1\eta^1\text{ZZ}$ to form an edge-sharing infinite chain of rare earth—oxygen polyhedra REO_7 . They may be viewed as “rod-like” building units in the construction of the overall framework structure. Each rod is then connected to four neighboring rods through the ligand benzene ring. The rods pack in a tetragonal fashion, resulting in $6.6 \times 6.6 \text{ \AA}^2$ square channels in the c direction, filled with solvent molecules.

$[\text{Tb}(\text{btc})(\text{DMF})_2]_n \cdot n\text{H}_2\text{O}$ was obtained by heating a mixture of $\text{Tb}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, 1,3,5-benzotricarboxylic acid (H_3btc) and caprolactam (molar ratio 1 : 1 : 1) in a mixture of DMF and EtOH at 55°C [74]. X-ray diffraction studies showed that each metal center is coordinated with six oxygen atoms from four carboxylate groups of four different ligands and two oxygen atoms from two terminal DMF, $\text{CN} = 8$. Each of the four ligands is then connected to another four RE(III) to form a very complicated 3D-network (Figure 3.15). The most attractive feature

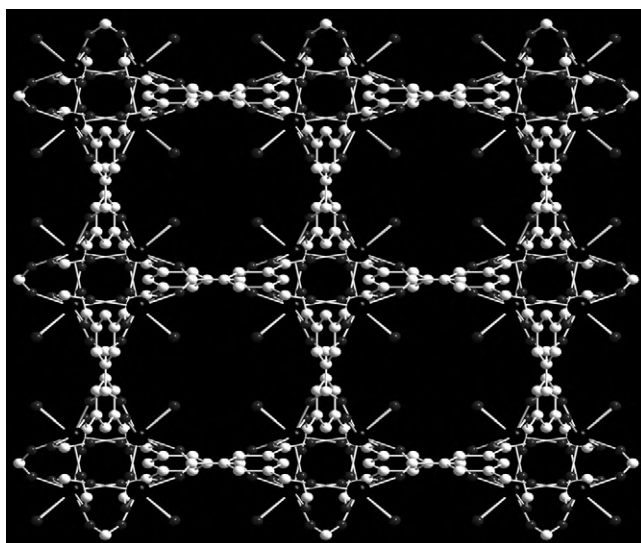


Figure 3.14 The structure of MOF-76 showing the $6.6 \times 6.6 \text{ \AA}^2$ square channels in the c -direction with the “rod-like” chains of rare earth—oxygen polyhedra REO_7 linked together via the benzene ring of 1,3,5-benzenetricarboxylate (RE, black; O, grey; C, white; H, omitted; DMF and H_2O guest molecules have been removed for clarity). (Redrawn from the CIF file of N.L. Rosi *et al.*, “Rod packings and metalorganic frameworks constructed from rod-shaped secondary building units,” *Journal of the American Chemical Society*, **127** (5), 1504–1518, 2005 [73].)

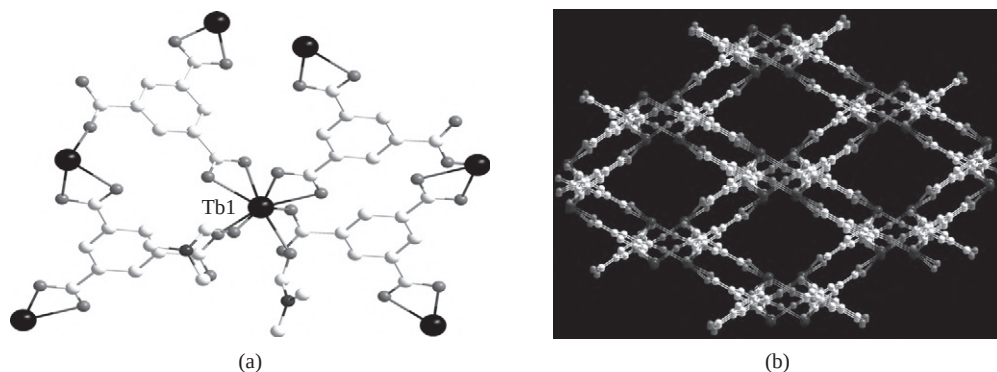


Figure 3.15 The structure of $[\text{Tb}(\text{btc})(\text{DMF})_2]_n \cdot n\text{H}_2\text{O}$. (a) Each Tb center is connected to six other Tb centers through four ligands. (b) The $13.5 \times 7.6 \text{ \AA}^2$ rectangle channels viewed down the c direction (Tb, black; O, grey; C, white; H, omitted; DMF and H_2O guest molecules in (b) have been removed for clarity). (Redrawn from the CIF file of Z. Li *et al.*, “Synthesis, structure, and luminescent and magnetic properties of novel lanthanide metal-organic frameworks with zeolite-like topology,” *Inorganic Chemistry*, **46** (13), 5174–5178, 2007 [74].)

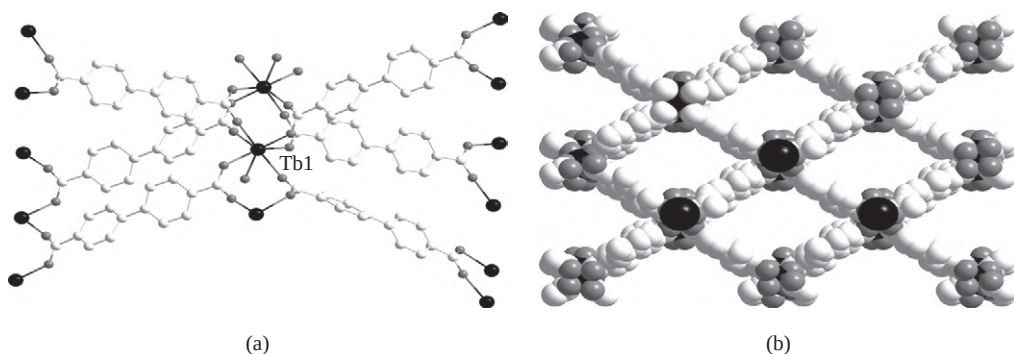


Figure 3.16 The structure of $[\text{Tb}(\text{bpdC})_{1.5}(\text{H}_2\text{O})]_n \cdot 0.5n\text{DMF}$. (a) The paddle-wheel building block. (b) The 3D-framework showing the large rhombic channels (Tb, black; O, grey; C, white; H, omitted; DMF guest molecules in (b) have been removed for clarity). (Redrawn from the CIF file of X. Guo *et al.*, “Synthesis, structure and luminescent properties of rare earth coordination polymers constructed from paddle-wheel building blocks,” *Inorganic Chemistry*, **44** (11), 3850–3855, 2005 [75].)

of the structure is the eight-membered channel consisting of four metal centers and four phenyl groups linked through carboxylic groups in the $[110]$ direction. The size of the channel is around $7.6 \times 13.5 \text{ \AA}^2$ and is filled with coordinating DMF and water molecules of crystallization. Experiments suggested that the dehydrated sample could absorb up to 15 water molecules per unit cell.

$[\text{Tb}(\text{bpdC})_{1.5}(\text{H}_2\text{O})]_n \cdot 0.5n\text{DMF}$ was synthesized by diffusion of triethylamine into a mixture of $\text{Tb}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ and 4,4'-biphenyldicarboxylic acid (H_2bpdC) (molar ratio 2 : 1) in a mixture of DMF and EtOH at 4°C then at 55°C [75]. Its crystal structure is shown in Figure 3.16a. The terbium atom is coordinated with six oxygen atoms from six bpdC^{2-} and one oxygen atom from a terminal aqua ligand, $\text{CN} = 7$. The crystallographically equivalent Tb(III) ions

are bridged by bpdc^{2-} with a mode of alternating double bidentate bridging and quadruple bidentate bridging $(\mu_2-\eta^1\eta^1)_2/(\mu_2-\eta^1\eta^1)_4$ to give an edge-sharing infinite chain of rare earth–oxygen polyhedra REO_7 in the [001] direction. The 1D-chains are linked by biphenyl groups in the [110] and $[\bar{1}10]$ directions to form a 3D-framework with remarkably large rhombic channels sized $25.2 \times 17.1 \text{ \AA}^2$ along the diagonals (calculated from the distances of metal ion centers) (Figure 3.16b).

3.2.2.5 Structures of Rare Earth Complexes with Carboxylic Acids Bearing Other Donor Atoms

Many carboxylic acids with other donor atoms, such as N, O, and S, have been used to prepare RE(III) complexes. Usually, the ligands are coordinated to RE(III) by using only their carboxylate groups, leaving any $-\text{OH}$, $-\text{NH}_2$ or $-\text{SH}$ groups untouched. However, the hydroxy oxygen atom of α - or β -hydroxyl carboxylic acids and the pyridyl nitrogen of α -pyridylcarboxylic acids are found to coordinate RE(III) together with the carboxylate groups to form stable five- or six-membered rings, resulting in intriguing structures with unique coordination modes in addition to interesting physical and chemical properties (Figure 3.17).

$[(\text{Lig})_2\text{Tb}(\text{H}_2\text{O})_2]_n \cdot n\text{ClO}_4$ ($\text{Hlig} = \text{L-lactic acid}$) was obtained through the hydrothermal reaction of L-ethyl lactate with $\text{Tb}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ [76]. Its crystal structure is shown in Figure 3.18. Each Tb(III) ion is coordinated by six O atoms from four different lactate ions and two water molecules, $\text{CN} = 8$. Each lactate ion links two Tb(III) ions, using one carboxylate oxygen and the hydroxy oxygen to chelate one Tb(III) ion while the other carboxylate oxygen connects to another Tb(III) ion, resulting in a lamellar 2D-layered framework in the ab plane, with perchlorate anions in between the layers (Figure 3.18b). Ferroelectric and magnetic property measurements revealed that this compound was the first “ferromagnetic and ferroelectric” metal–organic framework.

Mucic acid, (2*S*, 3*R*, 4*S*, 5*R*)-2,3,4,5-tetrahydroxyhexanedioic acid, is an important biopolyhydroxydicarboxylic acid ligand with a flexible chain that may provide a variety of coordination modes. Its complex with Tb(III), $[\text{Tb}(\text{Muc})_{1.5}(\text{H}_2\text{O})_2]_n \cdot 5n\text{H}_2\text{O}$ ($\text{H}_2\text{muc} = \text{mucic acid}$), was obtained by mixing stoichiometric amounts of TbCl_3 , mucic acid, and triethylamine in EtOH (Figures 3.19) [77]. In the asymmetric unit, there is one Tb(III), one and a half muc^{2-} , two coordination water molecules, and five lattice water molecules. Each Tb(III) is coordinated

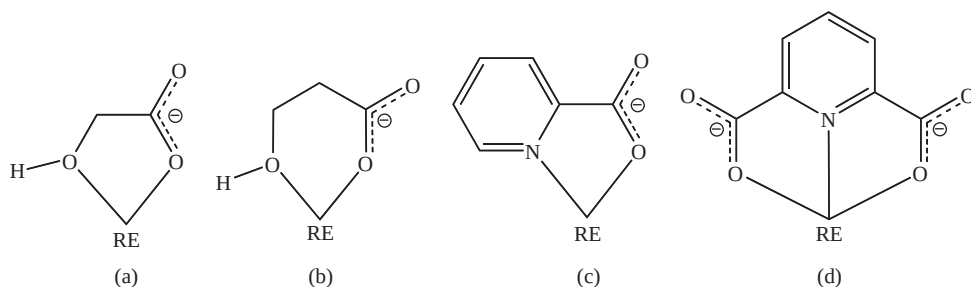


Figure 3.17 Coordination modes of (a) α -hydroxyl carboxylate; (b) β -hydroxyl carboxylate; (c) α -pyridinecarboxylate; and (d) 2,6-pyridinedicarboxylate.

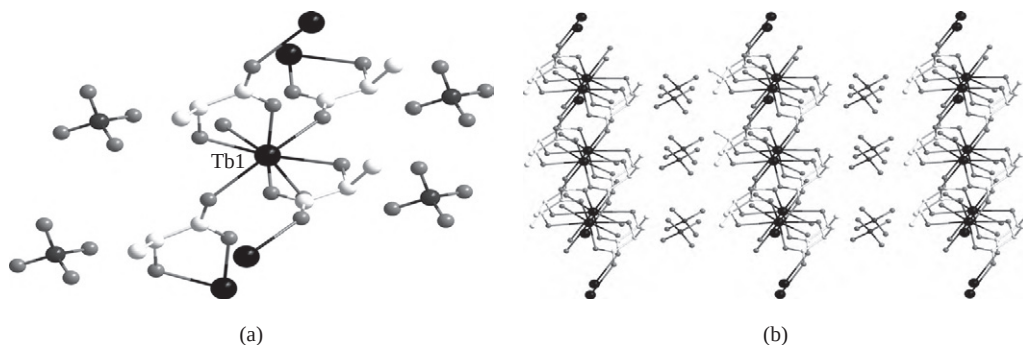


Figure 3.18 (a) Structure of $[(\text{Lig})_2\text{Tb}(\text{H}_2\text{O})_2]_n \cdot n\text{ClO}_4$ (Hlig = *L*-lactic acid). (b) The 2D $\text{Tb}(\text{lactate})_2^+$ frameworks–perchlorate ions sandwich structure viewed from the *b*-direction [Tb, black (large balls); Cl, black (small balls); O, grey; C, white; H, omitted]. (Redrawn from the CIF file of Q. Ye *et al.*, “Multiferroic homochiral metal-organic framework,” *Inorganic Chemistry*, **47** (3), 772–774, 2008 [76].)

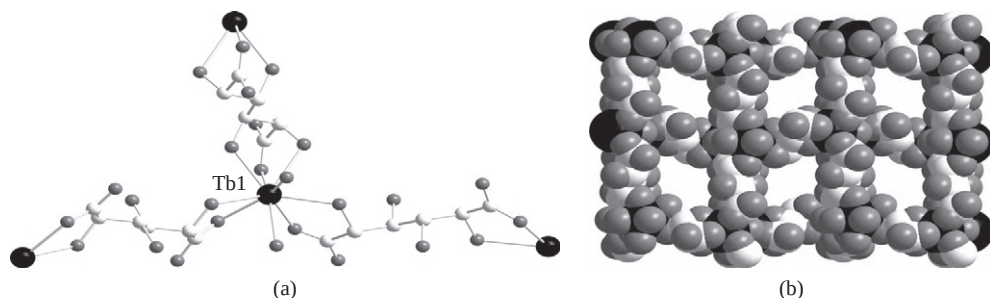


Figure 3.19 Molecular structure of (a) $[\text{Tb}(\text{Muc})_{1.5}(\text{H}_2\text{O})_2]_n$ and (b) square-shaped channels viewed in the *a*-direction with lattice water molecules omitted for clarity (Tb, black; O, grey; C, white; H, omitted). (Redrawn from the CIF file of K.L. Wong *et al.*, “A highly porous luminescent terbium-organic framework for reversible anion sensing,” *Advanced Materials*, **18** (8), 1051–1054, 2006 [77].)

by seven oxygen atoms from three acid ligands and two water molecules, $\text{CN} = 9$. Among the three organic ligands, two of them are symmetrically related, each coordinating two Tb(III) in a double-bidentate mode, with one carboxylato oxygen and the α -OH at one end, and one oxygen of the other carboxylate and the δ -OH at the other end. The third ligand is coordinated to two Tb(III) ions in a double-tridentate mode, with the β - and γ -OH also involved in the coordination. Each Tb(III) ion is linked to three other Tb(III) ions by three ligands to form a T-shape building motif, which interlinks to form a 2D-layered structure parallel to the *bc* plane. The hydrogen bonds between the mucate anions and the water molecules connect the neighboring layers together into a 3D-network, leading to approximately square-shaped ($9.9 \times 9.8 \text{ \AA}^2$) channels, filled with lattice water, in the *a* direction. Some remarkable properties of this complex include: (i) the framework does not collapse upon dehydration/re-hydration; (ii) anion uptake and removal; and (iii) the entrance and departure of the different anions can be monitored by examining the intensity of the characteristic emission of Tb at 545 nm.

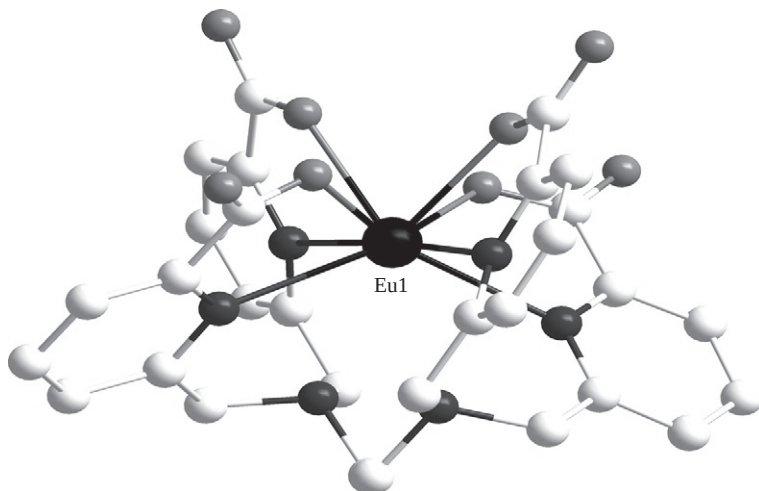


Figure 3.20 Crystal structure of $[\{\text{Eu}(\text{tpaen})\}\text{K}(\text{H}_2\text{O})_3]$ with K^+ and water molecules removed for clarity [Eu, black (large ball); O, grey; N, black (small balls); C, white; H, omitted]. (Redrawn from the CIF file of N. Chatterton *et al.*, “An efficient design for the rigid assembly of four bidentate chromophores in water-stable highly luminescent lanthanide complexes,” *Angewandte Chemie International Edition*, **44** (46), 7595–7598, 2005 [80].)

Dipicolinic acid or 2,6-pyridinedicarboxylic acid (H_2dipic), an excellent chromophore for Eu(III) and Tb(III) sensitization, forms stable tris complexes with RE(III) ions, $[\text{RE}(\text{dipic})_3]^{3-}$ [78]. The Eu(III) and Tb(III) complexes are very bright red and green emitters with quantum yields of 12 and 21%, respectively. All of their RE(III) analogs are isostructural and their second order NLO activities were reported. In the complexes, the RE(III) ions are coordinated by three tridentate dipic^{2-} with a symmetry close to D_3 , CN = 9 [79].

A decadentate ligand, N,N,N',N' -tetrakis[(6-carboxypyridin-2-yl)methyl] ethylenediamine (H_4tpaen) was reported to form the most bright green emitting Tb(III) complex, $[\text{Tb}(\text{tpaen})]^-$, with a quantum yield of 45%. The structure of the Eu(III) complex, $[\{\text{Eu}(\text{tpaen})\}\text{K}(\text{H}_2\text{O})_3] \cdot 4\text{H}_2\text{O}$ is shown in Figure 3.20 [80].

3.2.2.6 Structures of d–f Heteronuclear Complexes with Carboxylic Acids

The d–f heteronuclear or lanthanide–transition metal (abbreviated as Ln–M) complexes attract interest from both academic and industry because of the challenge for their synthesis, the novelty of their structures, and their potential application as advanced materials, such as molecular or nano magnets, bimetallic catalysts, and sensors. The complexes can be assigned to three categories based on the nature of the Ln–M interaction: (a) complexes with direct Ln–M bonding, (b) complexes with Ln–M interactions bridged by ligands, and (c) the complexes with ionically associated Ln–coordination units and M–coordination units. Most of the d–f heteronuclear complexes of carboxylic acids reported so far are found with type (b) structure, and very few of them are of structure type (c). The lanthanides and the transition metals in these complexes are far away from each other, and no direct Ln–M interactions have been observed.

Ligands bearing O, N, or S atoms as donors are used to incorporate both lanthanides and transition metals into the complexes, as lanthanides are hard Lewis acids and oxophilic,

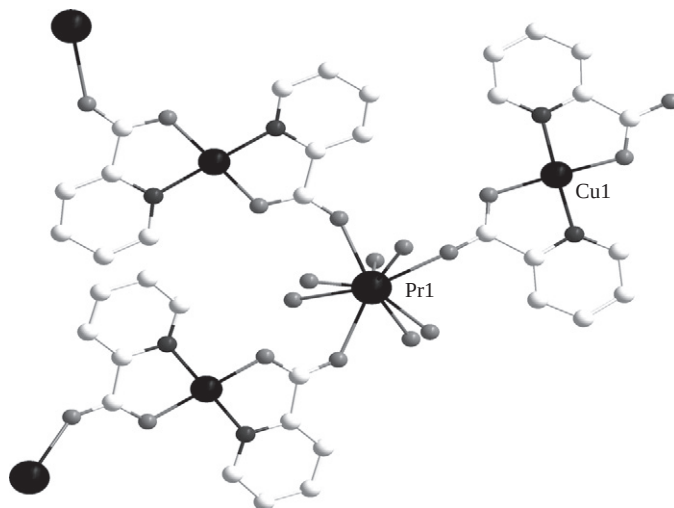


Figure 3.21 The chain structure of $[\text{PrCu}_2(\text{pic})_4(\text{H}_2\text{O})_6]_n^{3n+}$ [Pr, black (large ball); Cu, black (medium balls); O, grey; N, black (small balls); C, white; H, omitted]. (Redrawn from the CIF file of A.Q. Wu *et al.*, “Extended structures and magnetic properties of lanthanide-copper complexes with picolinic acids as bridging ligands,” *European Journal of Inorganic Chemistry*, **2005** (10), 1947–1954, 2005 [81].)

while transition metals are soft Lewis acids and prefer soft donors, such as N or S. Picolinate (pic^{1-}) are among the simplest ligands used to prepare d–f heteronuclear complexes. Complex $[\text{LnCu}_2(\text{pic})_4(\text{H}_2\text{O})_6]_n \cdot 3n\text{ClO}_4 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{and Sm}$) is a 1D-chain polymer (Figure 3.21) [81]. Each Cu(II) is coordinated by two oxygen and two nitrogen atoms from two picolates to form $\text{Cu}(\text{pic})_2$, a “metallo ligand” with two free carboxylato oxygen atoms. In addition, each of the Ln(III) is coordinated by three $\text{Cu}(\text{pic})_2$, of which two coordinate to another two Ln(III) ions, resulting a 1D-zigzag chain. With a very similar connectivity, complex $[\text{Ln}_2\text{Cu}_5(\text{pic})_{10}(\text{H}_2\text{O})_8]_n \cdot 6n\text{ClO}_4 \cdot 2n\text{H}_2\text{O}$ ($\text{Ln} = \text{Gd}, \text{Nd}, \text{Sm}, \text{Dy}, \text{Eu}, \text{Pr}, \text{and Yb}$) is a 2D-layered structure, where each of the Ln(III) is surrounded by four $\text{Cu}(\text{pic})_2$, with only three of them connecting to three additional Ln(III) ions. Very similar coordination modes for Ln(III) and the transition metal are also found in the d–f heteronuclear complexes with pyridine-2,3-dicarboxylate [82], pyridine-2,4-dicarboxylate [83], and pyridine-2,5-dicarboxylate [84] as ligands. However, for pyridine-2,6-dicarboxylate, the similar coordination mode is only observed in its Cu(II) complexes, where the Cu(II) ions are chelated by the nitrogen atom and two monodentate carboxylates, and the Ln(III) is coordinated by monodentate carboxylates and water [85]. Interestingly, the Ln and M are found to have their positions switched in its Mn(II), Co(II), Zn(II), Cd(II), and Ag(I) analogs [86–88].

d–f Heteronuclear complexes are also achievable with carboxylates that do not bear a nitrogen donor. The complexes are tetranuclear, pentanuclear or polymeric. Typically, the transition metals take the terminal positions while the lanthanides prefer to stay inside a chain or polymer to achieve high coordination numbers. The pentanuclear complexes $[\text{Cu}_3\text{Ln}_2(\text{ClCH}_2\text{COO})_{12}(\text{H}_2\text{O})_8] \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Ho}, \text{and Yb}$), possess a common linear structure with alternating Cu(II) and Ln(III) ions, $\text{Cu}(2) \cdots \text{Ln}(1) \cdots \text{Cu}(1) \cdots \text{Ln}(1) \cdots \text{Cu}(2)$ (Figure 3.22). In the structure, Cu(II) and Ln(III) are bridged by four carboxylates to form a dinuclear unit; two such dinuclear units are linked to a Cu(II) through two single

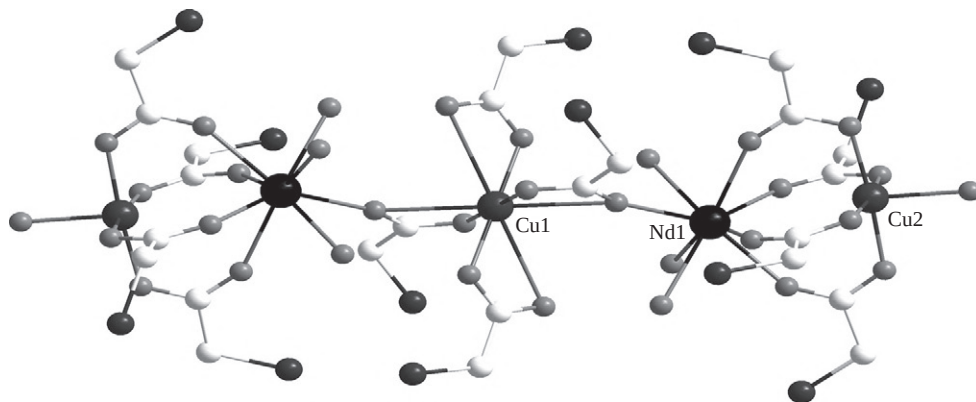


Figure 3.22 The chain structure of $[\text{Cu}_3\text{Pr}_2(\text{ClCH}_2\text{COO})_{12}(\text{H}_2\text{O})_8]$ [Pr, black (large ball); Cu, black (medium balls); Cl, black (small balls); O, grey; C, white; H, omitted]. (Redrawn from the CIF file of V.K. Voronkova *et al.*, “Exchange interaction and spin dynamics in the pentanuclear clusters $\text{Cu}_3\text{Ln}_2(\text{ClCH}_2\text{COO})_{12}(\text{H}_2\text{O})_8$ ($\text{Ln} = \text{Nd}^{3+}$, Sm^{3+} , Pr^{3+}),” *Applied Magnetic Resonance*, **25** (2), 227–247, 2003 [89].)

bidentate carboxylate bridges [89]. The tetranuclear complex, $[\text{Pd}_2\text{Sm}_2(\text{H}_2\text{O})_2(\text{CH}_3\text{COO})_{10}]$, is also of a linear structure with the two Pd(II) in the terminal positions [90].

An example of the complexes with ionically associated Ln–coordination units and M–coordination units is $[\{\text{Gd}_4(\text{ip})_7(\text{H}_2\text{O})_2\}\{\text{Cu}(\text{bipy})_2\}_2]_n$ (ip = isophthalate, bipy = 2,2′-bipyridine), where the nitrogen donor is supplied by the auxiliary ligand, bipy. Thus, Gd(III) ions are coordinated by the carboxylates to form charged cages. Inside each cage are two $[\text{Cu}(\text{bpy})_2]^+$ cations [91].

3.2.3 Solution Chemistry of Rare Earth Complexes with Carboxylic Acids

Compared with their polyaminopolycarboxylic acid analogs, the solution chemistry of RE(III)–carboxylic acid complexes have received much less attention. However, from the data reported so far, we can already see some of the general aspects of the complexes in solution, the species formed, their stability, and the thermodynamic properties, as well as their evolution with the change of the central atoms.

The study on the La(III) complexes with formate, acetate, and propionate in aqueous solution indicated that La(III) forms four complex species with these three monocarboxylates, $[\text{LaL}_n]$ ($n = 1-4$), and the linear relationship between $\log \beta_1$ and the pK_a of the ligands was confirmed (Table 3.1) [92]. This is because being hard acids, RE(III) ions favor complexation with hard bases, which leads to the stability constants of lanthanides with carboxylate ligands being proportional to the basicity of the ligands. A similar trend was observed for the systems with aromatic carboxylic acids (mellitic, pyromellitic, hemimellitic, trimellitic, trimesic, phthalic, isophthalic, terephthalic, and benzoic) as ligands [93]. However, with aliphatic dicarboxylates as ligands, the reversed trend is observed. Studies showed that $\log \beta_1$ decreased as the ΣpK_a increased from oxalate, malonate, succinate, glutarate to adipate [94, 95]. The phenomenon is the result of the change in the carbon chain in between the two carboxylates. While oxalate and

Table 3.1 The stability constants of La(III)–L complexes and the pK_a of HL (HL = formic acid, acetic acid, and propionic acid) (25°C, $I = 1.00$ M NaClO₄).

Ligand	Log β_1	Log β_2	Log β_3	Log β_4	pK_a
Formate	1.11	1.68	2.07	1.93	3.64
Acetate	1.53	2.44	2.67	3.28	4.56
Propionate	1.62	2.48	3.08	3.40	4.92

Table 3.2 The protonation constants of acetate and some dicarboxylates and the stability constants (log β_1) of their complexes with RE(III) (25°C, $I = 0.10$ M).

Ligand	$pK_{a_1}^a$	pK_{a_2}	La ³⁺	Pr ³⁺	Sm ³⁺	Eu ³⁺	Gd ³⁺	Dy ³⁺	Er ³⁺	Lu ³⁺
Acetate ^b	4.56		2.02	2.18	2.30	2.31	2.16	2.03	2.01	2.04
Malonate ^c	2.65	5.28	5.9	6.3	6.8	7.0	7.0	7.1	7.1	7.2
Succinate ^d	4.00	5.24	3.09	3.36	3.50		3.42	3.33	3.32	3.31
Glutarate ^d	4.13	5.03	2.99	3.17	3.24		3.19	3.13	3.09	3.16
Adipate ^d	4.26	5.03	2.95	3.09	3.19		3.09	3.04	3.05	3.19

^a pK_a for acetate [92]; pK_{a_1} , pK_{a_2} for dicarboxylates [94]. ^bLog β_1 [96]. ^cLog β_1 [97]. ^dLog β_1 [95].

malonate can chelate to a metal by forming a stable six-membered ring, the formation of seven-, eight-, and nine-membered rings will be required in order for succinate, glutarate, and adipate to chelate a metal. These are much less stable than the chelation by five- or six-membered rings due to the negative entropy contribution or the increasing loss in the configurational entropy in the alkyl chain associated with the expansion in ring size. In fact, X-ray crystal structure analysis indicated that, instead of forming seven-, eight-, or nine-membered chelating rings, the two carboxylato groups of succinate, glutarate, and adipate tend to coordinate different RE(III) to form polynuclear structures.

The primarily ionic nature of the RE(III)–carboxylate interaction suggests that a direct relationship between the ionic radii of the RE(III) and the stability of their complexes with carboxylates should exist; the stability constants of the complexes would increase monotonously from La(III) to Lu(III). However, the experimental results obtained indicate that this is only true for light rare earth metals from La(III) to Eu(III). Three different trends are observed for heavy rare earths from Gd(III) to Lu(III), that is, upward, flat, and downward. This is the so called “gadolinium break.” Acetate, malonate, succinate, glutarate, and adipate complexes fall into the second category. The log β_1 of the complexes remain almost unchanged from Gd(III) to Lu(III) (Table 3.2). There have been various interpretations of these trends, and the most widely accepted one is the change in the number of the hydration water molecules [98, 99].

3.3 Rare Earth Complexes with Polyaminopolycarboxylic Acids

The coordination chemistry of polyaminopolycarboxylic acids with rare earths has been an active area of rare earth chemistry since hydrazino-*N,N*-diacetic acid and ethylenediaminetetraacetic acid (H₄EDTA) were used for ion-exchange separations of rare earths 50

years ago [98]. Owing to the high stability of the complexes resulting from the hard Lewis acid character of rare earths and the multidentate coordination ability of polyaminopolycarboxylic acids and the distinctive optical and magnetic properties of rare earths, rare earth–polyaminopolycarboxylic acid complexes have found applications in optical sensing [100, 101], and magnetic resonance imaging (MRI) [102, 103]. This section will cover the synthesis, structure, and solution properties of some representative complexes.

3.3.1 Preparation of Rare Earth Complexes with Polyaminopolycarboxylic Acids

The synthesis is normally carried out by refluxing an aqueous mixture of polyaminopolycarboxylic acid and a selected rare earth oxide in a molar ratio of RE : L = 1 : 1. The resulting solution can be neutralized to pH 5–6 by adding a dilute solution of NaOH, KOH, $\text{NH}_3 \cdot \text{H}_2\text{O}$, NaHCO_3 , or NaHCO_3 . After filtration, the complex can be crystallized by evaporation or with the addition of EtOH. The rare earth oxide can be replaced by a rare earth carbonate or other soluble salts, such as chlorides, nitrates, perchlorates, or acetates [104]. The synthesis can also be done under hydrothermal conditions [105], which leads to complexes of polymeric structure, while most of the complexes obtained under ambient conditions are monomeric (see Section 3.3.2 for examples).

3.3.2 Structural Chemistry of Rare Earth Complexes with Polyaminopolycarboxylic Acids

Polyaminopolycarboxylic acids, with EDTA, DTPA, and DOTA as the representatives, are among the ligands capable of forming the most stable complexes with RE(III), due to the affinity of RE(III) for N and O donors and the chelating ability of the ligands. In the structures, the RE(III) ions are coordinated by ligands through monodentate carboxylate (η^1) groups and the nitrogen atoms, and the coordination numbers are usually nine for light rare earth, and eight for the heavy ones.

3.3.2.1 Structures of Rare Earth Complexes with EDTA, DTPA, and TTHA

As a hexadentate ligand, H_4EDTA coordinates to RE(III) through its two nitrogen atoms, and the four oxygen atoms from its four carboxylates, that is, (N_2O_4). Most of the RE– H_4EDTA complexes are mononuclear with a formula $\text{M}[\text{RE}(\text{H}_2\text{O})_n(\text{EDTA})] \cdot m\text{H}_2\text{O}$ ($\text{M} = \text{Na}^+$, K^+ , Cs^+ , NH_4^+ , and $[\text{C}(\text{NH}_2)_3]^+$; $n = 2$ or 3 ; $m = 0$ – 5), CN = 8 or 9. The structures and the coordination modes of the complexes seem to be dominated by two factors, that is, the size of the RE(III) and the property of the counter cation [104]. Complexes (I) $\text{Na}[\text{RE}(\text{H}_2\text{O})_3(\text{EDTA})] \cdot 5\text{H}_2\text{O}$ ($\text{RE} = \text{La}$ – Er , Y) and (II) $\text{K}[\text{RE}(\text{H}_2\text{O})_3(\text{EDTA})] \cdot 5\text{H}_2\text{O}$ ($\text{RE} = \text{La}$ – Ho) are isostructural and isomorphous with an orthorhombic space group $Fdd2$, where the RE(III) ion is coordinated by the hexadentate EDTA and three water molecules, CN = 9 (Figure 3.23). With Cs^+ as the counter cation, two series complexes were obtained: (III) $\text{Cs}[\text{RE}(\text{H}_2\text{O})_3(\text{EDTA})] \cdot 4\text{H}_2\text{O}$ ($\text{RE} = \text{Sm}$ and Gd) and (IV) $\text{Cs}[\text{RE}(\text{H}_2\text{O})_2(\text{EDTA})] \cdot 3\text{H}_2\text{O}$ ($\text{RE} = \text{Dy}$ and Ho). The coordination modes of (III) and (IV) are very similar to (I) and (II) with EDTA in a hexadentate mode (N_2O_4), except that (IV) has only two aqua ligands, CN = 8.

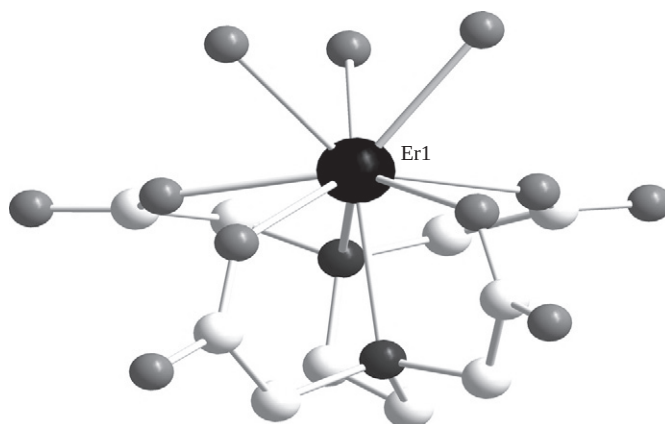


Figure 3.23 The structure of monomeric complex $[\text{Er}(\text{H}_2\text{O})_3(\text{EDTA})]^-$ [Er, black (large ball); O, grey; N, black (small balls); C, white; H, omitted]. (Redrawn from the CIF file of N. Sakagami *et al.*, “Crystal structures and stereochemical properties of lanthanide(III) complexes with ethylenediamine-*N,N,N',N'*-tetraacetate,” *Inorganica Chimica Acta*, **288** (1), 7–16, 1999 [104].)

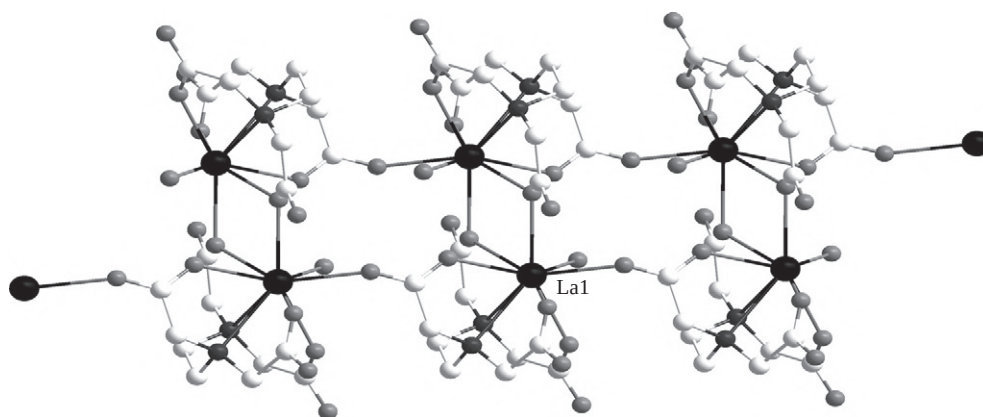


Figure 3.24 The structure polymeric $[\text{La}(\text{H}_2\text{O})(\text{EDTA})]_n^-$ [Nd, black (large balls); O, grey; N, black (small balls); C, white; H, omitted]. (Redrawn from the CIF file of N. Sakagami *et al.*, “Crystal structures and stereochemical properties of lanthanide(III) complexes with ethylenediamine-*N,N,N',N'*-tetraacetate,” *Inorganica Chimica Acta*, **288** (1), 7–16, 1999 [104].)

While the mononuclear complexes (I)–(IV) were crystallized under ambient conditions, two polymeric complexes, $[\text{RE}(\text{H}_2\text{O})(\text{HEDTA})]_n$ (RE = La and Nd) were obtained by hydro(solvo)thermal synthesis. In the structure, the HEDTA^{3+} ligand is octadentate with its two nitrogen atoms and four carboxylato oxygen atoms coordinating the central RE(III), and the remaining oxygen atom of the $\mu_2\text{-}\eta^1\eta^1$ carboxylate coordinating its neighboring RE(III) along the *a* direction to form a 1D-chain. The chain is then linked to another chain through the oxygen atoms of the $\mu_2\text{-}\eta^1\eta^1$ (O, O) carboxylate groups, affording a double-chained structure (Figure 3.24) [105].

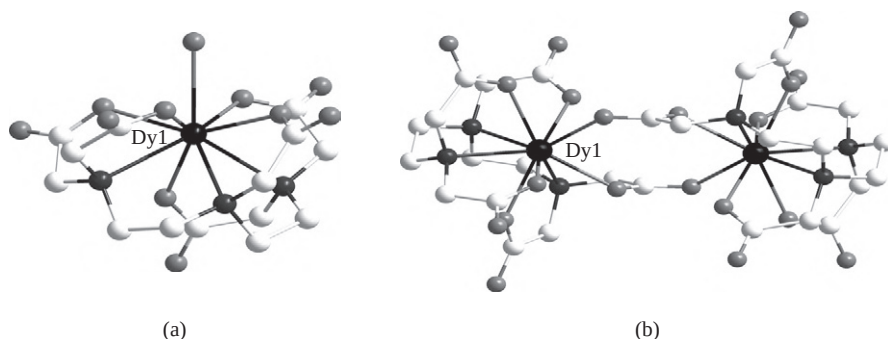


Figure 3.25 The structure of (a) $[\text{Dy}(\text{H}_2\text{O})(\text{DTPA})]^-$ and (b) $[\text{Dy}_2(\text{DTPA})_2]^{4-}$ [Dy, black (large balls); O, grey; N, black (small balls); C, white; H, omitted]. (Redrawn from the CIF files of J. Wang *et al.*, “Syntheses and structural determinations of the nine-coordinate rare earth metal: $\text{Na}_4[\text{Dy}^{\text{III}}(\text{dtpa})(\text{H}_2\text{O})]_2 \cdot 16\text{H}_2\text{O}$, $\text{Na}[\text{Dy}^{\text{III}}(\text{edta})(\text{H}_2\text{O})_3] \cdot 3.25\text{H}_2\text{O}$ and $\text{Na}_3[\text{Dy}^{\text{III}}(\text{nta})_2(\text{H}_2\text{O})] \cdot 5.5\text{H}_2\text{O}$,” *Journal of Coordination Chemistry*, **60** (20), 2221–2241, 2007 [106]; and Y. Inomata, T. Sunakawa and F.S. Howell, “The syntheses of lanthanide metal complexes with diethylenetriamine-N, N, N', N'', N''-pentaacetic acid and the comparison of their crystal structures,” *Journal of Molecular Structure*, **648** (1–2), 81–88, 2007 [107].)

H_5DTPA , diethylenetriaminepentacarboxylic acid, is an octadentate ligand (N_3O_5), and can form mononuclear and dinuclear complexes with RE(III). Similar to their EDTA analogs, the structures of the RE–DTPA complexes also vary on changing the counter cations. For example, $\text{M}_2[\text{Dy}(\text{H}_2\text{O})(\text{DTPA})] \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Na}^+$, $n = 8$; $\text{M} = \text{K}^+$, $n = 5$) are mononuclear with the Dy(III) coordinated by three nitrogen atoms and five monodentate carboxylates, and one aqua ligand, CN = 9 (Figure 3.25a) [106], while $\text{M}_4[\text{Dy}_2(\text{DTPA})_2] \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Cs}^+$, $n = 13$; $\text{M} = \text{NH}_4^+$, $n = 8$) are dinuclear with the two $\text{Dy}(\text{DTPA})^{2-}$ joined through the two $\mu_2\text{-}\eta^1\eta^1$ carboxylate groups, CN = 9 (Figure 3.25b) [107].

H_6TTHA , triethylenetetraaminehexaacetic acid, is a decadentate ligand with four nitrogen and six oxygen donors (N_4O_6). In its complexes with RE(III), the ten donor atoms can coordinate one central atom collectively or partially, which keeps water or other solvent molecules from entering the coordination sphere. The structures of the complexes reported so far are of four types, that is, (a) $[\text{RE}(\text{TTHA})]^{3+}$ or $[\text{RE}(\text{HTTTHA})]^{2+}$ ($\text{RE} = \text{La–Nd}$, CN = 10); (b) $[\text{RE}(\text{TTHA})]^{3+}$ or $[\text{RE}(\text{HTTTHA})]^{2+}$ ($\text{RE} = \text{Eu–Yb}$, CN = 9); (c) $[\text{RE}_2(\text{HTTTHA})_2]^{4+}$ ($\text{RE} = \text{Sm–Tb}$, Y, CN = 9); and (d) $[\text{RE}_2(\text{H}_2\text{O})_5(\text{TTHA})]_n$ ($\text{RE} = \text{Tm}$). Here the complexes of TTHA^{6-} and HTTTHA^{5-} are placed in the same groups because they have very similar coordination modes, as exemplified by the ten-coordination (N_4O_6) in $[\text{Nd}(\text{TTHA})]^{3+}$ and $[\text{Nd}(\text{HTTTHA})]^{2+}$ [108], and the nine-coordination (N_4O_5) in $[\text{Er}(\text{TTHA})]^{3+}$ or $[\text{Er}(\text{HTTTHA})]^{2+}$ [109, 110].

Apparently, both large and small RE(III) can form 1 : 1 mononuclear anionic complexes, $[\text{RE}(\text{TTHA})]^{3-}$ or $[\text{RE}(\text{HTTTHA})]^{2-}$, however with different coordination modes. The structures of $[\text{Nd}(\text{TTHA})]^{3+}$ and $[\text{Er}(\text{TTHA})]^{3+}$ are shown in Figure 3.26a and b, respectively. The larger Nd(III) is coordinated by N_4O_6 , CN = 10, whereas the smaller Er(III) is coordinated by N_4O_5 , CN = 9. The structure of a dinuclear complex, $[\text{Gd}_2(\text{HTTTHA})_2]^{4+}$, is shown in Figure 3.26c, wherein each of the Gd(III) is coordinated by $\text{N}_3\text{O}_4\text{O}'_2$ ($\text{O}' = \text{the oxygen atom}$

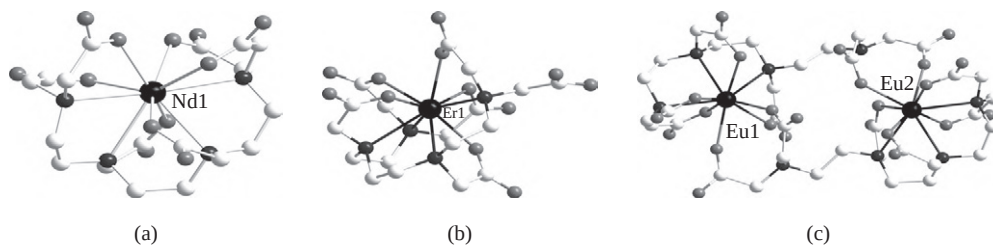


Figure 3.26 The structure of (a) $[\text{Nd}(\text{TTHA})]^{3+}$; (b) $[\text{Er}(\text{TTHA})]^{3+}$; and (c) polymer $[\text{Gd}_2(\text{DTPA})_2]^{4-}$ [RE, black (large balls); O, grey; N, black (small balls); C, white; H, omitted]. (Redrawn from the CIF files of J. Wang *et al.*, “Syntheses and structural determinations of the nine-coordinate rare earth metal: $\text{Na}_4[\text{Dy}^{\text{III}}(\text{dtpa})(\text{H}_2\text{O})_2] \cdot 16\text{H}_2\text{O}$, $\text{Na}[\text{Dy}^{\text{III}}(\text{edta})(\text{H}_2\text{O})_3] \cdot 3.25\text{H}_2\text{O}$ and $\text{Na}_3[\text{Dy}^{\text{III}}(\text{nta})_2(\text{H}_2\text{O})] \cdot 5.5\text{H}_2\text{O}$,” *Journal of Coordination Chemistry*, **60** (20), 2221–2241, 2007 [106]; and Y. Inomata, T. Sunakawa and F.S. Howell, “The syntheses of lanthanide metal complexes with diethylenetriamine-N, N, N', N', N''-pentaacetic acid and the comparison of their crystal structures,” *Journal of Molecular Structure*, **648** (1–2), 81–88, 2007 [107].)

from a different ligand), CN = 9. $[\text{Tm}_2(\text{H}_2\text{O})_5(\text{TTHA})]_n$ is a coordination polymer. There are two independent metals in the structure, Tm1 and Tm2. Tm1 is coordinated by $\text{N}_2\text{O}_3\text{O}'_1$ and two aqua ligands, CN = 8, while Tm2 is coordinated by N_2O_3 and three aqua ligands, CN = 8 [111].

3.3.2.2 Structures of Rare Earth Complexes with DOTA, HP-DO3A, and BT-DO3A

The high magnetic moment (7.9 BM) and the long electron-spin relaxation time (10^{-8} – 10^{-9} s) makes Gd(III) an ideal candidate for producing MRI contrast agents [102]. However, owing to the toxicity of free Gd^{3+} , the metal ions have to be encapsulated in the form of kinetically and thermodynamically stable complexes if they are to be applied in living diagnoses. The 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (H_4DOTA) was the first ligand, in addition to DTPA and its derivatives, to form complexes with RE(III) with high stability (about 10 orders of magnitude larger than the corresponding stability constant of EDTA) with slow dissociation kinetics [112]. Since then, extensive research has been done to develop better macrocyclic polyaminopolycarboxylic acid ligands. So far, at least three Gd(III) complexes of this family have been approved for clinical uses. They are (meglumine) $[\text{Gd}(\text{DOTA})(\text{H}_2\text{O})]$ (Dotarem[®], gadoterate meglumine), $[\text{Gd}(\text{HP-DO3A})(\text{H}_2\text{O})]$ (ProHance[®]), and $[\text{Gd}(\text{BT-DO3A})(\text{H}_2\text{O})]$ (Gadovist[®]), where HP-DO3A = 10-(2-hydroxypropyl)-1,4,7,10-tetraazacyclododecane-1,4,7-triacetate, BT-DO3A = 10-(1-(hydroxymethyl)-2,3-dihydroxypropyl)-1,4,7,10-tetraazacyclododecane-1,4,7-triacetate.

The structures of $[\text{Gd}(\text{DOTA})(\text{H}_2\text{O})]^-$ and $[\text{Gd}_2(\text{BT-DO3A})_2]$ are shown in Figure 3.27. In $[\text{Gd}(\text{DOTA})(\text{H}_2\text{O})]^-$, the nine-coordinated Gd(III) in the C_4 symmetric anion is coordinated by the four nitrogen atoms of the aza crown, four oxygen atoms from the carboxylates, and the ninth coordination site is occupied by an aqua ligand. The coordination geometry can be best described as a distorted monocapped square antiprism, with the four nitrogens forming the basal plane and four oxygens as the upper plane, with the water molecule located in

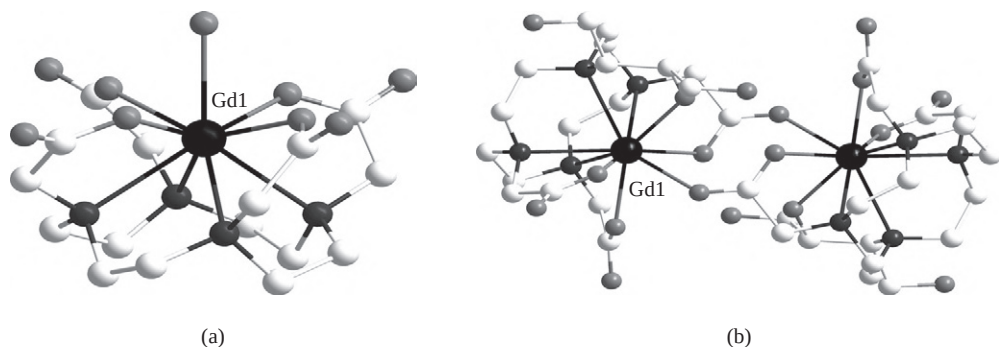


Figure 3.27 The structure of (a) $[\text{Gd}(\text{DOTA})]^-$ and (b) $[\text{Gd}_2(\text{BT-DO3A})_2]$ [RE, black (large balls); O, grey; N, black (small balls); C, white; H, omitted]. (Redrawn from the CIF files of C.A. Chang *et al.*, “Synthesis, characterization, and crystal structures of $\text{M}(\text{DO3A})$ ($\text{M} = \text{iron, gadolinium}$) and $\text{Na}[\text{M}(\text{DOTA})]$ ($\text{M} = \text{Fe, Y, Gd}$),” *Inorganic Chemistry*, **32** (16), 3501–3508, 1993 [113]; and J. Platzek *et al.*, “Synthesis and structure of a new macrocyclic polyhydroxylated gadolinium chelate used as a contrast agent for magnetic resonance imaging,” *Inorganic Chemistry*, **36** (26), 6086–6093, 1997 [115].)

the capping position [113]. The structure of $[\text{Gd}(\text{HP-DO3A})(\text{H}_2\text{O})]$ is very similar to that of $[\text{Gd}(\text{DOTA})(\text{H}_2\text{O})]^-$, where the four vertex oxygens are from the three carboxylates and the hydroxyl group [114].

The dinuclear complex, $[\text{Gd}_2(\text{BT-DO3A})_2]$, is centrosymmetrical, and only half of the molecule is unique. Each of the two $\text{Gd}(\text{III})$ ions is thus coordinated by N_4O_4 of one ligand, and then bridged to the other half of the molecule through two $\mu_2\text{-}\eta^1\eta^1$ carboxylate groups. The two $\text{Gd}(\text{III})$ ions each keep the distorted monocapped square antiprism coordination geometry, but with the carboxylato oxygen from the other ligand sitting in the capping position. It remains unclear why $[\text{Gd}_2(\text{BT-DO3A})_2]$ is dimeric while the other two complexes are mononuclear in the solid state, when experiments have shown that $\text{Gd}(\text{BT-DO3A})$ is a monomer in aqueous solution [115].

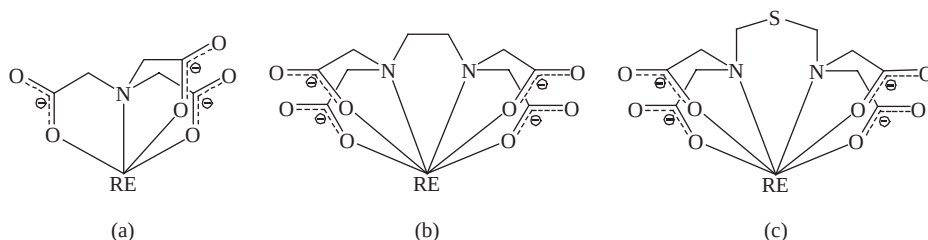
3.3.3 Solution Chemistry of Rare Earth Complexes with Polyaminopolycarboxylic Acids

The studies on solution chemistry of $\text{RE}(\text{III})$ –polyaminopolycarboxylic acid complexes started shortly after EDTA was found to be an effective agent for ion-exchange separation of rare earths [99]. Since then, linear and cyclic polyaminopolycarboxylic acids have been developed for both pure academic studies and practical applications, including lanthanide separation, lanthanide–actinide separation, optical sensing, and magnetic resonance imaging (MRI). As a result, the solution chemistry of their complexes with $\text{RE}(\text{III})$ has been explored extensively. In this section, we will use some representative ligands to briefly illustrate the general features of this chemistry.

Table 3.3 lists the $\log \beta_1$ and the ΣpK_a of $\text{Eu}(\text{III})$ complexes with iminodiacetic acid (IDA), nitrilotriacetic acid (NTA), N' -(2-hydroxyethyl)ethylenediamine- N,N,N' -triacetic acid (HEDTA), ethylenediamine- N,N,N',N' -tetraacetic acid (EDTA),

Table 3.3 The stability constants ($\log \beta_1$) of Eu(III)–L complexes and the ΣpK_a the ligands in aqueous solution.

Ligand	IDA	NTA	HEDTA	EDTA	TEDTA	DCTA	DTPA
ΣpK_a	11.91	14.11	17.69	21.09	22.28	23.72	27.95
$\log \beta_1$	6.73	11.52	15.35	17.99	14.82	18.99	22.91

**Figure 3.28** Coordination modes of (a) NTA; (b) EDTA; and (c) TEDTA.

thio-bis(ethylenenitrilo)tetraacetic acid (TEDTA), 1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid (DCTA), and diethylenetriamine-*N,N,N',N',N''*-pentaacetic acid (DTPA) [96]. For IDA, NTA, EDTA, and DTPA, the stability of the complexes ($\log \beta_1$) change linearly with ΣpK_a of the ligands due to the ionic nature of the RE(III)–O and RE(III)–N interactions, similar to the RE(III) complexes of carboxylic acids (Section 3.2.3). However, the trend was reversed for TEDTA, which is of a larger ΣpK_a (22.28) than EDTA (21.09), but with a significantly smaller $\log \beta_1$ (14.82 versus 17.99) [116]. This is considered to be a result of a change in the chelating ability of the ligands. For example, NTA and EDTA can coordinate RE(III) to form three and five 5-membered chelating rings, respectively (Figure 3.28), while IDA and DTPA can similarly coordinate RE(III) to form two and seven 5-membered chelating rings. Apparently, the more the chelating-5-membered rings, the higher the stability of the complex. HEDTA and DCTA can form the same number of 5-membered chelating rings as EDTA, but the coordination ability of –OH is weaker than that of –COO[–], and the two nitrogen atoms in DCTA are stronger bases than those in EDTA due to the cyclohexyl substitution. The reversed trend observed for EDTA and TEDTA is a result of changing one 5-membered chelating ring to the large 6-membered ring due to the replacement of the –CH₂CH₂– by –CH₂–S–CH₂– [117].

Although the ionic nature of the RE(III)–polyaminopolycarboxylic acid interaction suggests that the stability constants of the complexes would increase gradually along with a decrease in the ionic radii, different patterns of graphs of $\log \beta_1$ versus *Z* (atomic number) have been observed. Figure 3.29 shows the change in $\log \beta_1$ with *Z* for the IDA, NTA, TEDTA [thio-bis(ethylenenitrilo)tetraacetic acid], EDTA, and DTPA complexes [96, 98, 116]. There is a steady increase in $\log \beta_1$ from La to Sm or Eu, and then a slight decrease from Sm or Eu to Gd for all of the five ligand systems. Beyond Gd, two different trends are observed, that is, upward and downward. The $\log \beta_1$ data for DTPA and TEDTA complexes go slightly downward until the end of the series, while there is a steady increase in $\log \beta_1$ for IDA, NTA, and EDTA complexes. The trends are believed to be a reflection of the changes in the number of hydration water molecules [98, 99].

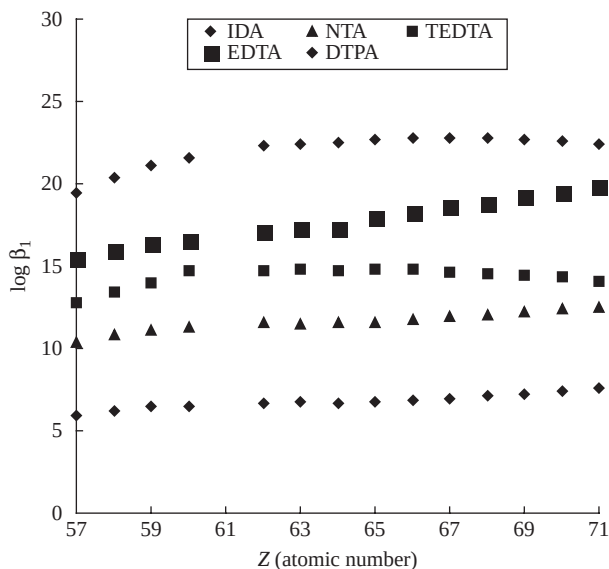


Figure 3.29 The formation constants of RE(III) complexes with IDA, NTA, TEDTA, EDTA, and DTPA.

3.4 Rare Earth Complexes with Amino Acids

Coordination chemistry of RE(III) with amino acids has been attracting much interest since the early 1970s after the discovery that certain RE(III) ions could be used as probes of calcium ion binding sites in proteins and enzymes [118, 119]. Since then, a large amount of work on the solution and structural chemistry of rare earth–amino acid complexes has been published. The solution studies involve all of the rare earth elements and 13 (Gly, Ala, Val, Leu, Phe, Met, Pro, Ser, Tyr, His, Lys, Trp, and Arg) of the 20 standard amino acids, and more than 100 of the RE(III)–amino acid complexes have been structurally characterized. This section will cover the synthetic, structural, and solution chemistry of these complexes.

3.4.1 Preparation of Rare Earth Complexes with Amino Acids

The preparation of the complexes starts with the amino acids and RE(III) salts, usually perchlorates, nitrates or chlorides due to their good solubility and availability. Most of the complexes are obtainable by mixing the salts and the ligands at a molar ratio of RE(III) : ligand = 1 : 1 in aqueous solutions, followed by slow evaporation, and the stoichiometry and the structure of the resulting products generally shows no dependence on the RE(III) to ligand ratio of the starting materials. Exceptions exist, however; two products with different stoichiometry have been isolated from the same reaction mixture [120]. Nevertheless, it may be necessary to adjust the RE(III) to ligand ratio to facilitate the growing of single crystals of the products.

3.4.2 Structural Chemistry of Rare Earth Complexes with Amino Acids

At pH 1–4, amino acids are in their zwitterions form. The ligands can thus be considered as simple carboxylates with a positively charged side group $-\text{NH}_3^+$ at its α -position. In fact, the

structures reported so far indicate that amino acids behave very similarly to monocarboxylate in terms of their coordination mode with the $-\text{NH}_3^+$ group only participating in forming hydrogen bonded networks. However, no mononuclear RE(III)–amino acid complexes have been reported so far, and only five coordination modes are found in the structures: η^1 ; η^2 ; μ_2 – $\eta^1\eta^1$ ZZ; μ_2 – $\eta^1\eta^1$ ZE; and μ_2 – $\eta^2\eta^1$ (Figure 3.1). The complexes are either dimeric or polymeric with RE(III) to ligand ratios of 1 : 1, 1 : 2 or 1 : 3. The coordination numbers of the RE(III) range from six to ten, with most of them being eight with a distorted square anti-prism geometry. Among the ligands, Gly and Pro are found to form three types of complexes with RE : L = 1 : 3, 1 : 2, and 1 : 1, while both Ala and Ser can form two types of complexes with RE : L = 1 : 2 and 1 : 1 for Ala, and RE : L = 1 : 2 and 2 : 3 for Ser, respectively. All of the other ligands can only form either 1 : 2 or 1 : 1 complexes [9].

3.4.2.1 Structures of 1 : 3 (RE : L) Complexes

The 1 : 3 (RE : L) complexes are only found when Gly or Pro are the ligands, but with a wide range of metal ions from the smallest Sc(III) to the largest La(III). Correspondingly, CN = 6, 8, 9, or 10 complexes are observed, all of which are of 1D-polymeric structures with either alternating double bridging and quadruple bridging, triple bridging, or double bridging connectivity.

Three types of alternating double bridging and quadruple bridging connections, that is, (I) $(\mu_2\text{--}\eta^2\eta^1)_2//(\mu_2\text{--}\eta^1\eta^1)_2(\mu_2\text{--}\eta^2\eta^1)_2$, (II) $(\mu_2\text{--}\eta^1\eta^1)_2//(\mu_2\text{--}\eta^1\eta^1)_2(\mu_2\text{--}\eta^2\eta^1)_2$, and (III) $(\mu_2\text{--}\eta^1\eta^1)_2//(\mu_2\text{--}\eta^1\eta^1)_2(\mu_2\text{--}\eta^1\eta^1)_2$, two types of triple bridging connections, (IV) $(\mu_2\text{--}\eta^2\eta^1)_2(\mu_2\text{--}\eta^1\eta^1)$ and (V) $(\mu_2\text{--}\eta^2\eta^1)_2$, and one type of double bridging connection, i.e. (VI) $(\mu_2\text{--}\eta^1\eta^1)_2$, have been identified in the 1 : 3 complexes (Figure 3.30). Gly forms type (I) structures with light La(III), and type (II) structures with smaller RE(III), including Pr, Nd, Sm, Ho, Er, and Y. However, the 1 : 3 complexes of Pro with Pr(III), Nd(III), and Gd(III) are all of type (III) structures. Three representatives of structure type (I) to (III) are shown in Figure 3.30a, b, and c. The three complexes have the same formula: $[\text{RE}_2\text{L}_6(\text{H}_2\text{O})_4]_n^{6n+}$, although their structures are different. In the $[\text{La}_2\text{Gly}_6(\text{H}_2\text{O})_4]_n^{6n+}$, four of the six carboxylates around La(III) are in the tridentate bridging coordination mode $(\mu_2\text{--}\eta^2\eta^1)$ [121], while there are only two and zero carboxylates in this mode for $[\text{Sm}_2(\text{Gly})_6(\text{H}_2\text{O})_4]_n^{6n+}$ [122] and $[\text{Pr}_2(\text{Pro})_6(\text{H}_2\text{O})_4]_n^{6n+}$ [123], respectively. Thus the coordination numbers of the RE(III) in the three structures are ten, nine, and eight. This is a result of the lanthanide contraction and steric effect: the La(III) ion, with large ionic radius, prefers the $\mu_2\text{--}\eta^2\eta^1$ coordination mode to achieve high coordination numbers, and Pro is bulkier than Gly.

The structures of the two triple bridging complexes are shown in Figure 3.30d and e. The coordination numbers for La(III) and Yb(III) are nine and eight, respectively [124, 125]. The double bridging structures are only found in the Pro complexes, $[\text{RE}_2(\text{Pro})_6(\text{H}_2\text{O})_6]_n^{6n+}$ [RE = Sm(III), Eu(III), Gd(III), Er(III), and Y(III)] (Figure 3.30f), where the two neighboring metal ions are linked by a double bridge $(\mu_2\text{--}\eta^1\eta^1)_2$, with each of them being further coordinated by a monodentate (η^1) Pro and three water molecules, CN = 8 [126].

3.4.2.2 Structures of 1 : 2(RE : L) Complexes

The 1 : 2(RE : L) complexes are inclined to form when Gly, Ala, Val, Phe, Met, Ile, His, Cys, and Pro are used as the ligands. Most of these complexes are dimeric, with the general formula

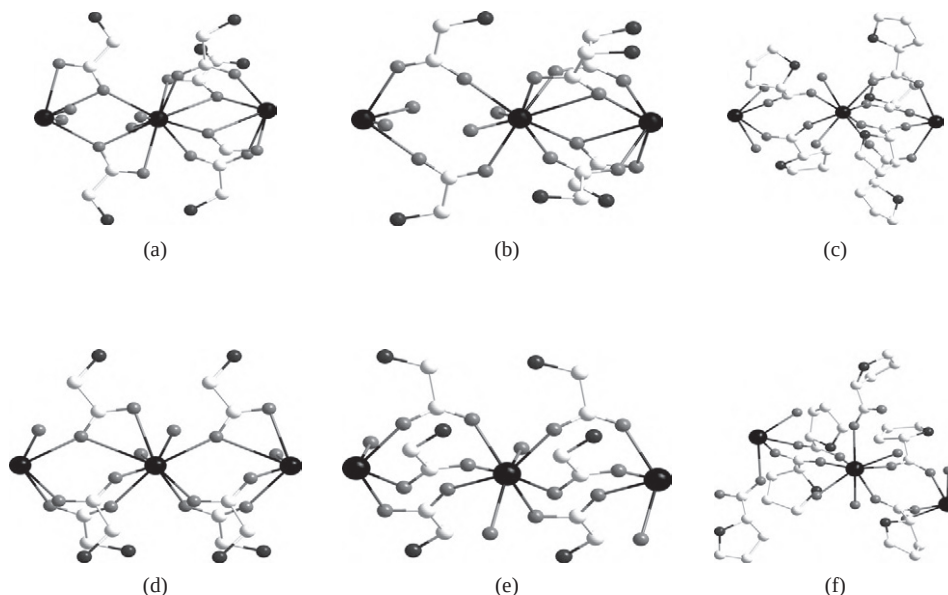


Figure 3.30 The structures of (a) $[\text{La}_2\text{Gly}_6(\text{H}_2\text{O})_4]_n^{6n+}$; (b) $[\text{Sm}_2\text{Gly}_6(\text{H}_2\text{O})_4]_n^{6n+}$; (c) $[\text{Pr}_2\text{Pro}_6(\text{H}_2\text{O})_4]_n^{6n+}$; (d) $[\text{La}_2\text{Gly}_6(\text{H}_2\text{O})_4]_n^{6n+}$; (e) $[\text{Yb}_2\text{Gly}_6(\text{H}_2\text{O})_4]_n^{6n+}$; and (f) $\text{Sm}_2(\text{Pro})_6(\text{H}_2\text{O})_6]_n^{6n+}$ [RE, black (large balls); O, grey; N, black (small balls); C, white; H, omitted]. (Redrawn from the CIF files of A. Ma *et al.*, “Crystal structure and infrared spectra of a lanthanum coordination compound with glycine, $\{[\text{La}(\text{Gly})_32\text{H}_2\text{O}](\text{ClO}_4)_3\}_n$,” *Journal of Coordination Chemistry*, **33** (1), 59–67, 1994 [121]; A. Ma *et al.*, “Synthesis and crystal structure of $\{[\text{Sm}_2(\text{Gly})_6(\text{H}_2\text{O})_4](\text{ClO}_4)_6(\text{H}_2\text{O})_5\}_n$,” *Wuji Huaxue Xuebao* (Chinese Journal of Inorganic Chemistry), **9** (4), 401–406, 1993 [122]; Z. Wang *et al.*, “Synthesis characterization and crystal structure of rare earth complexes with L-proline,” *Huaxue Xuebao* (Acta Chimica Sinica), **51** (3), 257–264, 1993 [123]; S.L. Gao *et al.*, “Catena-Poly[[[diaqualanthanum(III)]-tri- μ -glycinato] trichloride monohydrate],” *Acta Crystallographica Section E*, **E58**, m234–m236, 2002 [124]; F. Ren *et al.*, “Study on the regularity of crystal structures of complexes of rare earth perchlorate with glycine,” *Xibei Daxue Xuebao*, Ziran Kexueban (Journal of Northwest University, Natural Science Edition), **31** (2), 111–114, 2001 [125]; and J. Torres *et al.*, “Sm(III) complexation with amino acids. Crystal structures of $[\text{Sm}_2(\text{Pro})_6(\text{H}_2\text{O})_6](\text{ClO}_4)_6$ and $[\text{Sm}(\text{Asp})(\text{H}_2\text{O})_4]\text{Cl}_2$,” *Journal of the Chemical Society, Dalton Transactions*, (21), 4035–4041, 2002 [126].)

$[\text{RE}_2\text{L}_4(\text{H}_2\text{O})_8]\text{X}_6 \cdot n\text{H}_2\text{O}$ (RE = Pr, Nd, Sm, Eu, Ho, Er, and Y; X = Cl^- or ClO_4^- ; $n = 0\text{--}4$) with the exception of some Pro complexes, $[\text{RE}(\text{Pro})_2(\text{H}_2\text{O})_5]\text{Cl}_3$ (RE = Er, Ho, Dy, and Yb), which are 1D-polymers.

In a typical dimeric 1 : 2 complex, the two RE(III) ions are linked through a quadruple bridge $(\mu_2\text{-}\eta^1\eta^1)_4$. Each of the metal ions is further coordinated by four water molecules, CN = 8. A representative structure, $[\text{Eu}_2(\text{Ala})_4(\text{H}_2\text{O})_8]^{6+}$, is shown in Figure 3.31a. While most dimeric RE(III)–carboxylic acid complexes are centrosymmetric, with amino acids as ligands, similarly structured complexes are only obtainable when the racemic form of the ligands are used for the synthesis [127].

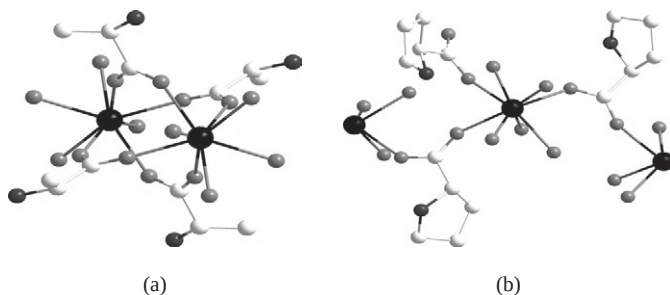


Figure 3.31 The structures of (a) $[\text{Er}_2(\text{Ala})_4(\text{H}_2\text{O})_8]^{6+}$ and (b) $[\text{Er}(\text{Pro})_2(\text{H}_2\text{O})_5]_n^{3n+}$ [RE, black (large balls); O, grey; N, black (small balls); C, white; H, omitted)]. (Redrawn from the CIF files of T. Glowiak *et al.*, “Ligand chirality effect on the structure and its spectroscopic consequences in $[\text{Ln}_2(\text{Ala})_4(\text{H}_2\text{O})_8](\text{ClO}_4)_6$ crystals,” *Polyhedron*, **15** (17), 2939–2947, 1996 [127]; and A.Z. Ma *et al.*, “Structure of an erbium coordination compound with L-proline, $\{[\text{Er}(\text{Pro})_2(\text{H}_2\text{O})_5]\text{Cl}_3\}_n$,” *Acta Crystallographica Section C*, **49** (5), 865–867, 1993 [128].)

Figure 3.31b shows the structure of $[\text{Er}(\text{Pro})_2(\text{H}_2\text{O})_5]_n^{3n+}$. The two adjacent Er(III) ions in the structure are joined together by a bridging carboxylate in the coordination mode $\mu_2\text{-}\eta^1\eta^1$, and each of the Er(III) is further coordinated by one monodentate (η^1) ligand and five water molecules, CN = 8 [128].

3.4.2.3 Structures of 1 : 1 and 2 : 3(RE : L) Complexes

A diverse range of structures have been revealed for the 1 : 1 complexes with the simple amino acids, Gly, Pro, and Ala, as well as the amino acids with side groups capable of metal coordination, such as Ser, Thr, Glu, and Asp. The structures can be dimeric, 1D-polymeric or 2D-layered.

The complexes of Gly and Pro are dimeric with the two RE(III) ions bridged by two carboxylate groups in a bidentate bridging mode $(\mu_2\text{-}\eta^1\eta^1)_2$. The structure of $[\text{Nd}_2(\text{Pro})_2(\text{H}_2\text{O})_{12}]_n^{6n+}$ is shown in Figure 3.32a [129]. However, the Ala complex, $[\text{Dy}(\text{Ala})(\text{H}_2\text{O})_6]_n^{3n+}$ is an infinite chain. Each of the Dy(III) ions is coordinated by six water molecules, and linked to its adjacent metal centers through single carboxylate bridges $\mu_2\text{-}\eta^1\eta^1$ (Figure 3.32b) [130].

There are only two structures reported for Ser and Thr, $[\text{Ho}_2(\text{Ser})_2(\text{H}_2\text{O})_{12}]_n\text{Cl}_{3n}$ and $[\text{Ho}_2(\text{Thr})_2(\text{H}_2\text{O})_{12}]_n\text{Cl}_{3n}$. The two complexes have very similar structures with an –OH group and one carboxylate O chelating to one Ho(III), and the other carboxylate O coordinating its neighboring Ho(III) to form a 1D-polymer (Figure 3.32c) [131].

The only known 2 : 3 complex with the only seven-coordinate RE(III)–amino acid complex reported so far is the dimeric Ser complex, $[\text{Er}_2(\text{Ser})_3(\text{H}_2\text{O})_8](\text{ClO}_4)_6$ [132]. In the structure, the two Er(III) ions are bridged through three carboxylates in their $\mu_2\text{-}\eta^1\eta^1$ coordination mode, and the coordination sphere of Er(III) is completed by four water molecules, CN = 7.

Both Glu and Asp have an extra carboxylic group, which deprotonates when coordinating RE(III) ions. Thus, Glu and Asp are negatively charged in the complexes. The coordination modes of Glu and Asp are shown in Figure 3.33. Several Glu complexes [RE = Pr, Nd(Y), Ho Er] have been reported, all displaying very similar 2D-layered structures. A typical Glu complex

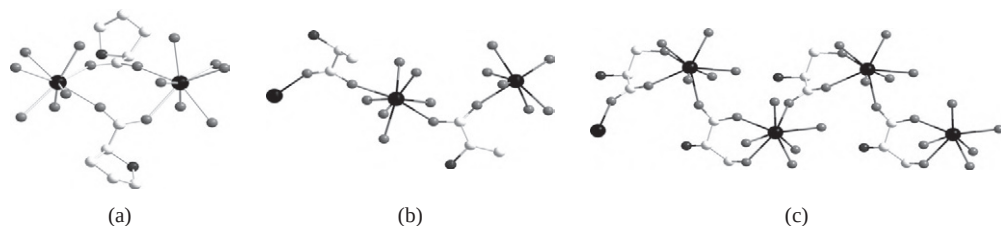


Figure 3.32 The structures of (a) $[\text{Nd}_2(\text{Pro})_2(\text{H}_2\text{O})_{12}]^{6+}$; (b) $[\text{Dy}(\text{Ala})(\text{H}_2\text{O})_6]_n$; and (c) $[\text{Ho}_2(\text{Ser})_2(\text{H}_2\text{O})_{12}]^{6n+}$ [RE, black (large balls); O, grey; N, black (small balls); C, white; H, omitted]. (Redrawn from the CIF files of T. Glowiak *et al.*, “Structures of neodymium(III) complexes with amino acids: (I) catena-poly{[triaquatrachloroneodymium(III)]- μ -(β -alanine-O,O')}”; (II) pentaquaquachloro- μ -(L-proline-O,O')-neodymium(III) hexaaqua- μ -(L-proline-O,O')-neodymium(III) pentachloride,” *Acta Crystallographica Section C*, **47** (1), 78–81, 1991 [129]; T. Glowiak *et al.*, “Absorption, luminescence and crystal structure studies of dysprosium compound with L- α -Alanine: $[\text{Dy}(\text{L-}\alpha\text{-AlaH})(\text{H}_2\text{O})_6]\text{Cl}_3$,” *Journal of the Less Common Metals*, **168** (2), 237–248, 1991 [130]; and T. Glowiak and C.N. Dao, “Structure of pentaqua(L-serine)holmium(III) trichloride,” *Acta Crystallographica Section C*, **49** (6), 1171–1173, 1993 [131].)

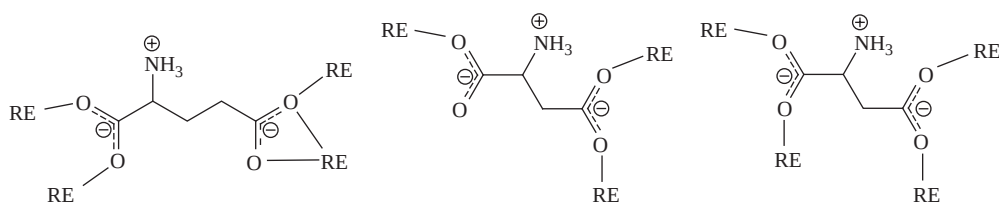


Figure 3.33 Coordination modes of Glu (left) and Asp (middle and right).

can be formulated as $[\text{RE}_2(\text{Glu})_2(\text{H}_2\text{O})_8]_n(\text{X})_4$ ($\text{X} = \text{ClO}_4^-$, Cl^- or NO_3^-) (Figure 3.34a). In the structure, two RE(III) ions are bridged to form a dimeric unit by two tridentate chelating(μ_2 - $\eta^2\eta^1$) γ -carboxylates and two bidentate bridging(μ_2 - $\eta^1\eta^1$) α -carboxylates from four ligands, and the dimeric units are linked to four other sets of dimeric units through the other ends of the ligands to form a layered structure. Each of the RE(III) ions is also coordinated by four water molecules, CN = 9 [133].

Only two Asp complexes have been structurally characterized by X-ray diffraction, but they are structurally distinctly different. $[\text{Sm}(\text{Asp})(\text{H}_2\text{O})_4]_n^{3n+}$ is a 2D-layered polymer [126], in which both the α - and β -carboxylates are in the μ_2 - $\eta^1\eta^1$ bridging coordination mode (Figure 3.34b), and each ligand is coordinated to four Sm(III) centers. Each of the metal centers is surrounded by four oxygen atoms, one from each ligand. The ligands then coordinate another eight metal centers to form a layered structure. $[\text{Ho}(\text{Asp})(\text{H}_2\text{O})_5]_n^{3n+}$ is an infinite chain [134]. Only the β -carboxylates are in bridging coordination mode μ_2 - $\eta^1\eta^1$; the α -carboxylates are monodentate η^1 (Figure 3.34c). Each Ho(III) is coordinated by five water molecules and three oxygen from different ligands, CN = 8.

As we have seen from the discussion above, the γ - and β -carboxylates are farther away from the positively charged $-\text{NH}_3^+$ than the α -carboxylate, and they are expected to coordinate

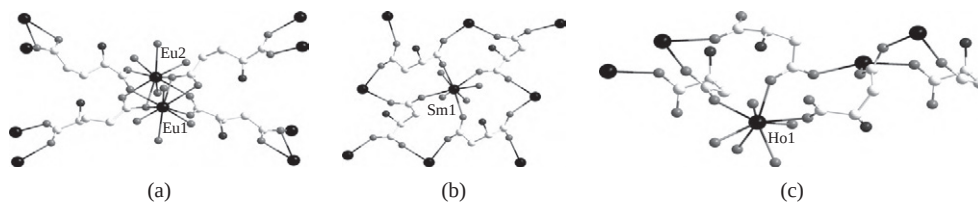


Figure 3.34 The structures of (a) $[\text{Eu}_2(\text{Glu})_2(\text{H}_2\text{O})_8]_n^{4n+}$; (b) $[\text{Sm}(\text{Asp})(\text{H}_2\text{O})_4]_n^{2n+}$; and (c) $[\text{Ho}(\text{Asp})(\text{H}_2\text{O})_5]_n^{2n+}$ [RE, black (large balls); O, grey; N, black (small balls); C, white; H, omitted]. (Redrawn from the CIF files of B. Barja *et al.*, “Gadolinium(III) and europium(III) L-glutamates: synthesis and characterization. *Inorganica Chimica Acta*, **359** (12), 3921–3926, 2006 [133]; J. Torres *et al.*, “Sm(III) complexation with amino acids. Crystal structures of $[\text{Sm}_2(\text{Pro})_6(\text{H}_2\text{O})_6](\text{ClO}_4)_6$ and $[\text{Sm}(\text{Asp})(\text{H}_2\text{O})_4]\text{Cl}_2$,” *Journal of the Chemical Society, Dalton Transactions*, (21), 4035–4041, 2002 [126]; and I. Csöregi *et al.*, “Crystal structure of holmium aspartate chloride hydrate $\text{Ho}(\text{L-Asp})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$,” *Acta Chemica Scandinavica*, **43** (7), 636–640, 1989 [134].)

RE(III) ions more effectively. This effect can help us to understand why they show two different coordination modes $\mu_2\text{-}\eta^2\eta^1$ versus $\mu_2\text{-}\eta^1\eta^1$ in Glu and $\mu_2\text{-}\eta^1\eta^1$ versus η^1 in Asp (Figure 3.34a and c). However, the effect is not significant enough to generate a sizable difference for RE(III)–O(carboxylate) distances between α -, β -, and γ -carboxylates.

3.4.3 Solution Chemistry of Rare Earth Complexes with Amino Acids

While studies on the crystal structures of RE(III)–amino acid complexes can give us clear pictures on the ways in which RE(III) ions and the amino acids bond to each other, their solution chemistry, which deals with the reactions in solution, the chemical species formed, their stability, as well as their distribution over certain pH ranges, can help us understand better the *in vivo* behaviors of RE(III) ions and their complexes with amino acids. Work on the solution chemistry of RE–amino acid complexes has been carried out since the early 1960s [9]. It has been found that the amino acids studied behave very similarly to one another, just as we have learned from their structural chemistry. Mononuclear species with 1 : 1 and 1 : 2 (RE : L) stoichiometry have been reported for all of the amino acids. In some studies, the presence of mononuclear species with stoichiometry 1 : 3, dinuclear species with stoichiometry 2 : 4 and 2 : 6, in addition to the hydrolyzed species, such as $[\text{RE}(\text{OH})\text{L}]^+$, $[\text{RE}(\text{OH})]^{2+}$, and $\text{RE}(\text{OH})_3(\text{s})$, have been confirmed [126, 135, 136].

Early studies on RE(III)–neutral amino acid and RE(III)–basic amino acid systems (14 neutral amino acids Gly, Ala, Val, Ile, Leu, Pro, Trp, Tyr, Met, Ser, Thr, Cys, Asn, and Gln; and three basic amino acids His, Lys, and Arg) indicate that they form only 1 : 1 and 1 : 2 (RE : L) mononuclear species $[\text{REL}]^{2+}$ and $[\text{REL}_2]^+$, with $\log \beta_1$ around 4–6 and $\log \beta_2$ around 6–8. Compared with the corresponding RE(III) complexes with acetic acid ($\log \beta_1 = 1.53$; $\log \beta_2 = 2.44$; $\text{pK}_a = 4.56$) (Table 3.1), a substantial increase in the complex stability is observed for all of the RE–amino acid complexes, indicating chelation between the carboxylato-oxygen, amino-nitrogen, and the RE(III) cations. Meanwhile, thermodynamic parameters and NMR studies showed that the –OH groups in Ser and Tyr are involved in the coordination of their

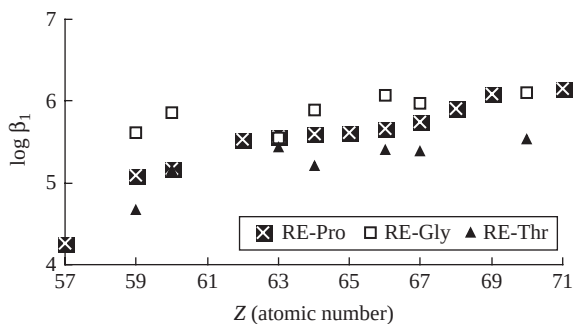


Figure 3.35 The stability constants ($\log \beta_1$) of the RE(III) complexes with Gly, Pro, and Thr.

complexes [137, 138]. The reactions and the equilibrium constants are shown in Equations (3.4)–(3.7).

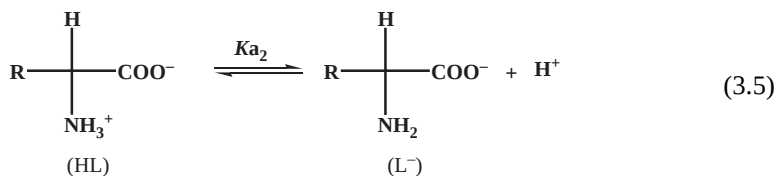
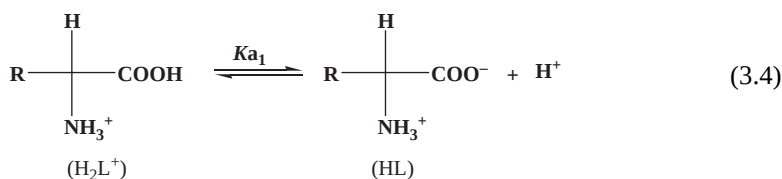


Figure 3.35 shows the evolution of the formation constants of the RE(III) complexes of Gly, Pro, and Thr with atomic numbers (Z) of the RE(III) [139, 140]. For all of the three series, the stability of the complexes increases from La to Sm or Eu, and then decreases from Eu to Gd (gadolinium break). From Gd to Lu, the stability shows a slow increase. The stability of the complexes are in the order of $[\text{RE}(\text{Gly})]^{2+} > [\text{RE}(\text{Pro})]^{2+} > [\text{RE}(\text{Thr})]^{2+}$, while the basicity of L^- is in the order of $\text{Pro} > \text{Gly} > \text{Thr}$ [the $(\text{p}K_{a1} + \text{p}K_{a2})$ for Thr, Gly, and Pro is 11.32, 11.98, and 12.87, respectively]. The reversed order between $[\text{RE}(\text{Gly})]^{2+}$ and $[\text{RE}(\text{Pro})]^{2+}$ could be a result of the bulkier volume of Pro compared with Gly.

Only a few studies have been done for the RE–basic amino acid system. A comprehensive study of RE(III) complexes with His revealed that $[\text{RE}(\text{HisH})]^{3+}$, $[\text{RE}(\text{His})_2]^+$, and $[\text{RE}(\text{His})]^{2+}$ are the major species formed in the solution, and hydroxo, such as $\text{RE}(\text{OH})^{2+}$ or $[\text{RE}(\text{His})_m(\text{OH})_n]^{(3-m-n)+}$, or polynuclear complex species are absent in the solution [141].

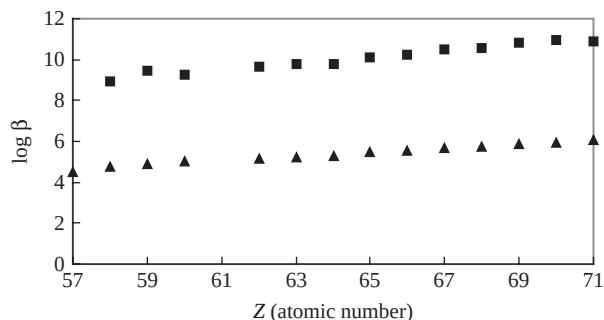


Figure 3.36 Stability constants of RE(III)–Asp complexes, $\log \beta_1$ (▲) and $\log \beta_2$ (■).

The two acidic amino acids Glu and Asp have an extra carboxyl group. They can be expressed as H_3Glu^+ or H_3Asp^+ when the α -carboxylates are also protonated. Most of the studies show that they form both $[\text{RE}(\text{L})]^{1+}$ and $[\text{RE}(\text{L})_2]^{1-}$ species in the solution with $\log \beta_1$ and $\log \beta_2$ around 5 and 9, respectively, which are close to the data for the neutral and basic amino acids [9]. This is an indication of the similar chelation modes among the RE–amino acid complexes, and the β - or γ -carboxy oxygen in Asp or Glu may not be involved in the chelation of the α -carboxy oxygen and the amino nitrogen with the RE(III).

While the research into RE–Glu systems has been limited and far from systematic, some excellent work has been done with the RE–Asp [9]. Figure 3.36 shows the $\log \beta_1$ and $\log \beta_2$ of the complexes from La to Lu. There is a steady increase from La to Lu for $\log \beta_1$, and the trend for $\log \beta_2$ is more complicated, although it is not atypical for RE(III) complexes.

Most of the studies on the RE(III) complexes with neutral and basic amino acids have shown that complexation takes place when $\text{pH} > 6$, and that $\text{RE}(\text{OH})_3$ precipitation forms if the $\text{pH} > 8$, and experiments done at $\text{pH} < 7$ or 7.5 are considered to be free of significant hydrolysis. However, a few studies did show that protonated complex species form at $\text{pH} < 2$, and the hydrolysis of RE(III) starts at $\text{pH} < 6$ [126, 135, 136]. The large discrepancies among the data could be a result of different experimental conditions [concentrations of the RE(III) and the ligands, the RE : L ratios] and various computing models used, as all of the experiments and the calculations are based on Bjerrum's method [142]. More detailed and systematic studies are thus definitely needed for the solution chemistry of RE(III)–amino acid complexes.

3.5 Summary and Outlook

Numerous RE(III) complexes with carboxylic acids, polyaminopolycarboxylic acids, and amino acids having intriguing topologies, diverse nuclearity, fascinating structures, and coordination modes have been reported, and their applications as catalysts, light emitters, optical sensors, MRI contrast agents, and magnets have been established. Efforts have been made to design and synthesize RE(III)–carboxylic acid complexes as advanced materials, and complexes having potential applications as storage materials, magnetic materials, Lewis acid catalysts, optical sensors, and so on have been reported. However, owing to the ionic nature of the RE(III)–O (carboxylate) bonds, it remains a challenge to predict a priori the structure of any given complexes. Making use of their multiple N- and O-donors and great

chelating ability, polyaminopolycarboxylic acids have been extensively utilized for the formation of thermodynamically and kinetically stable complexes of RE(III) ions, with the clinically proven Gd(III)–polyaminopolycarboxylic acid complexes being the culmination of such efforts. Research on RE(III) complexes with amino acids was stimulated by the success of using RE(III) as a probe for the Ca(II)-binding site in proteins in the early 1970s. Complexes with unique structures have since been isolated and structurally characterized. X-ray crystallographic and thermodynamic studies have revealed the strong similarity among the complexes formed by different amino acids in both the solid state and solution. However, the synthesis of such complexes remains a challenge as the structures of these species are hard to predict if at all possible, largely due to their relatively low stability. It is exactly because of this low stability, that solution studies aimed at the delineation of the different species at equilibrium have been difficult, and therefore, far from being systematic and definitive. These challenges should constitute the major tasks for future studies of these unique rare earth complexes.

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4

N-Based Rare Earth Complexes

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4.1 Introduction

Among the numerous rare earth complexes, those formed with N-based type ligands are of great importance due to their various physicochemical properties associated with the intriguing coordination environment [1]. However, the N-based ligands themselves can be perceived as high-energy materials that have been frequently employed, for example, for the construction of complexes possessing interesting optical or electrochemical properties with applications in nonlinear optic (NLO) materials, luminescent materials, electronic devices (switches or wires), and multi-electron catalysis. As a result, the intramolecular interaction of N-based rare earth complexes and the intrinsic nature of the rare earth metal centers endow the complexes with characteristic features that cannot be found in their non-coordination counterparts, enabling them to be used in different areas.

In an effort towards preparing N-based rare earth complexes, various ligands containing nitrogen atom(s) have been developed. Thus, various rare earth complexes containing amide type, N-heterocyclic type, or Schiff-base type ligands have been synthesized and their single crystal structures resolved by X-ray diffraction analyses. In addition, great progress has also been made on investigating the relationship between the N-based ligands and the properties of the rare earth complexes.

In this chapter, we seek to summarize the recent progress in the synthesis, crystal structure, and various physical properties of N-based rare earth complexes.

4.2 Rare Earth Complexes with Amide Type Ligands

4.2.1 Rare Earth Complexes with Aliphatic Amide Type Ligands

The aliphatic amine can be used to classify primary, secondary, tertiary, and quaternary amines. Except for the quaternary amine, the other three types of amines are able to coordinate with the

rare earth metals. The coordination ability of these aliphatic amine ligands with rare earth ions mainly relies on three factors, namely: the inductive effect arising from the electronegativity of the functional group substituted to the nitrogen atom, the space effect of the aliphatic amine, and the influence of the intermolecular hydrogen bonding interaction. Owing to the lack of integrated structural parameters, it is difficult to quantitatively depict the influence as a whole. In most instances, the factor affecting the coordination ability of the ligand was estimated according to experimental results. For example, when only the influence of the inductive effect is taken into consideration, the order of alkalinescence of the aliphatic amines is tertiary > secondary > primary. However, this order does not always persist if the influence of the space effect is taken into account. In fact, the order of the alkalinescence for aliphatic amines is secondary > primary > tertiary on the basis of experimental results.

Usually, the alkalinescence of the aliphatic amines is strong. In order to avoid the hydrolysis of the rare earth ions, it is necessary to maintain a strictly anhydrous environment when complexes of the rare earths with aliphatic amine ligands are synthesized. Instead of rare earth chloride, nitrate, or perchlorate salts, the rare earth triflate salts $\text{RE}(\text{CF}_3\text{SO}_3)_3$ are often used as the starting material. The most characteristic feature of $\text{RE}(\text{CF}_3\text{SO}_3)_3$ is the stability and ease of eliminating water. The rare earth triflate salts are usually prepared from the corresponding rare earth oxide and trifluoromethanesulfonic acid $\text{CF}_3\text{SO}_3\text{H}$ [2]. Adding the rare earth oxide to an aqueous solution of trifluoromethanesulfonic acid and removing the undissolved oxide by filtration, after evaporating the residue solution using a rotatory evaporator, the resulting solid is dried at 160–200 °C under vacuum, and $\text{RE}(\text{CF}_3\text{SO}_3)_3$ is obtained and used without further purification.

Some representative aliphatic amine ligands are summarized in Figure 4.1. The synthesis and structure characteristics of example complexes will be introduced in the following sections.

$[\text{La}(\mathbf{1})_4\cdot\text{CF}_3\text{SO}_3]\text{CH}_3\text{CN}\cdot(\text{CF}_3\text{SO}_3)_2$ Complex: The preparation of this complex [3] is analogous to the corresponding perchlorate first reported by Forsberg and Moeller. $\text{La}(\text{CF}_3\text{SO}_3)_3$ reacted with ethylenediamine (**1**) in a ratio of 1 : 8 in acetonitrile under N_2 in a dry Schlenk tube. The resulting cloudy mixture was heated to reflux for about 5 min, then the mixture was filtered. When the filtrate was evaporated and cooled to -20°C , a white crystalline solid was obtained. The lanthanum–ethylenediamine complex belongs to the triclinic system and crystallizes in the space group $P\bar{1}$ with $a = 0.9526(2)$ (nm), $b = 1.2919(2)$ (nm), $c = 1.4077(2)$ (nm),

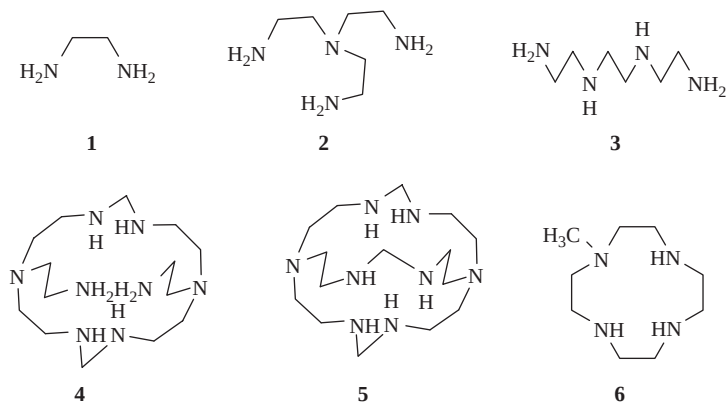


Figure 4.1 Six representative aliphatic amine type ligands.

$\alpha = 102.62(1)^\circ$, $\beta = 91.38(1)^\circ$, $\gamma = 98.03(1)^\circ$, $V = 1.6713(9) \text{ nm}^3$, and $Z = 2$. The structure of the $\text{La}(\mathbf{1})_4(\text{CF}_3\text{SO}_3)^{2+}$ cation is shown in Figure 4.2. As can be seen, the central lanthanum ion is nine-coordinate with eight nitrogen atoms from four ethyleneamines and one oxygen from a triflate anion. The coordination geometry can be described as a distorted tricapped trigonal prism. La–N bond lengths range from 0.2692(2) to 0.2741(2) nm with an average of 0.2705(2) nm, and the average ethylenediamine bite angle is 63.8° , ranging from 62.8° to 64.6° . The interligand N–N distance ranges from 0.315 to 0.341 nm. It seems that a weak hydrogen bonding interaction exists between the hydrogen of NH group and oxygen of the triflate, with the N–O distance ranging from 0.3000(4) to 0.3215(3) nm.

Pr(2)(3)(CF₃SO₃)₃ Complex: Raymond and coworkers [4] reported the synthesis and the crystal structure of the $\text{Pr}(\mathbf{2})(\mathbf{3})(\text{CF}_3\text{SO}_3)_3$ complex. 1 equiv of both **2** and **3** were added simultaneously via two syringes into the suspended acetonitrile solution containing anhydrous $\text{Pr}(\text{CF}_3\text{SO}_3)_3$. Most of the solid was dissolved after the addition of an appropriate amount of acetonitrile. The solution was then heated to reflux, briefly, and clarified by filtration. The resulting light green clear solution was evaporated to the required volume and cooled to about -20°C for 6 h. After decantation of the solution, the target crystals were obtained. Furthermore, additional crystals can be obtained if the mother liquor was cooled overnight again, with a total yield of about 72%. According to the data from the crystal structure, the formula of this complex can be expressed as $\text{Pr}(\mathbf{2})(\mathbf{3})(\text{CF}_3\text{SO}_3)_3$. It belongs to the triclinic system and crystallizes in a space group $P-1$ with $a = 0.9526(1) \text{ (nm)}$, $b = 1.0660(1) \text{ (nm)}$, $c = 1.7080(3) \text{ (nm)}$, $\alpha = 74.28(1)^\circ$, $\beta = 76.91(1)^\circ$, $\gamma = 85.50(1)^\circ$. The complex is nine-coordinate with eight amine donors and one oxygen donor from a coordinating triflate anion. The coordinated triflate anion is disordered. Figure 4.3 illustrates the labeling diagram for the cation $[\text{Pr}(\mathbf{2})(\mathbf{3})(\text{CF}_3\text{SO}_3)]^{2+}$ on a schematic drawing of the complex. It is worth noting that the bond lengths and angles in this complex provide some information with respect to the appropriate encapsulation bridge lengths as well as typical values for these particular ligands. The tertiary amine Pr–N(1) distance in **2** is about of 0.2737(7) nm. The bond lengths of the three primary amines (N2, N3,

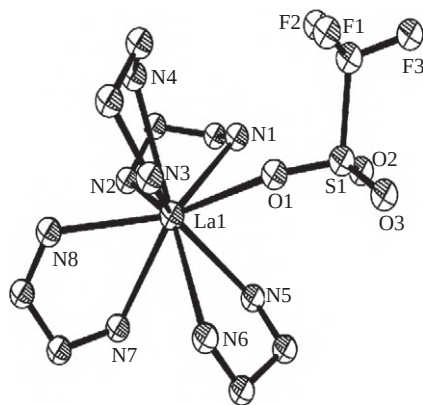


Figure 4.2 Structure of $[\text{La}(\mathbf{1})_4\text{CF}_3\text{SO}_3]^{2+}$ [3]. (Reproduced with permission from H. Paul, P.H. Smith and K.N. Raymond, "A lanthanide-amine template synthesis. Preparation and molecular structures of $\text{Ln}(\text{L})(\text{CH}_3\text{CN})(\text{CF}_3\text{SO}_3)_3$ [$\text{L} = 1,9\text{-bis}(2\text{-aminoethyl})\text{-}1,4,6,9,12,14\text{-hexaazacyclohexadecane}$; $\text{Ln} = \text{La}, \text{Yb}$] and $\text{La}(\text{en})_4(\text{CH}_3\text{CN})(\text{CF}_3\text{SO}_3)_3$," *Inorganic Chemistry*, **24**, 3469, 1985. © 1985 American Chemical Society.)

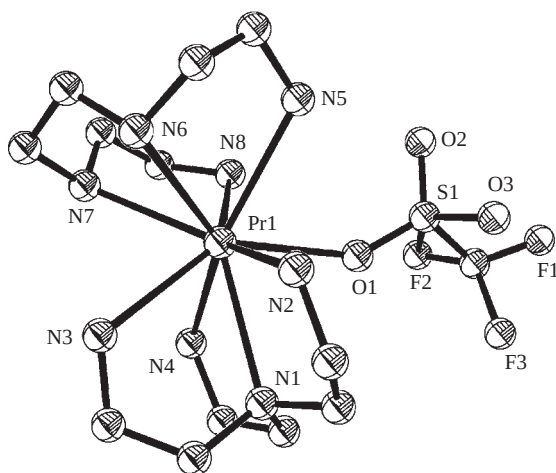


Figure 4.3 Structure of $[\text{Pr}(\mathbf{2})(\mathbf{3})\text{CF}_3\text{SO}_3]^{2+}$ [4]. (Reproduced with permission from H. Paul, Z.E.R. Smith, C.W. Lee and K.N. Raymond, "Characterization of a series of lanthanide amine cage complexes," *Inorganic Chemistry*, **27**, 4154, 1988. © 1988 American Chemical Society.)

N4) Pr–N(2), Pr–N(3), and Pr–N(4) of **2** are 0.2634 (7), 0.2642(7), and 0.2685(7) nm, respectively. The average of the three primary amine Pr–N bonds of **2** is 0.2654(7) nm, which is significantly shorter than the tertiary amine Pr–N(1) distance. The primary amine (N5, N8), Pr–N(5), Pr–N(8) distances of **3** are 0.2690(7) and 0.2690(7) nm. The bond lengths of secondary amines (N6, N7), Pr–N(6), Pr–N(7) of **3** are 0.2683(7) and 0.2687(7) nm. The average of the two primary amine Pr–N bonds of **3** is 0.2680 nm, in comparison with 0.2654 nm for the average of the two secondary amine Pr–N bonds of **3**. Obviously, the average length of the second amine Pr–N bonds of tren [tetradentate amine 2,2',2''-tris(2-aminoethyl) amine] [4] (is almost the same as the primary amine Pr–N bonds. The average of all ethylene-bridged N–N distances is 0.268 nm, that for **2** is 0.287 nm, and that for **3** is 0.285 nm. The nitrogen hydrogens are involved in a weak hydrogen bonding network to the triflate oxygens.

RE(4)(CF₃SO₃)₃CH₃CN [RE = La, Yb; **4** = 1,9-bis(2-aminoethyl)-1,4,6,9,12,14 hex azacyclo hexadecane: With the use of a rare earth ion as a template, the complexes of RE(4)(CF₃SO₃)₃CH₃CN complexes (Figure 4.1) [4] can be easily synthesized. For example, La(4)(CF₃SO₃)₃CH₃CN was prepared by the reaction of 2 equiv of **2** with 3 equiv of bis(dimethylamino)methane in the presence of 1 equiv of lanthanum triflate salt in acetonitrile at 70–80 °C for 8 h. White crystals were obtained (yield 78%) after the reaction mixture was clarified by filtration, evaporated under vacuum, and then purified by repeated crystallization. For the complex of Yb(4)(CF₃SO₃)₃CH₃CN, although the reaction time extends to 24 h, only about 11% yield was obtained. Using this particular formaldehyde derivative, bis(dimethylamino)methane as a coupling reagent is critical to the synthesis in this method. The reaction of this compound with an amine produces dimethylamine, which is volatile and eventually leaves the reaction mixture as a gas. Thus it drives the reaction towards the desired product. No water, which often results in the hydrolysis of rare earths, was produced during the whole reaction process. Furthermore, the small bite angle of the N–CH₂–N moiety favors a high coordination number around the rare earth metal. As can be seen, although

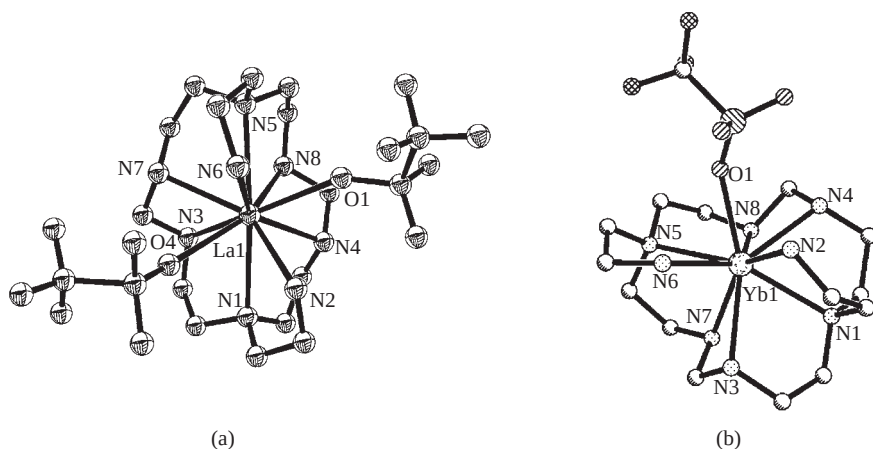


Figure 4.4 Structure of $[\text{La}(\mathbf{4})(\text{CF}_3\text{SO}_3)_2]^+$ and $[\text{Yb}(\mathbf{4})(\text{CF}_3\text{SO}_3)_2]^+$ [4]. (Reproduced with permission from H. Paul, Z.E.R. Smith, C.W. Lee and K.N. Raymond, "Characterization of a series of lanthanide amine cage complexes," *Inorganic Chemistry*, 27, 4154, 1988. © 1988 American Chemical Society.)

the two complexes have the same composition they adopt significantly different structures. For $[\text{La}(\mathbf{4})(\text{CF}_3\text{SO}_3)_2]\text{CF}_3\text{SO}_3\text{CH}_3\text{CN}$, the coordination number is ten, however, a nine-coordinate ytterbium ion is found in $[\text{Yb}(\mathbf{4})(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)_2\text{CH}_3\text{CN}$, Figure 4.4a and b. Owing to the smaller size of Yb^{3+} , one of the CF_3SO_3^- anions was packed outside. This phenomenon is often observed in rare earth coordination chemistry. In other words, the role of the metal in determining the macrocyclic ligand structure was evaluated by comparing $[\text{La}(\mathbf{4})(\text{CF}_3\text{SO}_3)_2]\text{CF}_3\text{SO}_3\text{CH}_3\text{CN}$ and $[\text{Yb}(\mathbf{4})(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)_2\text{CH}_3\text{CN}$.

For $[\text{La}(\mathbf{1})(\text{CF}_3\text{SO}_3)_2]\text{CF}_3\text{SO}_3\text{CH}_3\text{CN}$, the ten-coordinated lanthanum complex includes eight amine nitrogens from **4** and two oxygens from two triflate anions, Figure 4.4a. The coordination geometry can be described as a bicapped square antiprism. If one ignores the orientation of the triflate anions, the complex has a noncrystallographic C_2 axis passing through the La ion and bisecting the O–La–O angle. The longest La–N distance among the eight La–N bonds comes from the tertiary amine La–N, which is 0.2819(3) and 0.2816(3) nm, respectively. The bond lengths of primary amine La–N are 0.2669(4) and 0.2677(7) nm. The secondary amine La–N lengths are 0.2756(3), 0.2701(3), 0.2685(3), and 0.2751(3), respectively. From these data, it can be seen that the longest La–N bond comes from the tertiary amine La–N. However, the primary amine La–N bond is the shortest one. Clearly, the space factor plays a crucial role. However, the ytterbium ion in $[\text{Yb}(\mathbf{4})(\text{CF}_3\text{SO}_3)_2]\text{CF}_3\text{SO}_3\text{CH}_3\text{CN}$ is nine-coordinate with eight amine nitrogens from **L** and only one oxygen donor from a coordinated triflate anion. The coordination geometry can be described as a monocapped square antiprism, Figure 4.4b. The Yb–N bond lengths range from 0.2442(3) to 0.2611(3) nm with an average of 0.2523 nm. Compared with the La–N bond, the Yb–N distance is slightly larger, which may be indicative of an increased intraligand N–N repulsion due to the shorter Yb–N distance.

In comparison with the complex of $[\text{Yb}(\mathbf{4})(\text{CF}_3\text{SO}_3)_2]\text{CF}_3\text{SO}_3\text{CH}_3\text{CN}$, a more encapsulated ytterbium complex $[\text{Yb}(\mathbf{5})(\text{CF}_3\text{SO}_3)_3]\text{CH}_3\text{CN}$ [5] was synthesized by a template reaction of 2 equiv of $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ with 10 equiv of bis(dimethylamino)methane in the presence of 1 equiv of ytterbium triflate. The most exciting feature of this complex is its

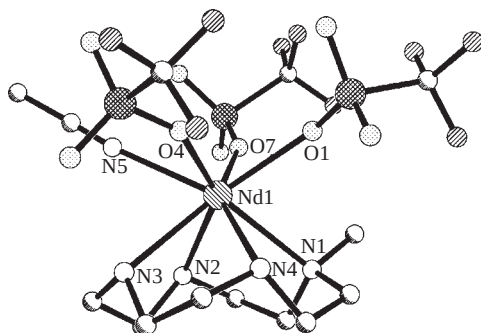


Figure 4.5 Structure of $\text{Nd}(\mathbf{6})\text{CH}_3\text{CN}(\text{CF}_3\text{SO}_3)_2$ [7]. (Redrawn from P. Wei, T. Jin and G. Xu, "Synthesis and crystal structure of neodymium complex of 1-methyl-1,4,7,10-tetraazacyclododecane," *Acta Chimica Sinica*, **50**, 883, 1992.)

apparent stability towards hydrolysis. With the addition of water, the acetonitrile solution of $[\text{Yb}(\mathbf{4})(\text{CF}_3\text{SO}_3)_2]\text{CF}_3\text{SO}_3\text{CH}_3\text{CN}$ forms precipitates of $\text{Yb}(\text{OH})_3$ immediately. In contrast, $[\text{Yb}(\mathbf{5})(\text{CF}_3\text{SO}_3)_3]\text{CH}_3\text{CN}$ remains dissolved in water without producing a precipitate of $\text{Yb}(\text{OH})_3$.

1-Methyl-1,4,7,10-tetraazacyclododecane: This complex (**6**, Figure 4.2) was synthesized by Jin and coworkers using a straight synthesis method [6, 7]. By the reaction of 1 equiv of **6** with 1 equiv of a rare earth triflate salt ($\text{RE} = \text{La, Nd, Gd, and Eu}$) under N_2 and in an anhydrous environment in acetonitrile, the corresponding rare earth complexes were successfully obtained. Except for $\text{La}(\mathbf{6})\text{CH}_3\text{CN} \cdot (\text{CF}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$, almost all the rare earth complexes possess the same composition as $\text{RE}(\mathbf{6})\text{CH}_3\text{CN} \cdot (\text{CF}_3\text{SO}_3)_3$ ($\text{RE} = \text{Nd, Gd, and Eu}$). In the structure of $\text{Nd}(\mathbf{6})\text{CH}_3\text{CN}(\text{CF}_3\text{SO}_3)_3$, the eight-coordinate neodymium ion coordinates with four amine nitrogen atoms from macrocycle ligand **6**, one nitrogen atom is from one acetonitrile molecule, and three oxygen atoms are from three triflate anions, Figure 4.5. The coordination geometry can be described as a square antiprism. The bond lengths of its triflate anion $\text{Nd}-\text{O}$ range from 0.2395(3) to 0.2412(4) nm, with an average of 0.2404 nm. The average $\text{Nd}-\text{N}$ distance of the tetraaza heterocycle $\text{Nd}-\text{N}$ is 0.2612 nm, ranging from 0.2575 to 0.2661 nm. Owing to the π -d coordination interaction from the acetonitrile to the lanthanum ion, the acetonitrile $\text{Nd}-\text{N}$ (0.2564 nm) length is shorter compared with the average $\text{Nd}-\text{N}$ distance of the tetraaza heterocycle $\text{Nd}-\text{N}$. As a result of the larger ionic radius of lanthanum, the coordination number of complex $\text{La}(\mathbf{6})\text{CH}_3\text{CN} \cdot (\text{CF}_3\text{SO}_3)_3 \cdot \text{H}_2\text{O}$ is nine with an addition of one molecule water.

4.2.2 Rare Earth Complexes with Silyl Amide Type Ligands

The silyl amide type ligands have been used extensively in rare earth chemistry, as well as in actinide and transition metal chemistry, to stabilize electronically unsaturated metal centers due to the available lone pair on the nitrogen donor atom. Because of the relatively larger steric encumbrance, the rare earth complexes with silyl amide type ligands often exhibit low coordination numbers. As a consequence, the large and electropositive rare earth metal centers are accessible to external reagents, which make them more active in many reactions.

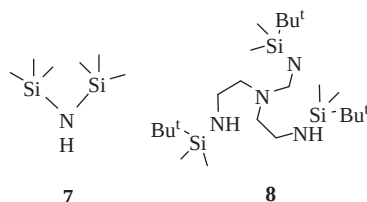


Figure 4.6 Two representative silyl amide type ligands.

For example, according to the salt elimination reaction, some rare earth complexes with silyl amide type ligands can be used to prepare rare earth metallic compounds, which are further used in the homogenous catalytic reaction of C–H, C–C, and C–X bond formation [8]. The most time-honored method to synthesize this type of rare earth complexes involves the reaction of anhydrous rare earth chlorides (usually the metal chloride–THF adduct, THF = tetrahydrofuran) with a theoretical amount of the alkali metal salts of the silyl amide ligands. The rare earth complexes containing the ligand–alkali metal are first obtained, which can be further used as precursors to form the organometal compounds according to the salt elimination reaction. In some cases, the anhydrous rare earth chloride dissolved in diethylether also proved to be effective for the synthesis of these complexes. The first preparation of the simple rare earth silyl amide complexes $\text{Ln}(\mathbf{4})_3$ was reported by Bradley *et al.* over 30 years ago [9]. Since then, many rare earth complexes with silyl amide type ligands have been prepared. Figure 4.6 shows two representative silyl amide type ligands.

The bis(trimethylsilyl)amido **7**, a very common ligand, is often used to coordinate with rare earth ions with low coordination number. To date, many homoleptic trivalent and divalent rare earth complexes in the form of $\{\text{RE}[\text{N}(\text{SiMe}_3)_2]_3\}^{n-}$ [$n=0$ for RE(III), 1 for RE(II)] have been structurally characterized either in the solid state or in the gas phase for Sc(III), Ce(III), Pr(III), Nd(III), Eu(II), Eu(III), Dy(III), Er(III), Yb(II), and Yb(III) [10]. Usually, the pyramidal arrangement of the central MN_3 core is the common feature existing in this series of homoleptic rare earth complexes in addition to the analogous U(III) derivative. For example, in complex $\text{Eu}(\mathbf{7})_3$ the europium ion and three nitrogen atoms are coplanar [10e]. The center ion was found to be disordered between two equivalent positions above and below the plane of the three N atoms. The Si–N–Si plane for each ligand is tilted relative to the normal to the coplane, establishing a D_3 propeller arrangement for the three $\text{N}(\text{SiMe}_3)_2$ ligands. The central europium ion was three-coordinate with three nitrogen atoms from three bis(trimethylsilyl)amido ligands. The Eu–N bond length is 0.2259 nm and the pyramidal N–M–N angle is 116.6° , similar to those in the transition metal **7** complexes.

Through the reaction of europium diiodide with sodium bis(trimethylsilyl)amide **7** in 1,2-dimethoxyethane (dme), the +2 charged six-coordinate yellow complex $\text{Eu}(\mathbf{7})_2(\text{dme})_2$ was obtained [11]. The whole coordination polyhedron has a C_2 symmetry with the two bulky silylamide groups in a manner of surprising closeness to one another, Figure 4.7. This induces an increase in the N–Eu–N angle to 134.5° , larger than that in complex $\text{Eu}(\mathbf{7})_3$. The center atom is six-coordinate and bound to two nitrogen atoms from two bis(trimethylsilyl)amido ligands and four oxygen atoms of the dme ligands. The mean Eu–N bond distance is 0.253 (4) nm and the Eu–O distances are 0.2634 (4) and 0.2756 (4) nm, respectively. The ethane carbon atoms in the 1,2-dimethoxyethane ligand are disordered.

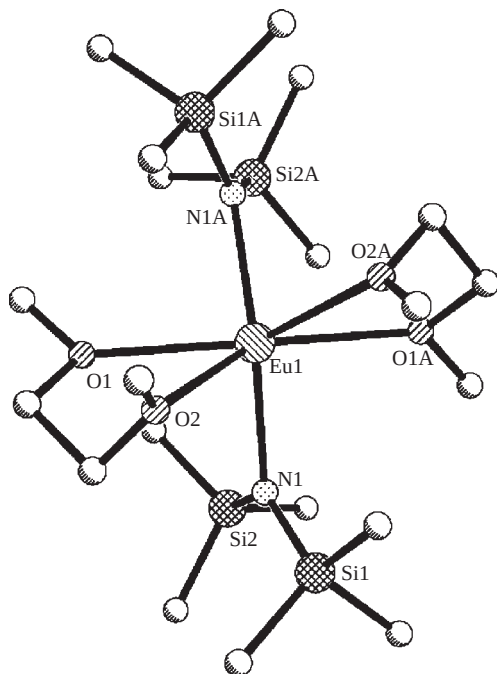


Figure 4.7 The structure of complex $\text{Eu}(\mathbf{7})_2(\text{dme})_2$ [11]. (Reproduced with permission from T.D. Tilley, A. Zalkin, R.A. Andersen and D.H. Templeton, "Divalent lanthanide chemistry. Preparation of some four- and six-coordinate bis[(trimethylsilyl)amido] complexes of europium(II). Crystal structure of bis[bis(trimethylsilyl)amido]bis(1,2-dimethoxyethane) europium(II)," *Inorganic Chemistry*, **20**, 551, 1981. © 1981 American Chemical Society.)

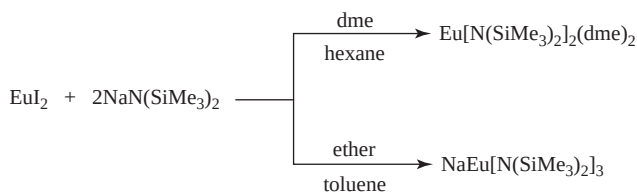


Figure 4.8 Synthesis of two types of europium complexes.

It must be pointed out that when ether rather than dme was employed as the solvent, a discrete different anionic complex $\text{NaEu}(\mathbf{7})_3$ can be isolated after crystallization (Figure 4.8) [10d].

Comparison in the crystal structure of $\text{NaEu}(\mathbf{7})_3$ with $\text{Eu}(\mathbf{7})_2(\text{dme})_2$ and $\text{Eu}(\mathbf{7})_3$ is shown in Figure 4.9. As can be seen, the europium complex $\text{NaEu}(\mathbf{7})_3$ crystallizes in a monoclinic space group and contains two chemically equivalent but crystallographically independent molecules. In each molecule, the sodium ion, three nitrogen atoms, and the europium ion are coplanar. The central europium ion was three-coordinate with three nitrogen atoms from three ligands. However, the nitrogen atom adopts a different mode. The coordination number of N(1) and N(4) is three with three donors from one europium atom and two silicon atoms. The N(2), N(3),

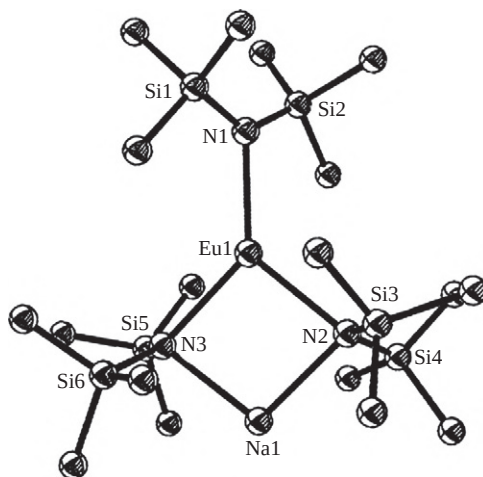


Figure 4.9 The structure of complex $\text{NaEu}(\mathbf{7})_3$ [10d]. (Reproduced with permission from T.D. Tilley, R.A. Andersen and A. Zalkin, "Divalent lanthanide chemistry. Preparation and crystal structures of sodium tris[bis(trimethylsilyl)amido]europate(II) and sodium tris[bis(trimethylsilyl)amido]ytterbate(II), $\text{NaM}[\text{N}(\text{SiMe}_3)_2]_3$," *Inorganic Chemistry*, **23**, 2271, 1984. © 1984 American Chemical Society.)

$\text{N}(5)$, and $\text{N}(6)$ are four-coordinate due to their additional coordination with one sodium atom. Compared with the six-coordinate complex $\text{Eu}(\mathbf{7})_2(\text{dme})_2$, the average $\text{Eu}-\text{N}$ bond length, 0.2446 nm, is slightly shorter. However, this distance is still 0.0019 nm longer than that in the +3 charged complex $\text{Eu}(\mathbf{7})_3$. Similar to a previous report [12], the change in these bond length is in accordance with the change in metal radii as a function of oxidation state and coordination number.

The quadridentate triamidoamines $[\text{N}(\text{CH}_2\text{CH}_2\text{NR})_3]^{3-}$ ($\text{R} = \text{SiMe}_3$, SiMe_2Bu^t) have become established as an important class of ligands for the main group metals, transition metals, and actinide elements. Compared with the closely crowded ligand **7**, the triamidoamine ligands $[\text{N}(\text{CH}_2\text{CH}_2\text{NR})_3]$ ($\text{R} = \text{SiMe}_3$, SiMe_2Bu^t) are expected to satisfy a lower steric demand. In 1998, Scott and coworkers reported the synthesis of rare earth complexes ($\text{RE} = \text{Y}$, La) with $[\text{N}(\text{CH}_2\text{CH}_2\text{NR})_3]^{3-}$ ($\text{R} = \text{SiMe}_2\text{Bu}^t$) ligand **8** [13]. When the more sterically demanding triamidoamines $\text{R} = \text{SiPri}_3$ and SiMePha were used, no product was isolated. The complexes were obtained by the reaction between pure $\text{Li}_3[\text{N}(\text{CH}_2\text{CH}_2\text{NR})_3]$ ($\text{R} = \text{SiMe}_2\text{Bu}^t$) and anhydrous $[\text{MCl}_3(\text{thf})_n]$ in THF. Adopting a similar method, a cerium complex with ligand **8** in the form of $\text{Ce}[\text{N}(\text{CH}_2\text{CH}_2\text{NR})_3]_3$ ($\text{R} = \text{SiMe}_2\text{Bu}^t$) was also obtained [14]. When this compound was further reacted with a halogen, very different complexes of $[\{\text{Ce}(\mathbf{8})\}_2(\mu\text{-Cl})]$ (Figure 4.10a), $[\{\text{Ce}(\mathbf{8})\}_2(\mu\text{-Br})]$, and $[\text{Ce}(\mathbf{8})\text{I}]$ (Figure 4.10b) were obtained. It has been found that the fascinating mixed valent $\text{Ce}(\text{III}/\text{IV})$ exists in complexes $[\{\text{Ce}(\mathbf{8})\}_2(\mu\text{-Cl})]$ and $[\{\text{Ce}(\mathbf{8})\}_2(\mu\text{-Br})]$. However, the weakest oxidizing agent, iodine, unexpectedly gave the purple cerium(IV) iodide complex $[\text{Ce}(\mathbf{8})\text{I}]$. The complex $[\{\text{Ce}(\mathbf{8})\}_2(\mu\text{-Cl})]$ belongs to a trigonal space group $P\text{-}31c$ with the cell parameters $a = 1.25843(5)$ nm, $c = 2.5433(2)$ nm, $\gamma = 120^\circ$, $V = 3.488$ nm³, and $Z = 2$. In the crystal, the threefold symmetric (triamidoamine)cerium fragments are crystallographically equivalent. The presence of cerium with a mixed-valence in $[\{\text{Ce}(\mathbf{8})\}_2(\mu\text{-Cl})]$ was proved by the ¹H NMR result of this complex due to the observation of only one set of nuclear

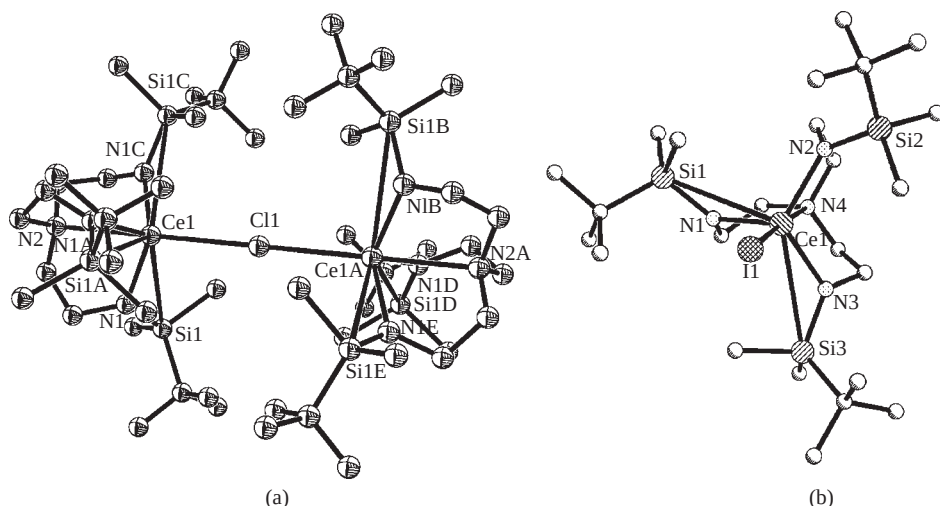


Figure 4.10 The structure of complex (a) $[\{\text{Ce}(\mathbf{8})\}_2(\mu\text{-Cl})]$ and (b) $[\text{Ce}(\mathbf{8})\text{I}]$ [14]. (Reproduced with permission from C. Morton *et al.*, ‘Stabilization of cerium(IV) in the presence of an iodide ligand: remarkable effects of Lewis acidity on valence state,’ *Journal of the American Chemical Society*, **121**, 11255, 1999. © 1999 American Chemical Society.)

and magnetic resonances for the triamidoamine ligands between 220 and 300 K. Different to $[\{\text{Ce}(\mathbf{8})\}_2(\mu\text{-Cl})]$, $[\text{Ce}(\mathbf{8})\text{I}]$ crystallizes in the monoclinic space group $P2_1/n$.

4.3 Rare Earth Complexes with N-Heterocyclic Type Ligands

As for N-heterocyclic type ligands, four species namely pyridine type ligands, imidazole type ligands, porphyrin type ligands, and phthalocyanine type ligands were involved. The synthesis and structure characteristics of this type of complexes will be detailed below:

4.3.1 Rare Earth Complexes with Pyridine Type Ligands

Owing to the weak alkalescence and strong π - d conjugated interaction, pyridine type ligands possess stronger coordination ability in comparison with amine type ligands. Anhydrous conditions appear not to be necessary when such types of rare earth complexes are synthesized. Therefore, investigations into this type of complexes started very early on. Some representative ligands are listed in Figure 4.11.

4.3.1.1 Rare Earth Complexes with 2,2'-Bipyridine (**9**) Type Ligands

To date, different types of rare earth complexes with 2,2'-bipyridine ligands have been reported. For instance, Wood and coworkers reported the synthesis and crystal structure of a series of rare earth complexes $\text{RE}(\mathbf{9})_2(\text{NO}_3)_3$ [15]. Crystal structures of dimeric Eu(III)-chelated complexes based on *p*-methoxybenzoate [16a], *o*- or *p*-aminobenzoate [16b], and *p*-methylbenzoate [16c] with **9** are well known. Recently, dimeric and polymeric Ln(III) complexes ($\text{Ln} = \text{La}$,

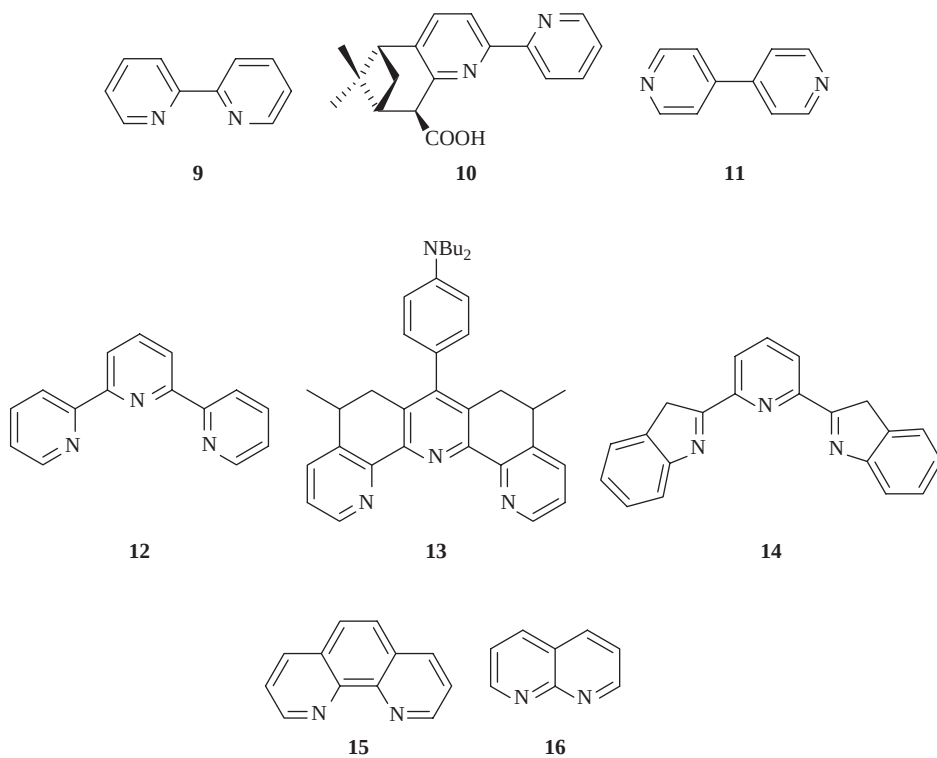


Figure 4.11 Eight representative pyridine type ligands.

Sm) based on β -diketonates with bipyridine (bipy) were studied [17]. Even more recently, a series of chiral rare earth complexes with modified 2,2'-bpy type ligand **10** were also investigated [18]. Research results revealed that a solvent-adaptive crystallization process exists in this system. When the complex was prepared from a mixture of Pr(III) ion and ligand **10** in the same metal-to-ligand ratio (1 : 2.25), two distinct self-assembly pathways led to two diastereoselective enantiopure architectures, a 2D-trinuclear array (in methanol) $[\text{Pr}_3\{(+)-(\mathbf{10})\}(\mu_3\text{-OH})(\text{H}_2\text{O})_3](\text{ClO}_4)_2$ and a 3D-tetranuclear pyramidal polyhedron (in acetonitrile) $[\text{Pr}_4\{(+)-(\mathbf{10})\}_9(\mu_3\text{-OH})](\text{ClO}_4)_2$. Interestingly, the mixture containing compound $[\text{Pr}_4\{(+)-(\mathbf{10})\}_9(\mu_3\text{-OH})](\text{ClO}_4)_2$ and the minor species in CD_3CN could be recovered back into compound $[\text{Pr}_3\{(+)-(\mathbf{10})\}(\mu_3\text{-OH})(\text{H}_2\text{O})_3](\text{ClO}_4)_2$ in the presence of water. The crystal structures of $[\text{Pr}_4\{(+)-(\mathbf{10})\}_9(\mu_3\text{-OH})](\text{ClO}_4)_2$ (a) and $[\text{Pr}_3\{(+)-(\mathbf{10})\}(\mu_3\text{-OH})(\text{H}_2\text{O})_3](\text{ClO}_4)_2$ (b) are shown in Figure 4.12. For $[\text{Pr}_4\{(+)-(\mathbf{10})\}_9(\mu_3\text{-OH})](\text{ClO}_4)_2$, the coordination polyhedron is a pseudo-trigonal-pyramidal structure and the three tridentated ligands **10** coordinated to the praseodymium ion through two nitrogen atoms from bipyridine and one oxygen atom from the carboxylate wrap helically around this stereogenic metal center, forming a chiral complex. The basis of this metallic framework is a pseudoequilateral triangle, which is held together by six bridging ligands that are divided into two sets of three, and a $\mu_3\text{-OH}$ group, whose oxygen atom is situated on the pyramidal pseudo- C_3 axis. The fourth metal cation is situated above the triangular base on the pseudo- C_3 axis on the same side as the $\mu_3\text{-OH}$ group.

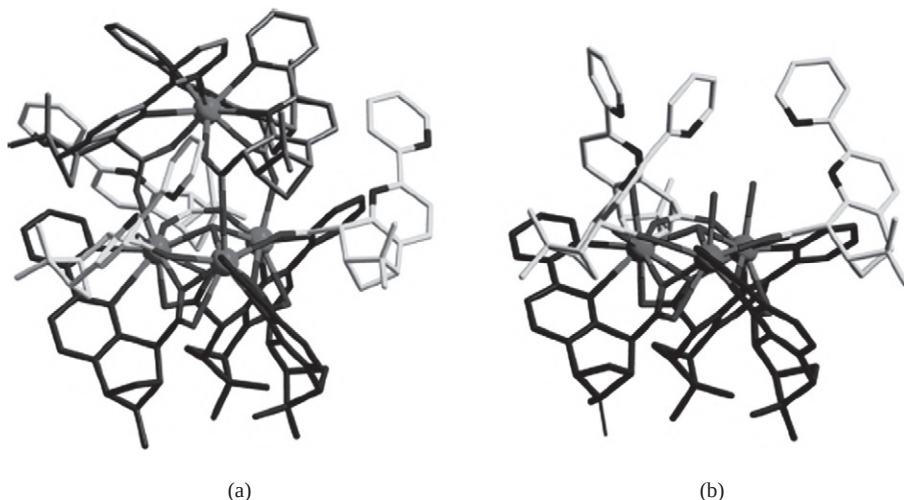


Figure 4.12 The structure of (a) $[\text{Pr}_4\{(+)\text{-(10)}\}_9(\mu_3\text{-OH})](\text{ClO}_4)_2$ and (b) $[\text{Pr}_3\{(+)\text{-(10)}\}(\mu_3\text{-OH})(\text{H}_2\text{O})_3](\text{ClO}_4)_2$ [18b]. (Reproduced with permission from O. Mamula, M. Lama, H.S. Evans and S. Shova, "Switchable chiral architectures containing PrIII ions: an example of solvent-induced adaptive behavior," *Angewandte Chemie International Edition*, 2006, **45**, 4940. © Wiley-VCH Verlag GmbH & Co. KGaA.)

4.3.1.2 Rare Earth Complexes with 4,4'-Bipyridine (11) Type Ligands

Complexes of rare earth salts with 4,4'-bipyridine for nitrate [19], picrate [20], and chloride [21] counteranions, have been reported. Using the mixed solvent of ethanol and water, these complexes can be easily synthesized and complexes of mononuclearity, binuclearity, or higher nuclearity structures were obtained. Among them, only the nitrate complexes have been thoroughly investigated. The complexation properties of these compounds are sensitive to the solvent of crystallization. Sometimes, any slight variation in the nature of the solvent, acidity, basicity, or the ratio of the mixed solvent leads to a drastic change in the complexes formed. According to the careful examination over more than 20 $\text{RE}(\text{NO}_3)_3$ complexes in the Cambridge Structural Database with **11**, and 4,4'-bpy ligands, bpy may be classified into three structurally distinct series: 4,4'-bpy, $[4,4'\text{-bpyH}]^+$ obtained from 4,4'-bpy and hydrogen ion, and 4,4'-bpy cation–nitrate anion pairs [22]. Usually, the nitrate anions bind in a chelating manner to the rare earth cation in all cases. However, 4,4'-bpy has three modes, the neutral 4,4'-bpy without coordination, $[4,4'\text{-bpyH}]^+$, and the coordination complexes between the nitrogen of pyridine and the rare earth ion. In some case, all these three modes can be included in the same complex, for example, the compound of $[4,4'\text{-bpyH}]_2[(\mu_2\text{-}4,4'\text{-bpy})\text{Nd}_2(\text{NO}_3)_8(\text{H}_2\text{O})_4] \cdot 3(4,4'\text{-bpy})$, Figure 4.13 [23]. The complex belongs to a monoclinic space group $P2_1/c$ with $a = 1.8723(10)$ (nm), $b = 1.0720(6)$ (nm), $c = 1.8027(10)$ (nm), $\beta = 94.43(5)^\circ$, $Z = 2$. The neodymium ion is ten-coordinate with one nitrogen atom from 4,4'-bpy, six oxygens from the bidentate nitrate, one oxygen from the unidentate nitrate, and two oxygens from water. The bond length of Nd–N is 0.2701 (6) nm. The Nd–O (w) distances are 0.2429 (7) and 0.2460 (6) nm, respectively. The bond length of Nd–O formed from the unidentate nitrate is 0.2531 (6) nm and of the others formed from bidentate nitrate amounts 0.2529 (6), 0.2611 (6), with an average of 0.2566 nm.

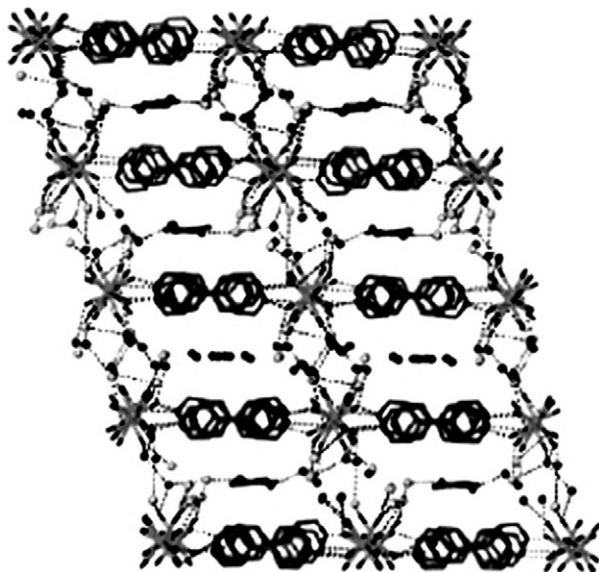


Figure 4.14 Full packing diagram shows a 3D hydrogen-bonded network with channels containing either bpy and water guests or water guest only [27]. (Reprinted with permission from L. Cunha-Silva, A. Westcott, N. Whitford, and M.J. Hardie, "Hydrogen-bonded 3-D network structures of lanthanide aquo ions and 4,4'-bipyridine with carbaborane anions," *Crystal Growth and Design*, **6**, no. 3, 726–735, 2006. © 2006 American Chemical Society.)

moiety into the 4-position of the central pyridinic ring, which can induce an intraligand charge-transfer transition from the amino donor to the pyridine acceptor group [28]. Interestingly, in order to force a cisoid conformation, a dimethylene annelation between the central pyridine ring and the distal quinoline moieties was introduced into the molecule. This is also helpful to stabilize their rare earth complexes by prohibiting the coordination of the solvent molecule. On treatment of ligand **13** with 1 equiv of $\text{RE}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ($x = 6$ for $\text{RE} = \text{La}$, Gd , and $x = 5$ for $\text{RE} = \text{Dy}$, Yb , and Y) in the mixed solvent of dichloromethane and acetonitrile, brown-orange complexes of $\text{RE}(\text{13})(\text{NO}_3)_3$ were obtained in good yield after repeated crystallization from hot acetonitrile and a dichloromethane–pentane mixture, respectively. The complex $[\text{Gd}(\text{13})(\text{NO}_3)_3 \cdot \frac{1}{2}\text{CH}_3\text{CN} \cdot \frac{1}{2}\text{H}_2\text{O}]$ belongs to a centrosymmetric space group with $a = 4.8415$ (nm), $c = 1.0628$ (nm), $\gamma = 120^\circ$, $V = 7.1913$ nm³, and $Z = 18$ (Figure 4.15). Because of the intermolecular hydrogen bonding between non-coordinated oxygen atoms of the nitrato and protonated NR_2 -phenyl unit, the molecule adopts a head-to-tail configuration. The central metal is nine-coordinate with three nitrogens from ligand **13** and six oxygens from nitrato ligands. The bite angle and distance between the two distal phenyl rings are $\Gamma = 87.9^\circ$ and $d = 0.685$ nm, respectively, which are significantly smaller than in other complexes with tpy type ligands, for instance $12\text{Lu}(\text{NO}_3)_3$ ($\Gamma = 105^\circ$, $d = 0.823$ nm) [29]. The $\text{Gd}-\text{N}_{\text{central}}$ bond length, 0.2445(9) nm, is remarkably shorter than that for the complex formed with the tpy ligand **14** [30]. It is worth noting that no additional solvent molecule is coordinated to the metal in $[\text{Gd}(\text{13})(\text{NO}_3)_3 \cdot \frac{1}{2}\text{CH}_3\text{CN} \cdot \frac{1}{2}\text{H}_2\text{O}]$. This seems unusual in the complexes formed

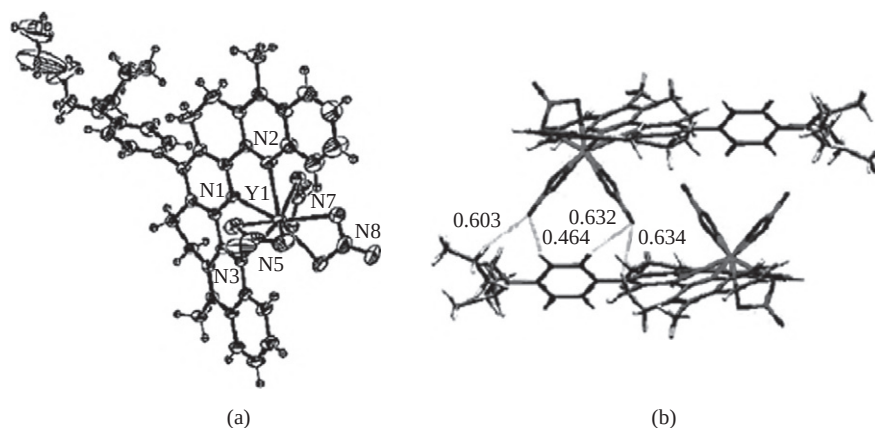


Figure 4.15 The structure of (a) complex $[\text{Gd}(\mathbf{13})(\text{NO}_3)_3] \cdot \frac{1}{2}\text{CH}_3\text{CN} \cdot \frac{1}{2}\text{H}_2\text{O}$ and (b) the head-to-tail stacking [29]. (Reprinted with permission from E. Terazzi, *et al.*, “Molecular control of macroscopic cubic, columnar, and lamellar organizations in luminescent lanthanide-containing thermotropic liquid crystals,” *Journal of the American Chemical Society*, **127**, no. 3, 888–903, 2005. © 2005 American Chemical Society.)

from rare earth metals with other tpy type ligands, whose coordination number is generally 10 or even 11, in which the rare earth metal forms additional coordination bond(s) with solvent molecules such as water, acetonitrile, and methanol. This might be ascribed to the largerr steric hindrance of the ligand **13**. It has also been revealed that the metal f electrons also contribute to the NLO activity of $\text{Ln}(\mathbf{13})(\text{NO}_3)_3$.

4.3.1.4 Rare Earth Complexes with 1,10-Phenanthroline (**15**) Type Ligands

When 1,10-phenanthroline (phen) was reacted with rare earth salts of nitrate, acetate, thiocyanate, and chloride, rare earth complexes with an RE : phen ratio of 1 : 2 can be obtained. Because of the weaker coordination ability of the perchlorate, the RE : phen ratio of coordination compounds for perchlorate (RE = Dy, Er, Yb) will increase to 1 : 3 or even 1 : 4 in the case of RE = La, Pr, Nd. Similar to the 2,2'-bipyridine type ligands, phen often has two modes in the complexes, one as the neutral phen without coordination and the other coordinating with the rare earth ion. For instance, in the complex of $[\text{Nd}(\mathbf{15})_3(\text{NCS})_3] \cdot \text{EtOH}$ (Figure 4.16a) [31], the rare earth ion is nine-coordinate and bound to six nitrogen atoms from the three bidentate 1,10-phenanthroline ligands and three nitrogen atoms from the three monodentate thiocyanate groups. In addition, no coordinated water molecule or ionic thiocyanate group is present. If the system has a bridging group, binuclear or multinuclear complexes can be obtained. Li and coworkers reported the synthesis and crystal structure of the dinuclear complex $[\text{Ho}_2(\mathbf{15})_4(\text{H}_2\text{O})_4(\text{OH})_2](\mathbf{15})_2(\text{NO}_3)_4$ (Figure 4.16b) [32]. This complex can be easily synthesized from the reaction of nitrated Ho_2O_3 with 1,10-phenanthroline in $\text{CH}_3\text{OH}-\text{H}_2\text{O}$. Single crystal X-ray diffraction analysis shows that $[\text{Ho}_2(\mathbf{15})_4(\text{H}_2\text{O})_4(\text{OH})_2](\mathbf{15})_2(\text{NO}_3)_4$ crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with the cell dimensions: $a = 1.1241$ (1) nm, $b = 1.1439$ (1) nm, $c = 1.4058$ (1) nm, $\alpha = 93.989$ (7)°, $\beta = 98.173$ (7)°, $\gamma = 108.19$ (1)°.

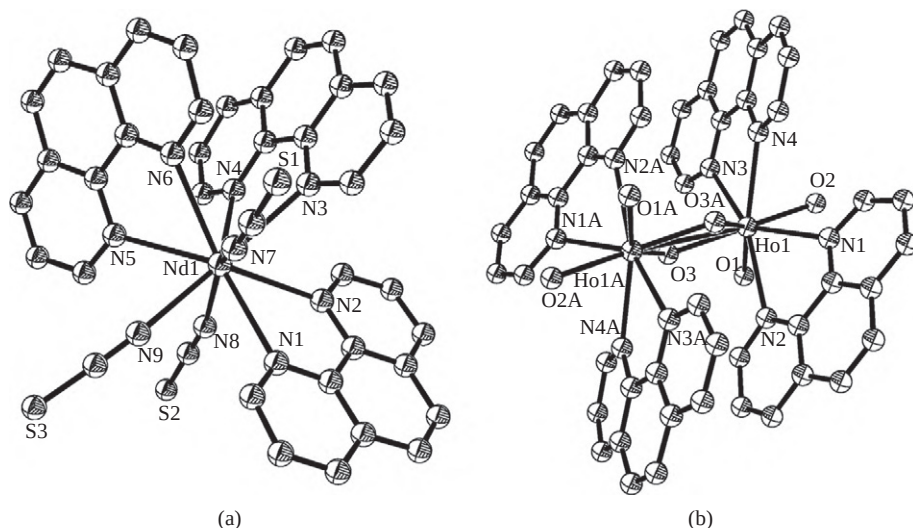


Figure 4.16 The structures of (a) $\text{Nd}(\mathbf{15})_3(\text{NCS})$ and (b) $[\text{Ho}(\mathbf{15})_4(\text{H}_2\text{O})(\text{OH})]^{4+}$ [31, 32]. (Reproduced from *Polyhedron*, 22, S.A. Cotton *et al.*, “Synthesis of complexes of 2,2':6',2''-terpyridine and 1,10-phenanthroline with lanthanide thiocyanates; the molecular structures of $[\text{Ln}(\text{terpy})_2(\text{NCS})_3]$ ($\text{Ln} = \text{Pr}, \text{Nd}$), $[\text{Nd}(\text{terpy})_2(\text{NCS})_3] \cdot 2\text{EtOH}$ and $[\text{Ln}(\text{phen})_3(\text{NCS})_3] \cdot \text{EtOH}$ ($\text{Ln} = \text{Pr}, \text{Nd}$),” 1489, 2003, with permission from Elsevier; and redrawn from D.Y. Wei, Y.Q. Zheng and J.L. Lin, “Synthesis, crystal structure and magnetic property of $[\text{Ho}_2(\text{phen})_4(\text{H}_2\text{O})_4(\text{OH})_2](\text{phen})_2(\text{NO}_3)_4$,” *Acta Chimica Sinica*, 7, 1248, 2002.)

$V = 1.6874(4) \text{ nm}^3$, and $Z = 1$. The compound is a square antiprism, consisting of the centrosymmetric dinuclear $[\text{Ho}_2(\mathbf{15})_4(\text{H}_2\text{O})_4(\text{OH})_2]_4^+$ cation, uncoordinated **15** molecules, and nitrate anions. The holmium atom is eight-coordinate with four nitrogens from the **15** ligands, two oxygens from H_2O molecules, and two oxygens from hydroxo groups.

4.3.1.5 Rare Earth Complexes with 1,8-Naphthylridine (**16**) Type Ligands

Rare earth complexes with 1,8-naphthylridine (ntd) ligands can be formulated as $\text{RE}(\text{ntd})_n\text{X}_3(\text{H}_2\text{O})_x$. When the complexes were synthesized with perchlorate [$\text{X} = (\text{ClO}_4)^-$], the coordination number of n changes along with the rare earth species. For $\text{RE} = \text{La}, \text{Ce}$, and Pr , n amounts to 6. Along with the decrease in the rare earth ionic radius to $\text{RE} = \text{Nd}, \text{Sm}$, and, Eu , the coordination number of the **16** ligand changes to 5. Owing to the comparatively stronger coordination ability, when the rare earth complexes were prepared with nitrate, the coordination number of ligands **16** in $\text{RE}(\mathbf{16})_n\text{X}_3(\text{H}_2\text{O})_x$ [$\text{X} = (\text{NO}_3)^-$] becomes even smaller. This is exemplified by the coordination number of two for $\text{RE}(\mathbf{16})_n\text{X}_3(\text{H}_2\text{O})_x$ [$\text{X} = (\text{NO}_3)^-$, $\text{RE} = \text{Y}, \text{Sm} - \text{Yb}$]. However, as expected, the coordination number of ligands **16** increases to three when the rare earth metal with larger ionic radius such as La and Nd was taking part in the reaction. Figure 4.17 shows the crystal structure of complex $[\text{Pr}(\mathbf{16})_6](\text{ClO}_4)_3$ [33]. The crystal is monoclinic with a space group of $P2_1/c$. The cell dimensions are $a = 1.3748(3) \text{ nm}$, $b = 1.6979(6) \text{ nm}$, $c = 2.2949(8) \text{ nm}$, $\beta = 107.34(1)^\circ$, $V = 5.11314 \text{ nm}^3$, and $Z = 4$. Each **16** ring acts as a bidentate ligand, making the praseodymium atom 12-coordinate. The coordination polyhedron

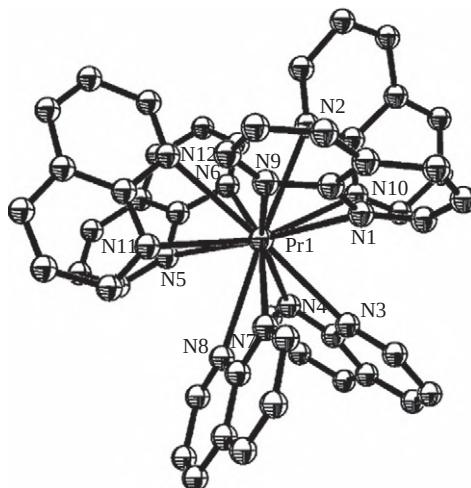


Figure 4.17 The structure of $[\text{Pr}(\mathbf{16})_6]^{3+}$ [33]. (Reproduced with permission from A. Clearfield, R. Gopal and R.W. Olsen, "Crystal structure of hexakis(1,8-naphthyridine)praseodymium(III) perchlorate," *Inorganic Chemistry*, **16**, 911, 1977. © 1977 American Chemical Society.)

is a distorted icosahedron, which results principally from the unequal nitrogen–nitrogen interatomic distance. The one appearing within individual ntd ring amounts to 0.2257 (12) nm, while that between adjacent nitrogen atoms in two different ntd rings ranges from 0.2890 (16) to 0.3195 (16) nm.

4.3.2 Rare Earth Complexes with Imidazole Type Ligands

The imidazole ring was found to exist in a number of biologically important molecules including histidine, iron-heme systems, purines, and several metalloproteins. In particular, its 5,6-dimethyl derivative [5,6-dimethyl-1-(α -D-ribofuranosyl)benzimidazole] is an integral part of the structure of vitamin B₁₂. As a result, a massive research effort has been expended upon the chemistry of imidazoles and benzimidazoles with particular emphasis on the synthesis of new compounds for pharmacological screening and discovering new antibacterial and anthelmintic agents. Being the moderately intensive organic base, imidazole and benzimidazole are amphoteric as they can accept proton(s) at the N-3 position and lose one proton from the N-1 position. To retain the aromaticity of the whole imidazole ring, imidazoles and benzimidazoles usually act as unidentate ligands when coordinating with rare earth ions, which obviously restricts the application of this type of ligand. To resolve this problem, some functional groups such as a pyridine ring have been introduced into the imidazole and benzimidazole derivatives to increase their coordination ability. Some representative ligands are shown in Figure 4.18.

4.3.2.1 Rare Earth Complexes with *N*-Methylimidazole (**17**) Type Ligands

N-Methylimidazole is a powerful donor solvent that can stabilize species which are difficult to isolate in other solvents. In 1994, Evans and coworkers reported the synthesis and crystal

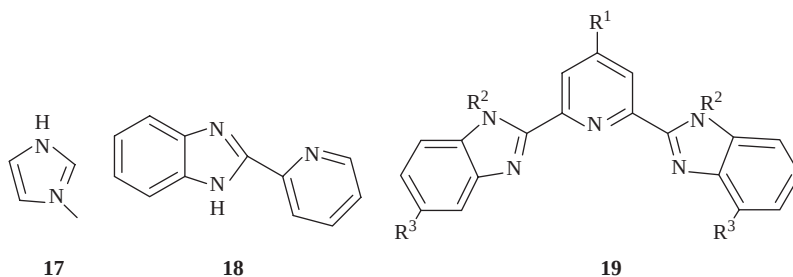


Figure 4.18 Four representative imidazole type ligands.

structure of a series of +2 and +3 charged samarium complexes with *N*-methylimidazole ligand [34]. By reacting SmI_2 with 4 equiv of *N*-methylimidazole at room temperature, a divalent complex of $\text{SmI}_2(\mathbf{17})_4$ was first isolated. Direct crystallization of $\text{SmI}_2(\mathbf{17})_4$ from THF led to the formation of the dimer crystal $[\text{SmI}(\mu\text{-I})(\mathbf{17})_3]_2$. However, crystallization from **17** solvent over a long period led to the hydrolyzed and oxidized complexes $\{[(\mathbf{17})_4\text{Sm}](\mu\text{-OH})\}_3(\mu_3\text{-OH})_2\text{I}_4$ and $\text{Sm}(\mathbf{17})_8\text{I}_3$. Meanwhile, hydroxide complex $[(\mathbf{17})_5\text{Sm}(\mu\text{-OH})]_2\text{I}_4$ was also isolated from crystallization of the trivalent samarium complex $\text{Sm}(\mathbf{17})_8\text{I}_3$ in **17**. The crystal structures and comparison between crystallographic data are shown in Figure 4.19. Through the iodide anion bridging, in the crystal of $[\text{SmI}(\mu\text{-I})(\mathbf{17})_3]_2$, the two samarium ions form a dimer structure, with each of them exhibiting an octahedral coordination environment. The donor atoms consist of three nitrogen atoms from three terminal **17**, one iodide atom from terminal iodide, and two iodide atoms from two bridging iodide ligands. The $\text{Sm}\text{-I}_{\text{bridging}}$ bond lengths are 0.328(1) and 0.3307(1) nm, longer than that of $\text{Sm}\text{-I}_{\text{terminal}}$, 0.3237(1) nm. The $\text{Sm}\text{-N}$ distance is in the range of 0.2621(7) to 0.2641(6) nm. As opposed to the divalent samarium-containing complex $[\text{SmI}(\mu\text{-I})(\mathbf{17})_3]_2$ with a six-coordinate number, the trivalent samarium ion is completely surrounded by **17** with an eight-coordinate number in $\text{Sm}(\mathbf{17})_8\text{I}_3$, probably due to the soft nature of Sm^{2+} in comparison with Sm^{3+} , which prefers to coordinate with the softer iodide anion over the harder **17** donor atom. However, the $\text{Sm}\text{-N}$ distance in $\text{Sm}(\mathbf{17})_8\text{I}_3$ is revealed to be in the range of 0.2563(6)–0.2596(6) nm, similar to that found in $[\text{SmI}(\mu\text{-I})(\mathbf{17})_3]_2$. At the first glance, this result appears strange but can be rationalized by the conflicting trend in the ionic radius and coordination number of the samarium ion in these two complexes. In $\text{Sm}(\mathbf{17})_8\text{I}_3$, the trivalent samarium ion with a smaller ionic radius should lead to a smaller $\text{Sm}\text{-N}$ distance for this complex. In fact, the larger coordinated number for the trivalent samarium ion in the same complex also results in an increase in the $\text{Sm}\text{-N}$ distance. As a total consequence, both complexes exhibit a similar $\text{Sm}\text{-N}$ distance. In addition, as the hydrolyzed product of $[\text{SmI}(\mu\text{-I})(\mathbf{17})_3]_2$, $\{[(\mathbf{17})_4\text{Sm}](\mu\text{-OH})\}_3(\mu_3\text{-OH})_2\text{I}_4$ can be depicted as a dodecahedron. The samarium ion is eight-coordinate with four nitrogen atoms from the terminal **17** and four oxygen atoms from four bridging hydroxides. The $\text{Sm}\text{-O}_{(\mu\text{-OH})}$ bond length is in the range of 0.2323(11)–0.2358(10) nm. However, the $\text{Sm}\text{-N}$ bond length ranges from 0.2538(16) to 0.2631(12) nm, overlapping the two distinct $\text{Sm}\text{-N}$ distances in $[\text{SmI}(\mu\text{-I})(\mathbf{17})_3]_2$. Unlike $\text{Sm}(\mathbf{17})_8\text{I}_3$ and $\{[(\mathbf{17})_4\text{Sm}](\mu\text{-OH})\}_3(\mu_3\text{-OH})_2\text{I}_4$, the hydrolyzed product of $\text{Sm}(\mathbf{17})_8\text{I}_3$ is seven-coordinate. In the crystal, all the terminal ligands are **17** and all of the bridging ligands are hydroxides.

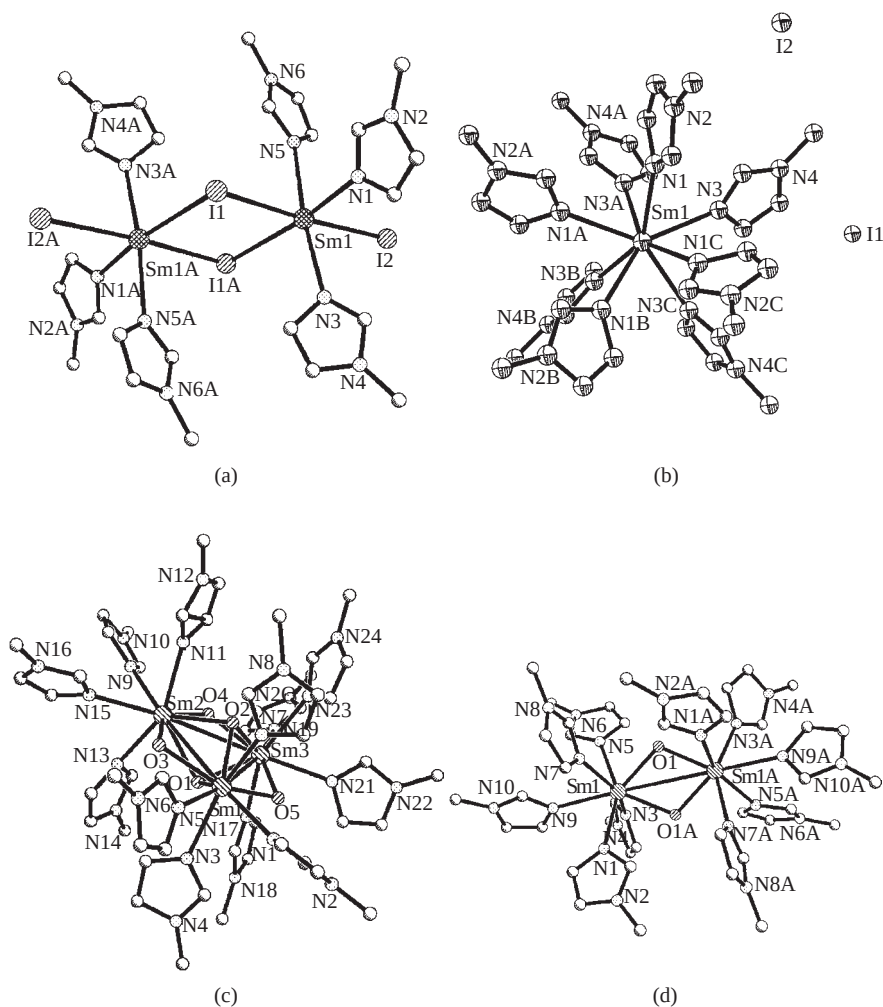


Figure 4.19 The structures of four complexes $[\text{SmI}(\mu\text{-I})(\mathbf{17})_3]_2$, $\text{Sm}(\mathbf{17})_8\text{I}_3$, $\{[(\mathbf{17})_4\text{Sm}](\mu\text{-OH})\}_3(\mu_3\text{-OH})_2\text{I}_4$, and $[(\mathbf{17})_5\text{Sm}(\mu\text{-OH})_2]\text{I}_4$ [34]. (Reproduced with permission from W.J. Evans, G.W. Rabe and J.W. Ziller, "Utility of N-methylimidazole in isolating crystalline lanthanide iodide and hydroxide complexes: crystallographic characterization of octasolvated $[\text{Sm}(\text{N-MeIm})_8]\text{I}_3$ and polynuclear $[\text{SmI}(\mu\text{-I})(\text{N-MeIm})_3]_2$, $[(\text{N-MeIm})_5\text{Sm}(\mu\text{-OH})_2]\text{I}_4$, and $\{[(\text{N-MeIm})_4\text{Sm}(\mu\text{-OH})_3(\mu_3\text{-OH})_2]\text{I}_4$," *Inorganic Chemistry*, **33**, 3072, 1994. © 1994 American Chemical Society.)

4.3.2.2 Complex $[\text{Sm}(\text{N}_3\text{C}_{12}\text{H}_8)_2(\text{N}_3\text{C}_{12}\text{H}_9)_2][\text{Sm}(\text{N}_3\text{C}_{12}\text{H}_8)_4](\text{N}_3\text{C}_{12}\text{H}_9)_2$

By reaction of the rare earth ion ($\text{RE} = \text{Y}, \text{Tb}, \text{Yb}, \text{La}, \text{Sm}, \text{Eu}$) with 2-(2-pyridine)-benzimidazole, **18**, two types of complexes $(\text{NC}_{12}\text{H}_8(\text{NH}_2)_2)[\text{RE}(\text{N}_3\text{C}_{12}\text{H}_8)_4]$ ($\text{RE} = \text{Y}, \text{Tb}, \text{Yb}$) and $[\text{RE}(\text{N}_3\text{C}_{12}\text{H}_8)_2(\text{N}_3\text{C}_{12}\text{H}_9)_2][\text{RE}(\text{N}_3\text{C}_{12}\text{H}_8)_4](\text{N}_3\text{C}_{12}\text{H}_9)_2$ ($\text{RE} = \text{La}, \text{Sm}, \text{Eu}$) were obtained [35]. The reaction was carried out by melting the amine without any solvent and the type of the complex obtained was determined by the melting temperature and the

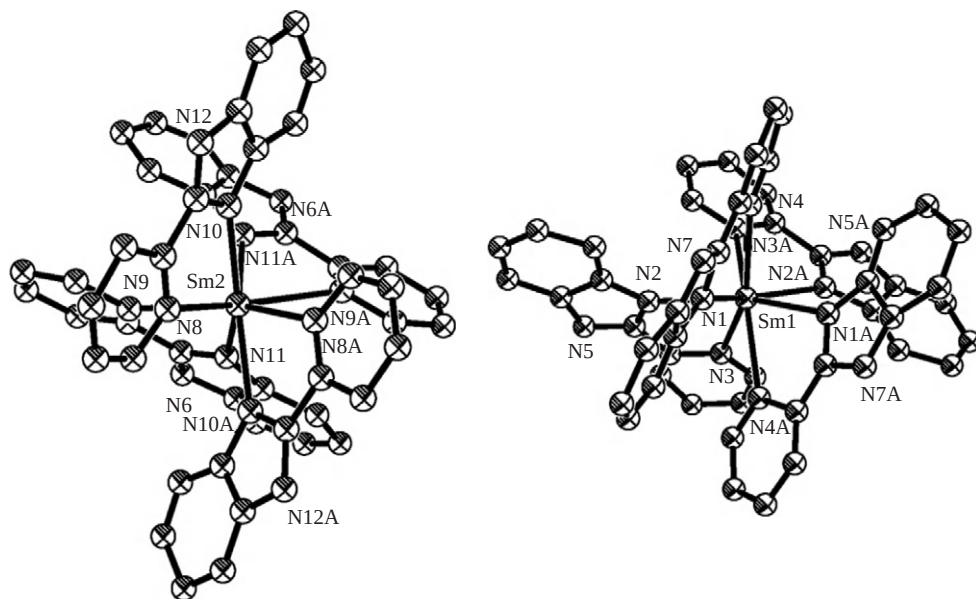


Figure 4.20 The structure of $[\text{Sm}(\text{N}_3\text{C}_{12}\text{H}_8)_2(\text{N}_3\text{C}_{12}\text{H}_9)_2][\text{Sm}(\text{N}_3\text{C}_{12}\text{H}_8)_4](\text{N}_3\text{C}_{12}\text{H}_9)_2$ [35]. (Reproduced with permission from K. Muller-Buschbaum and C.C. Quitmann, “Two new groups of homoleptic rare earth pyridylbenzimidazolates: $(\text{NC}_{12}\text{H}_8(\text{NH})_2)[\text{Ln}(\text{N}_3\text{C}_{12}\text{H}_8)_4]$ with $\text{Ln} = \text{Y}, \text{Tb}, \text{Yb}$, and $[\text{Ln}(\text{N}_3\text{C}_{12}\text{H}_8)_2(\text{N}_3\text{C}_{12}\text{H}_9)_2][\text{Ln}(\text{N}_3\text{C}_{12}\text{H}_8)_4](\text{N}_3\text{C}_{12}\text{H}_9)_2$ with $\text{Ln} = \text{La}, \text{Sm}, \text{Eu}$,” *Inorganic Chemistry*, **42**, 2742, 2003. © 2003 American Chemical Society.)

rare earth ionic radius. The crystal structure of the complex $[\text{Sm}(\text{N}_3\text{C}_{12}\text{H}_8)_2(\text{N}_3\text{C}_{12}\text{H}_9)_2][\text{Sm}(\text{N}_3\text{C}_{12}\text{H}_8)_4](\text{N}_3\text{C}_{12}\text{H}_9)_2$ is shown in Figure 4.20. The coordination polyhedron of the cation $[\text{Sm}(\text{N}_3\text{C}_{12}\text{H}_8)_2(\text{N}_3\text{C}_{12}\text{H}_9)_2]^+$ can be described as a stronger distorted square antiprism, which is similar to its anion $[\text{Sm}(\text{N}_3\text{C}_{12}\text{H}_8)_4](\text{N}_3\text{C}_{12}\text{H}_9)_2^-$. The complex crystallizes in an isotypic tetragonal space group with the cell parameters, $a = 1.6901(2)$ (nm), $c = 3.7595(4)$ (nm), and $Z = 4$. The central samarium ion is eight-coordinate with eight nitrogen atoms from four 2-(2-pyridine)benzimidazoles. The Sm–N distance is in the range of 0.244(2)–0.260(2) nm, with the shortest length from the pyridyl-N species. Despite the difference in the chemical formula from this complex, another type of complex $[\text{NC}_{12}\text{H}_8(\text{NH})_2][\text{RE}(\text{N}_3\text{C}_{12}\text{H}_8)_4]$ ($\text{RE} = \text{Y}, \text{Tb}, \text{Yb}$) obtained from the same reaction also crystallizes in the same isotypic tetragonal space group. However, it must be pointed out that 2-(2-pyridine)benzimidazole was chosen as the counterion to satisfy the charge balance instead of $[\text{Sm}(\text{N}_3\text{C}_{12}\text{H}_8)_2(\text{N}_3\text{C}_{12}\text{H}_9)_2]^+$ in the complex $[\text{Sm}(\text{N}_3\text{C}_{12}\text{H}_8)_2(\text{N}_3\text{C}_{12}\text{H}_9)_2][\text{Sm}(\text{N}_3\text{C}_{12}\text{H}_8)_4](\text{N}_3\text{C}_{12}\text{H}_9)_2$.

4.3.2.3 Rare Earth Complexes with Bis(benzimidazole)pyridine (19) Type Ligands

In recent years, scientific researchers have focused their attention on developing rare earth-containing materials for functional devices by taking advantage of the fascinating optical and magnetic properties of the rare earth metals to endow materials with enhanced physicochemical properties. One tactic to realize this purpose relies on the design and synthesis

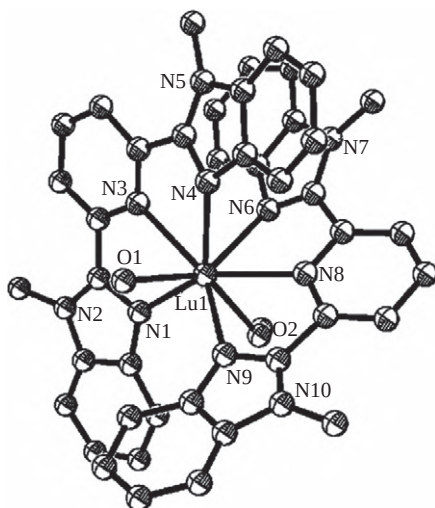


Figure 4.21 The structure of $[\text{Lu}(\mathbf{19})_2](\text{CH}_3\text{OH})(\text{H}_2\text{O})]^{3+}$ [37]. (Reproduced with permission from C. Piguet, A.F. Williams, C. Bernadine and J.C.G. Bünzli, "Structural and photophysical properties of lanthanide complexes with planar aromatic tridentate nitrogen ligands as luminescent building blocks for triple-helical structures," *Inorganic Chemistry*, **32**, 4139, 1993. © 1993 American Chemical Society.)

of novel pre-organized ligands. Among these, a series of terdentate chelating ligands, bis(benzimidazole)pyridine derivatives, were prepared and their rare earth complexes for nitrate and perchlorate reported [36]. Research results indicate that this type of ligand can effectively encapsulate the rare earth ion and therefore provide a rigid and protective environment for this ion, leading to the formation of complexes with pre-determined structure and thermodynamic, magnetic, and spectroscopic characteristics. For example, by complexation with the rare earth ions, the shape of the ligands **19** transfers from an I-shape to a V-shape [36c], which effectively improves the liquid crystal property of this ligand. In 1993, Piguet *et al.* reported the preparation and crystal structure of a series of rare earth complexes with bis(benzimidazole)pyridine type ligands for perchlorate [37]. The synthesis process can be simply depicted as follows: $\text{Lu}(\text{ClO}_4)_3 \cdot 7\text{H}_2\text{O}$ in methanol was slowly added to a solution of bis(benzimidazole)pyridine **19** in methanol at 70 °C. After being cooled, the crude precipitate was filtered and dissolved in acetonitrile, then methanol was allowed to diffuse in for 8 days to give a transparent complex $[\text{Lu}(\mathbf{19})_2](\text{CH}_3\text{OH})(\text{H}_2\text{O})(\text{ClO}_4)_3 \cdot 3\text{CH}_3\text{OH}$, Figure 4.21. The crystal belongs to a monoclinic system and the cell unit contains the cation $[\text{Lu}(\mathbf{19})_2](\text{CH}_3\text{OH})(\text{H}_2\text{O})]^{3+}$, three uncoordinated perchlorate anions, and three methanol molecules. The center lutetium ion is eight-coordinate with six nitrogen atoms from two tridentate bis(benzimidazole)pyridine ligands, one oxygen from a methanol molecule, and one oxygen from one water molecule, leading to a low-symmetry coordination sphere around the metal ion. The Lu–N distance ranges from 0.237(1) to 0.246(1) nm, with an average of 0.2415(1) nm. The Lu–O distance from the water-O and methanol-O species is 0.229(1) and 0.235(1) nm, respectively.

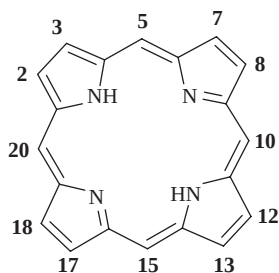


Figure 4.22 The structure of porphyrin.

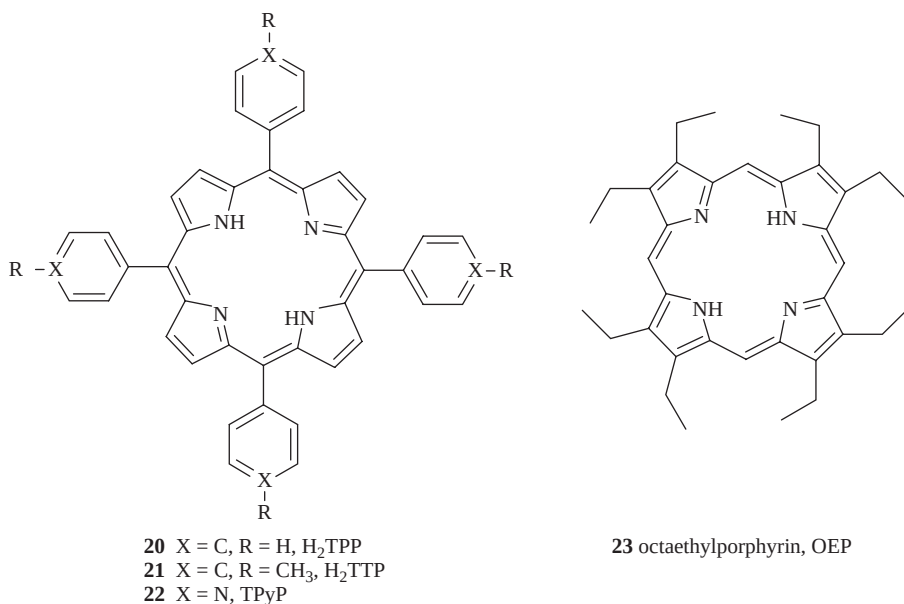


Figure 4.23 Four representative porphyrin type ligands.

4.3.3 Rare Earth Complexes with Porphyrin Type Ligands

Substituting some or all of the hydrogen atom(s) of the porphyrin ring leads to the formation of so-called porphyrin derivatives, porphyrin (Por) (Figure 4.22).

To date, few porphyrin derivatives have been revealed to exist in natural plant and animals despite that a large number of porphyrin derivatives have been artificially synthesized. Usually, artificial porphyrin derivatives are prepared by substituting the hydrogen atoms at the 5, 10, 15, and 20 positions of porphyrin ring, but the natural porphyrin derivatives are the product substituted at the 2, 3, 7, 8, 12, 13, 17, and 18 positions [38]. Some of the most representative porphyrin derivatives are shown in Figure 4.23.

The significance of porphyrins can be interpreted from their involvement in the most important processes of natural life. For example, chlorophyll, the magnesium porphyrin derivative, is related to photosynthesis and hemoglobin, the iron porphyrin derivative existing in the blood

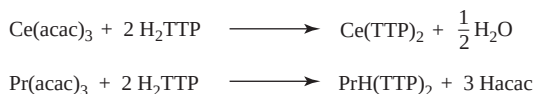


Figure 4.24 Synthesis of homoleptic sandwich-type double-decker porphyrinato rare earth complexes $\text{Ce}(\text{TTP})_2$ and $\text{PrH}(\text{TTP})_2$.

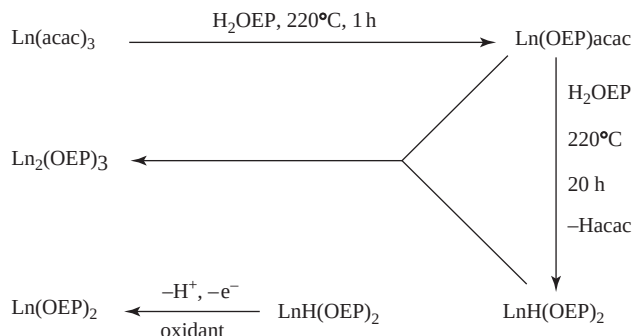


Figure 4.25 Schematic representation of the formation of double-decker and triple-decker porphyrinato rare earth complexes from monoporphyrins.

of mankind and animals, directly participates in life-maintaining processes by transporting O_2 [39]. Nowadays, as a result of the discovery of the large number of applications of the rare earth metals and the conjugated structure of the porphyrin ring, novel porphyrin rare earth complexes display characteristic features that cannot be found in their non-coordinated counterparts, enabling them to be used in different areas, for example, as artificial receptors for molecular recognition, as fluorescent probes for the exploration mechanisms of biologically important reactions, as shift reagents in the research of nuclear magnetic resonance, and as catalysts in organic chemistry. As the rare earth metals tend to coordinate to porphyrin with higher coordinate numbers, common sandwich type double- or triple-decker porphyrinato have been synthesized.

Owing to the lack of an effective preparation method, the development of porphyrinato rare earth complexes were relatively restrained in comparison with their phthalocyaninato rare earth analogs. The first sandwich type bis(porphyrinato) rare earth complex was reported in 1983 [40]. By prolonging the reaction time and replacing **20**, H_2TPP with **21**, H_2TTP , Buchler *et al.* accidentally obtained double-decker $\text{Ce}(\text{TTP})_2$ and $\text{HPr}(\text{TTP})_2$ when they repeated Wong's procedure for preparing monomeric porphyrinato rare earth compounds, Figure 4.24 [41]. By adopting the same procedure with 1,2,4-trichlorobenzene (TCB) as the solvent, a series of porphyrinato rare earth complexes were also prepared by the reaction between H_2TPP and $\text{RE}(\text{acac})_3 \cdot n\text{H}_2\text{O}$ (acac = acetylacetonate in a ratio of 1 : 3 for $\text{RE} = \text{La} - \text{Gd}$, except for Pm). The reaction procedure was also suitable for other porphyrin species such as **23**, H_2OEP . In 1986, Buchler obtained a substantial amount of the triple-decker $\text{RE}_2(\text{OEP})_3$ in addition to double-decker $\text{RE}(\text{OEP})_2$ using the same reaction procedure [42]. One step-by-step mechanism has been proposed for the formation of triple-decker $\text{RE}_2(\text{OEP})_3$, Figure 4.25. Accordingly, the bis(porphyrinato) rare earth complexes were first produced by reaction of H_2OEP and

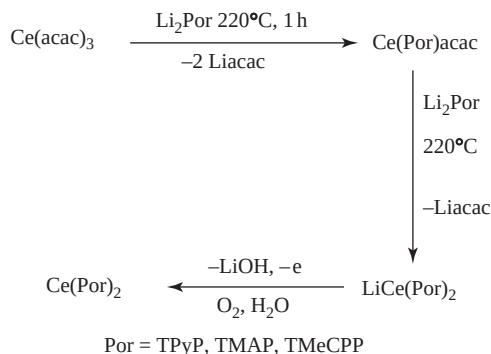


Figure 4.26 Schematic representation of the synthesis of the double-decker bis(porphyrinato) cerium complexes from Li_2Por and $\text{Ce}(\text{acac})_3$.

$\text{RE}(\text{acac})_3 \cdot n\text{H}_2\text{O}$. Along with prolonging the reaction time, metal free H_2OEP will further react with the double-deckers $\text{RE}(\text{OEP})_2$ to form the triple-decker $\text{RE}_2(\text{OEP})_3$. However, it must be pointed out that attempts to synthesize double-decker or triple-decker porphyrinato rare earth complexes with smaller ionic radius for $\text{RE} = \text{Dy-Lu}$ by the same procedure failed. Systematic investigation over a series of sandwich rare earth complexes with porphyrins H_2OEP and H_2TPP revealed that the rare earth ionic size is a critical factor in determining the ease, species, and stability of sandwich type complexes, double-decker or triple-decker. With the decrease in the rare earth ion radius, the repulsion between the two facing porphyrin rings becomes more enhanced, resulting in an increasing difficulty in inserting the rare earth ion into the center of bis(porphyrinato) compounds.

Encouraged by the synthesis of bis(phthalocyaninato) rare earth double- or triple-decker compounds, a more active porphyrin intermediate, $\text{Li}_2(\text{TPP})$, generated from metal free H_2TPP and butyllithium in TCB under an inert gas such as Ar or N_2 , was used to prepare sandwich porphyrinato rare earth complexes [43]. The yield was found to decrease along with the increase in the rare earth ionic radius, from 76% for Eu to only 4% for Lu. After the synthesis of bis(porphyrinato) complexes with rare earth metals other than cerium, some neutral and water-soluble bis(porphyrinato) cerium complexes, namely $\text{Ce}(\text{IV})(\text{Por})_2$ (Por = TpyP, TMAP, TMeCPP), $[\text{Ce}(\text{III})(\text{Por})_2]^{7+}$ (Por = TM_4PyP , TE_4PyP), and $[\text{Ce}(\text{IV})(\text{TTM}_4\text{AP})_2]^{8+}$ were also synthesized by Jiang and coworkers [44] and Buchler and coworkers [45] by employing the reaction between $\text{Li}_2(\text{Por})$ (Por = TpyP, TMAP, TMeCPP) and cerium acetylacetonate $\text{Ce}(\text{acac})_3 \cdot n\text{H}_2\text{O}$ in refluxing TCB for a prolonged reaction time, Figure 4.26. Recently, Aida reported the synthesis and optical resolution of some D_2 -chiral bis(porphyrinato) complexes of cerium and zirconium [46]. These optically active bis(porphyrinato) metal complexes can be used as probes to investigate the rotation dynamics of the porphyrin ligands around the metal center as the ligand rotation corresponds to the racemization. Investigation revealed that rotation of porphyrin ligands in the cerium double-decker complex is relatively simple, resulting in the easy racemization of the corresponding optically active bis(porphyrinato) cerium complexes. In contrast, the thermally-induced porphyrin ligand rotation hardly occurs in the zirconium analog.

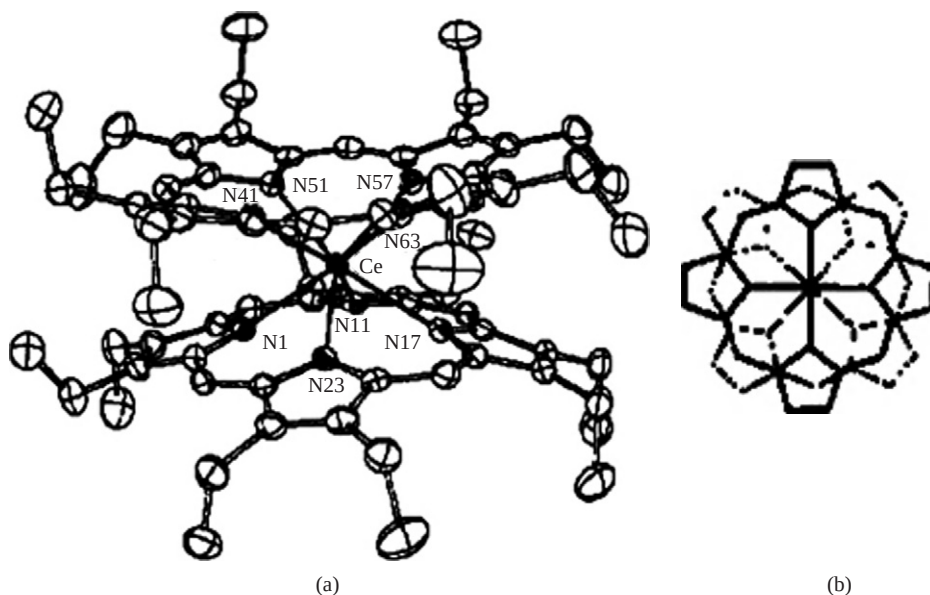


Figure 4.27 (a) Ortep plot of one molecule and (b) stick bond model projection of $\text{Ce}(\text{OEP})_2$ [42]. (Reprinted with permission from J.W. Buchler, *et al.*, “Metal complexes with tetrapyrrole ligands. 40. Cerium(IV) bis(octaethylporphyrinate) and dicerium(III) tris(octaethylporphyrinate): parents of a new family of lanthanoid double-decker and triple-decker molecules,” *Journal of the American Chemical Society*, **108**, no. 13, 3652–3659, 1986. © 1986 American Chemical Society.)

4.3.3.1 $\text{Ce}(\text{OEP})_2$

$\text{Ce}(\text{OEP})_2$ was the first homoleptic porphyrinato metal double-decker complex to be structurally characterized by X-ray crystallography [42]. In the crystalline state, the central cerium ion is eight-coordinate with eight nitrogen atoms from two porphyrin rings. The coordination geometry can be described as a square antiprism. The eight Ce–N bond lengths do not significantly differ from each other, with an average of about 0.2475(1) nm. The skew angle between two porphyrin ring is 41.8° , very similar to that for its bis(phthalocyaninato) analog. The four pyrrole nitrogen atoms of each macrocycle are coplanar and the mean separation of these two parallel planes formed by N1–N11–N17–N23 and N41–N51–N57–N63 is 0.2752 nm. The π – π interaction distance between the two average planes of the 24 atom (C_{20}N_4) framework of the OEP rings amounts to 0.3464 nm. As shown in Figure 4.27a, both the macrocycles are severely distorted from planarity with a mean dihedral angle δ of 15.5° .

4.3.3.2 $\text{Ce}_2(\text{OEP})_3$

$\text{Ce}_2(\text{OEP})_3$ is the only homoleptic porphyrinato triple-decker whose molecular structure has been determined by the X-ray crystallographic method [42]. The crystal structure of $\text{Ce}_2(\text{OEP})_3$ and comparison of the crystallographic data between $\text{Ce}(\text{OEP})_2$ and $\text{Ce}_2(\text{OEP})_3$ are shown in Figure 4.28. As can be seen, for each $\text{Ce}_2(\text{OEP})_3$ molecule, there are three octaethylporphyrinate (OEP) dianions, which are surrounded by two Ce(III) ions, resulting in a neutral

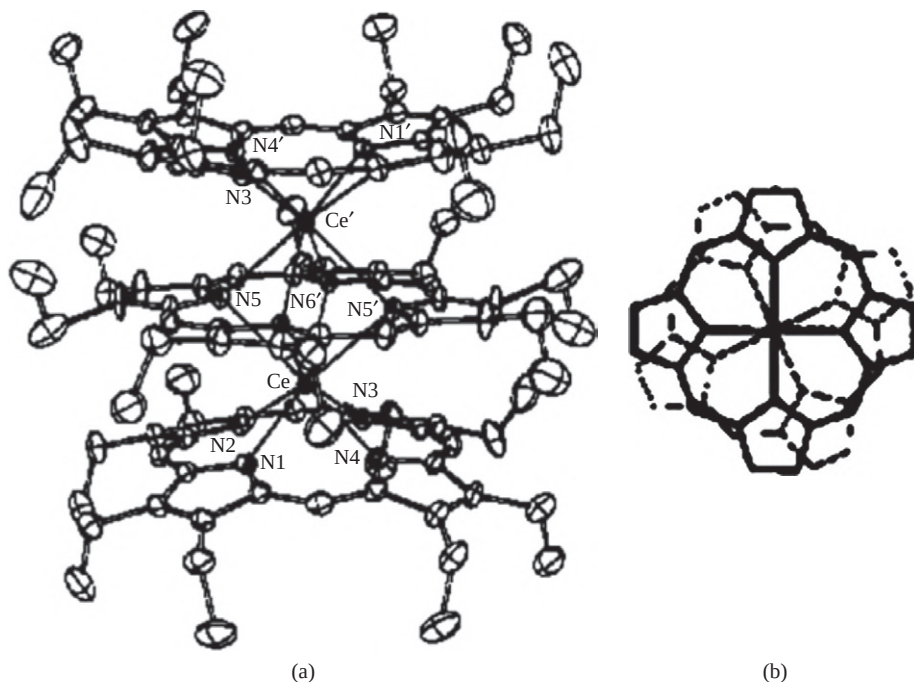


Figure 4.28 (a) Ortep plot of one molecule and (b) stick bond model projection of $\text{Ce}_2(\text{OEP})_3$ [42]. (Reprinted with permission from J.W. Buchler, *et al.*, “Metal complexes with tetrapyrrole ligands. 40. Cerium(IV) bis(octaethylporphyrinate) and dicerium(III) tris(octaethylporphyrinate): parents of a new family of lanthanoid double-decker and triple-decker molecules,” *Journal of the American Chemical Society*, **108**, no. 13, 3652–3659, 1986. © 1986 American Chemical Society.)

triple-decker molecule, Figure 4.28. Compared with the double-decker counterpart $\text{Ce}(\text{OEP})_2$, the triple-decker $\text{Ce}_2(\text{OEP})_3$ is more distorted from the ideal square antiprism. The two external OEP rings have the same orientation with respect to the planar internal macrocycle. The distance between the central cerium and the mean 4Np plane of the external and internal OEP ring is 0.1394 and 0.1876 nm, respectively. Clearly, the Ce(III) ions are not equidistant from their neighboring macrocycle rings as the internal OEP ring is shared by two metal ions, which cannot coordinate with the metal ion as effectively as the external OEP. Similarly, the Ce–N bond lengths are divided into two classes. The average Ce–N distance, connected to the pyrrole nitrogen atoms of the internal ring, is 0.2758 nm, slightly longer in comparison with those associated with the pyrrole atoms of the external rings, 0.2501 nm. The mean Ce–N bond length is 0.263 nm, slightly longer than that found in double-decker $\text{Ce}(\text{OEP})_2$ because of the stronger coordination bonding interaction of pyrrole nitrogen with Ce(IV) than with Ce(III). The mean planes of the 4Np atoms and the independent 12 core atoms of the internal porphyrin are quasicoincident coplanar. The separation between the mean planes of the 24 core atoms of the external ring and the 12 core atoms of the internal ring is approximately 0.354 nm. Compared with that in the double-decker analog $\text{Ce}(\text{OEP})_2$, the distance indicates a weaker π – π interaction between neighboring OEP rings in the triple-decker compound.

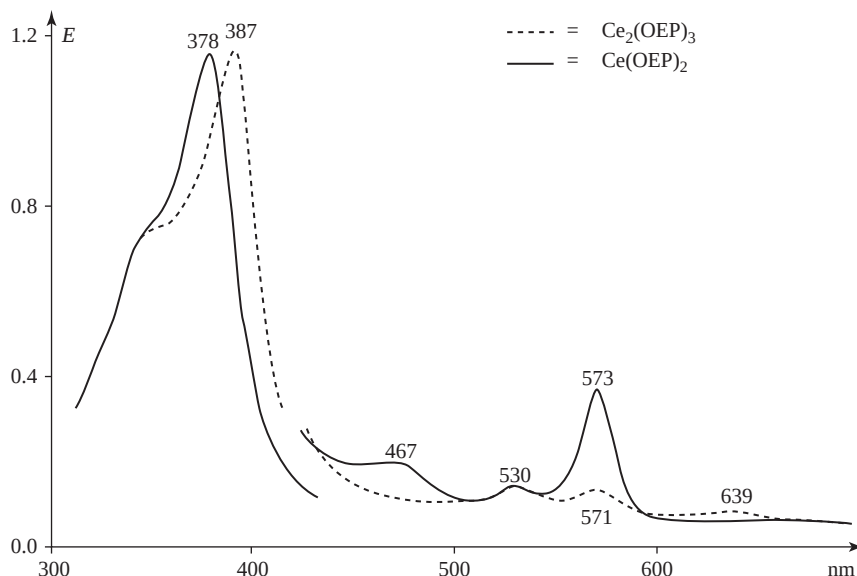


Figure 4.29 Electronic absorption spectra of $\text{Ce}(\text{OEP})_2$ (solid line) and $\text{Ce}_2(\text{OEP})_3$ (dashed line) [42]. (Reprinted with permission from J.W. Buchler, *et al.*, “Metal complexes with tetrapyrrole ligands. 40. Cerium(IV) bis(octaethylporphyrinate) and dicerium(III) tris(octaethylporphyrinate): parents of a new family of lanthanoid double-decker and triple-decker molecules,” *Journal of the American Chemical Society*, **108**, no. 13, 3652–3659, 1986. © 1986 American Chemical Society.)

4.3.3.3 Electronic Absorption Spectra

The electronic absorption spectrum of $\text{Ce}(\text{IV})(\text{OEP})_2$ exhibits similar UV–vis (ultraviolet–visible) features to that of monomeric metalloporphyrins except for some new optical bands resulting from the strong π – π interaction between the por macrocycles, Figure 4.29. There is a strong porphyrin Soret band at 378 nm, blue-shifted as compared with the monoporphyrrinato rare earth complexes. Meanwhile, there are two weak porphyrin Q-bands with maximums at 530 and 573 nm, respectively. In comparison with the monoporphyrrinato rare earth complexes, a new absorption band appears at 467 nm in the electronic absorption spectrum of $\text{Ce}(\text{IV})(\text{OEP})_2$, which is attributed to a π – π transition arising from the molecular orbitals delocalized over both OEP macrocycles. A similar phenomenon was also observed for the triple-deckers $\text{RE}_2(\text{OEP})_3$ ($\text{RE} = \text{La}–\text{Gd}$). However, the porphyrin Soret band is located at 387 nm, less blue-shifted in comparison with that for the double-decker analog $\text{Ce}(\text{IV})(\text{OEP})_2$. Additionally, the band centered at 467 nm in the double-decker disappears in the triple-decker, indicating the relatively weakened π – π interaction in the triple-decker because of the larger OEP–OEP distance. This was also revealed by the X-ray molecular structural analysis result of the double- and triple-deckers as detailed above.

4.3.3.4 Near-IR Spectra

Oxidation of the neutral tetravalent cerium OEP double-decker into its mono-oxidized form results in the appearance of a new absorption peak at 1240 nm in the near-IR

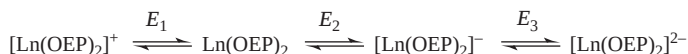


Figure 4.30 Schematic representation of three reversible one-electron processes.

(near-infrared) region. In fact, all the neutral porphyrinato rare earth(III) double-decker complexes RE(III)(Por)_2 exhibit a characteristic IR band at 1 200–1 500 nm. However, this band disappears in the porphyrinato double-decker complexes in which a monoanion radical $\text{Por}^{\cdot-}$ does not exist, such as Ce(IV)(Por)_2 and LnH(TTP)_2 . This absorption band can be ascribed to the intramolecular charge transfer between the $(\text{OEP})^{2-}$ donor and the $(\text{OEP})^-$ acceptor. Systematic study over the series of RE(OEP)_2 ($\text{RE} = \text{La}, \text{Pr}–\text{Lu}$) complexes indicates that a good linear correlation exists between the energy of the near-IR absorption band and the radius of the central trivalent rare earth metal. With the decreasing distance between the porphyrin rings due to the dwindling of rare earth ionic radius, the intramolecular charge transfer energy increases in the same order.

4.3.3.5 Electrochemical Properties

Buchler and coworkers studied the electrochemistry of OEP double-deckers for the series of trivalent rare earth elements ($\text{RE} = \text{La}–\text{Lu}$) and observed three reversible monoelectron processes, namely one monoelectron reversible reduction and two monoelectron oxidations, Figure 4.30 [43c]. Figure 4.31 displays the change in the oxidation and reduction potentials (E_1 , E_2 , and E_3) together with the wavenumber of the near-IR absorption maxima of the double-deckers RE(OEP)_2 as a function of the rare earth ionic radius. As can be seen, along with the increase in the ionic radius, both of the oxidation potentials show a linear increase, but the reduction potential takes a relatively slight change. Comparison reveals that the change in the energy of near-IR absorption as a function of the rare earth ionic size obeys the similar trend as shown by the first oxidation potential, reflecting the correlation between the electrochemical and spectroscopic properties. The linear relationship revealed also indicates the porphyrin ring-centered nature of the oxidation and reduction processes for RE(OEP)_2 . Alternatively, if these oxidation and reduction processes are metal ion-centered, Lu(OEP)_2 should display the highest oxidation potential because of the highest electron negativity of the lutetium cation among the whole series of trivalent rare earth ions. As shown in Figure 4.31, the lowest oxidation potential was observed for Lu(OEP)_2 . It is worth pointing out that the first electrochemical reduction of Ce(IV)(OEP)_2 is metal ion-centered rather than porphyrin ring-centered because of the presence of tetravalent cerium in this complex.

4.3.3.6 Heteroleptic Bis(porphyrinato) Rare Earth Double-Decker Complexes

Except for the homoleptic bi(porphyrinato) and tri(porphyrinato) rare earth complexes, complexes with different porphyrin macrocycles were also investigated. To date, some sandwich type heteroleptic bis(porphyrinato) rare earth double-deckers have been synthesized. However, few have been structurally characterized via single crystal X-ray diffraction analysis [47]. Among these, Ce(IV)(OEP)(TPP) is the only structurally characterized neutral heteroleptic bis(porphyrinato) rare earth double-decker complex [48]. Using an improved short route, Coutsolelos and coworkers prepared and isolated a series of heteroleptic bis(porphyrinato)

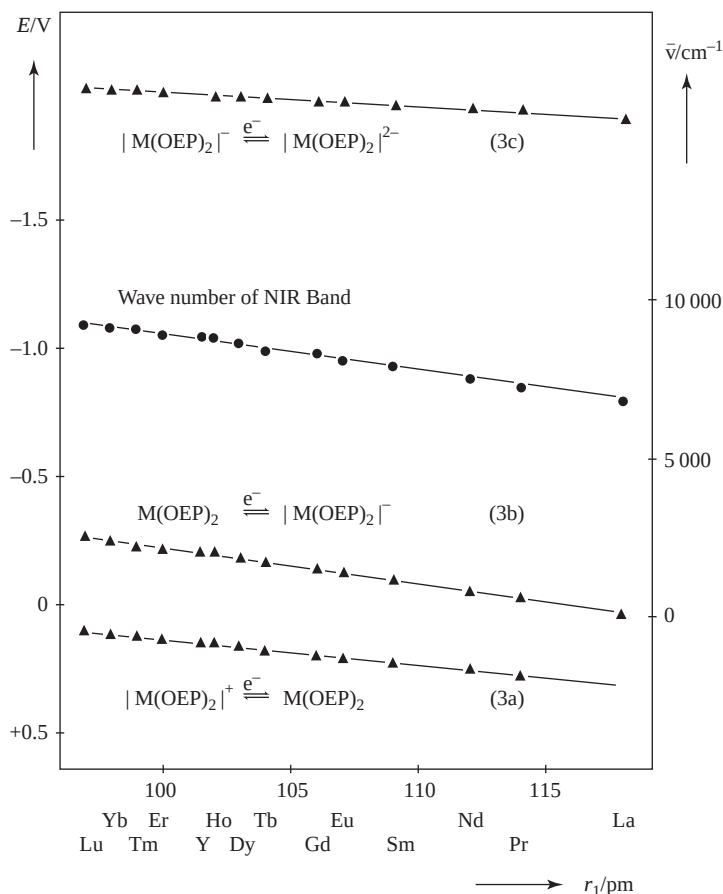


Figure 4.31 Redox potentials E and wavenumber $\tilde{\nu}$ of the near-IR absorption maxima of the sandwich complexes $M(\text{OEP})_2$ as functions of the ionic radii r_1 of the trivalent central metal M [43c]. (Reprinted with permission from J.W. Buchler, and B. Scharbert, "Metal complexes with tetrapyrrole ligands. 50. Redox potentials of sandwichlike metal bis(octaethylporphyrinates) and their correlation with ring-ring distances," *Journal of the American Chemical Society*, **110**, no. 13, 4272–4276, 1988. © 1988 American Chemical Society.)

rare earth double-decker complexes in the reduced form $\text{RE(III)H(OEP)(TPP)}$ ($\text{RE} = \text{Nd} - \text{Lu}$). In this series, the two compounds for $\text{RE} = \text{Sm}$ and Gd were structurally characterized. Figure 4.32 shows the crystal structure of $\text{HSm(III)(OEP)(TPP)}$. As can be seen, the coordination polyhedron of the Sm(III) is a square antiprism containing one +3 charged samarium ion and two different porphyrin rings. In comparison with the TPP ligand, the OEP ligand is more deformed. The skew angle between two porphyrin rings is 45.016° . The central samarium ion is eight-coordinate with four nitrogen atoms from TPP pyrroles and four nitrogen atoms from OEP pyrroles. Contrary to the homoleptic analog Ce(OEP)_2 , the Sm(III) ion in $\text{HSm(III)(OEP)(TPP)}$ is not equidistant from its neighboring porphyrin rings. The mean $\text{Sm}-\text{N}(\text{TPP})$ bond length is $0.2538(4)$ nm, slightly shorter than that for $\text{Sm}-\text{N}(\text{OEP})$, 0.2563 nm.

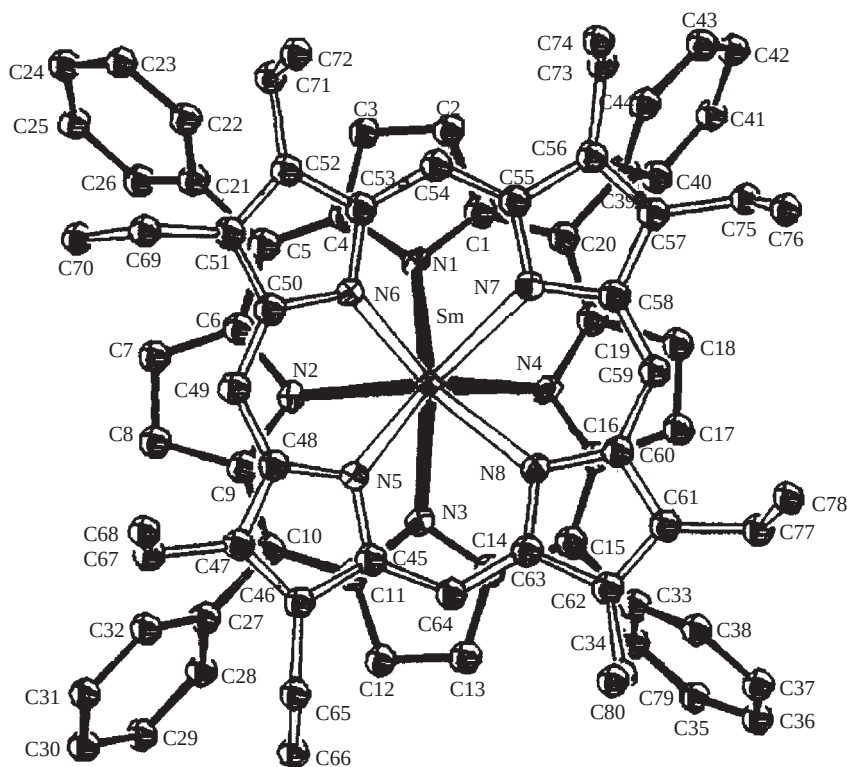


Figure 4.32 The structure of complex $\text{Sm(III)H(OEP)(TPP)}$ [48]. (Reprinted with permission from G.A. Spyroulias, *et al.*, "Synthesis, characterization, and X-ray study of a heteroleptic samarium(III) porphyrin double decker complex," *Inorganic Chemistry*, **34**, no. 9, 2476–2479, 1995. © 1995 American Chemical Society.)

This is also true for HGd(OEP)(TPP) . However, these results are in good contrast to those found for Ce(IV)(OEP)(TPP) . In the neutral heteroleptic bis(porphyrinato) cerium double-decker, the mean Ce-N(TPP) bond length, 0.2480(1) nm, is slightly longer than Ce-N(OEP) , 0.2471(1) nm, suggesting that the proton may locate on the OEP ring and the complex may be denoted as Sm(HOEP)(TPP) .

4.3.3.7 Monomeric Porphyrinato Rare Earth Complexes

The first monomeric porphyrinato rare earth complex was reported in 1974 [49]. However, only a few reports on these systems have appeared in the literature since then. In 1991, Schaverien and Orpent reported the synthesis of the monomeric porphyrinato lutetium complex $\text{Lu(OEP)[CH(Si(CH}_3)_2)]$ from the reaction between $\text{Lu}\{\text{CH[Si(CH}_3)_3]_2\}_3$ and H_2OEP in toluene [50]. Figure 4.33 displays its molecular structure. The complex belongs to the monoclinic system and crystallizes in a space group $P2_1/c$ with $a = 1.4879(6)$ nm, $b = 2.0644(10)$ nm, $c = 1.4161(5)$ nm, $\beta = 96.38(3)^\circ$, $V = 4.323(3)$ nm³, and $Z = 4$. The coordination geometry can be described as square-pyramidal. In the crystal, the porphyrin

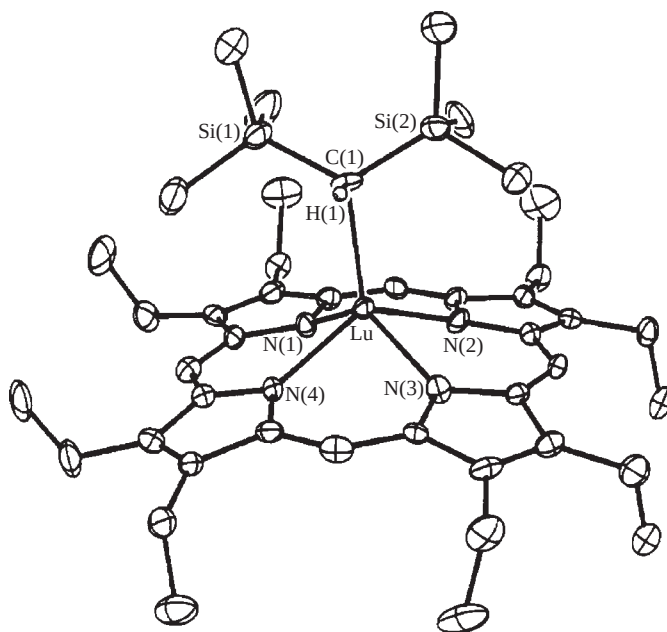


Figure 4.33 Structure of monomeric complex Lu(OEP)[CH(Si(CH₃)₂)₂] [50]. (Reprinted with permission from C.J. Schaverien, and A.G. Orpen, "Chemistry of (octaethylporphyrinato)lutetium and -yttrium complexes: synthesis and reactivity of (OEP)MX derivatives and the selective activation of O₂ by (OEP)Y(μ-Me)₂AlMe₂," *Inorganic Chemistry*, **30**, no. 26, 4968–4978, 1991. © 1991 American Chemical Society.)

skeleton is highly distorted. The central ion was five-coordinate, surrounded by four nitrogen atoms from porphyrin pyrroles and one carbon atom from the group of [CH(Si(CH₃)₂)₂]. The Lu–N(OEP) bond length is 0.2236(7), 0.2253(6), 0.2296(7), and 0.2256(6) nm, respectively, with an average of 0.226 nm. The distance between the lutetium atom and the mean N₄ plane of porphyrin ligand is 0.0918 nm.

The first cationic monomeric porphyrinato rare earth complex was reported in 1999 by Wong *et al.* via the protonolysis of a rare earth amide with porphyrin [51]. An excess amount of RE[N(SiMe₃)₂]₃ · x[LiCl(THF)₃], generated *in situ* from the reaction of anhydrous RECl₃ with 3 equiv of Li[N(SiMe₃)₂] in THF, was treated with H₂TMPP, leading to the cationic monomeric porphyrinato rare earth complexes [RE(III)(TMPP)(H₂O)₃]Cl·4THF (RE = Yb, Er, Y). The crystal structure of [Yb(III)(TMPP)(H₂O)₃]Cl·4THF is shown in Figure 4.34. The crystal is a square-antiprism and crystallizes in the monoclinic space group *Cc*. The central terbium ion is eight-coordinate with four porphyrin nitrogen atoms and four oxygen atoms from THF. The mean bond length for Tb–N is 0.2301 nm and for Tb–O, 0.2307 nm. Similar to the double- or triple-decker counterparts, in this monomeric porphyrinato rare earth compound the porphyrin ring also exhibits a distorted saddle. The separation of the terbium ion from the mean N₄ plane of porphyrin ligand and four oxygen atoms is 0.1082 and 0.164 nm, respectively. It is worth noting that [Yb(III)(TMPP)(H₂O)₃]Cl·4THF has been revealed to exhibit a catalytic role in the cyclotrimerization of phenyl isocyanate.

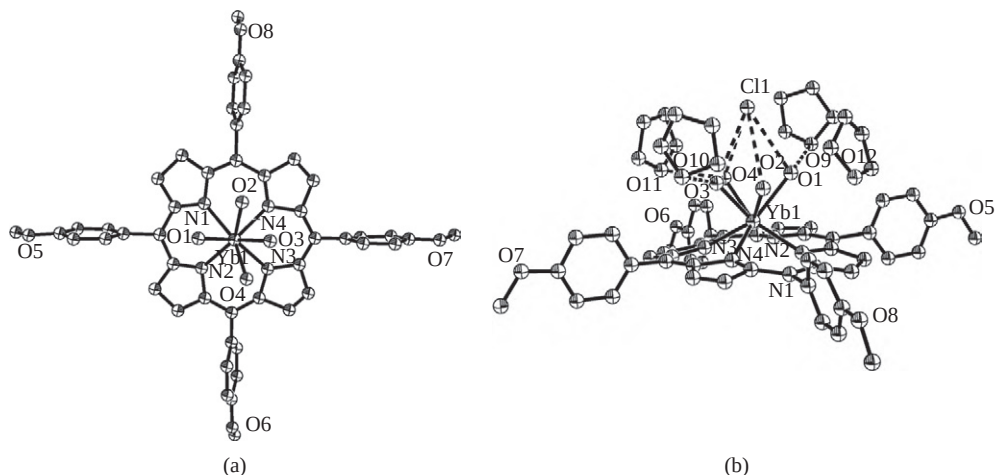


Figure 4.34 (a) Perspective view and (b) side view of compound $[\text{Yb}(\text{III})(\text{TMPP})(\text{H}_2\text{O})_3]\text{Cl}$ [51]. (Reproduced from W. Wong *et al.*, “Synthesis and crystal structures of cationic lanthanide (β) monophyrinate complexes,” *Journal of the Chemical Society, Dalton Transactions*, 615, 1999 (doi: 10.1039/a809696a), by permission of The Royal Society of Chemistry.)

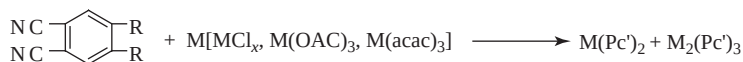
4.3.4 Rare Earth Complexes with Phthalocyanine Type Ligands

Phthalocyanines are two-dimensional 18 π -electron conjugated systems, which are the structural analogs of porphyrins. The first phthalocyanine compound was reported at the beginning of last century [52]. Since then, this series of tetrapyrrole derivatives have been investigated extensively, resulting in a wide range of technological applications in the fields of dyes and pigments, chemical sensors, electrochromism, photodynamic reagents, read-write optical disks, deodorants, nonlinear optics, electrocatalysis, and liquid crystals [53].

The phthalocyanine molecule contains four isoindole nitrogen atoms, which are able to complex with a range of metal ions of large ionic radius (for example, rare earths, actinides, Group 4 transition metals, and some main group metals) to form sandwich type double- and triple-decker complexes. The first bis(phthalocyaninato) metal compound $\text{Sn}(\text{Pc})_2$ was reported in 1936 [54] and the analogous rare earth complexes [55] have been known since the mid-1960s. The early research interest was focused on the double- or triple-deckers with the same phthalocyanine macrocycle ligand, namely homoleptic sandwich type complexes. However, heteroleptic sandwich type complexes with different tetrapyrrole ligands have attracted increasing research interest in recent years [56].

There are several ways to synthesize the homoleptic bis(phthalocyaninato) rare earth complexes $\text{RE}(\text{III})(\text{Pc}')_2$, Figure 4.35. The simplest way is to heat a mixture of a metal salt and phthalonitrile in a ratio of approximately 1 : 8 to 280–290 °C followed by chromatographic separation of the product [57]. Alternatively, this cyclic tetramerization method towards $\text{RE}(\text{III})(\text{Pc}')_2$ could be conducted with an organic base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a promoter [58]. In addition, a ligand condensation method also plays an important role in the synthesis of homoleptic bis(phthalocyaninato) rare earth complexes. This procedure is based on the reaction of $\text{H}_2\text{Pc}'$ or $\text{Li}_2(\text{Pc}')$ with rare earth salts in a solvent with a

1 Cyclic tetramerization



2 Ligands condensation

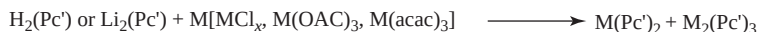


Figure 4.35 Schematic representation of the formation of double-decker and triple-decker phthalocyanines.

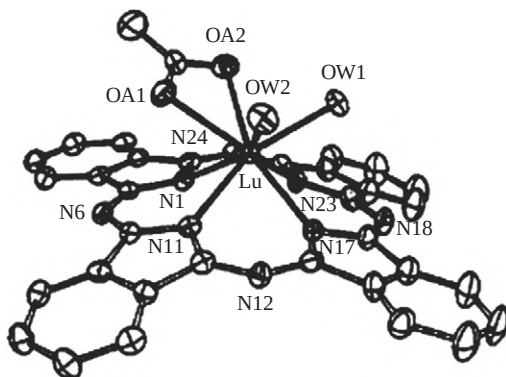


Figure 4.36 The structure of $\text{LuPc}(\text{CH}_3\text{COO})$ [61a]. (Reprinted with permission from J. Fischer, R. Weiss, *et al.*, "Synthesis, structure, and spectroscopic and magnetic properties of lutetium(III) phthalocyanine derivatives: $\text{LuPc}_2 \cdot \text{CH}_2\text{Cl}_2$ and $[\text{LuPc}(\text{OAc})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$," *Inorganic Chemistry*, **24**, no. 20, 3162–3167, 1985. © 1985 American Chemical Society.)

high boiling point such as TCB (1,2,4-trichlorobenzene). It is believed that in these reactions, the protonated double-deckers $\text{M}(\text{III})\text{H}(\text{Pc}')_2$ are the initial products, which undergo oxidation in air to give the deprotonated analogs $\text{RE}(\text{III})(\text{Pc}')_2$ [59]. If the reaction was completed in the presence of reducing agents, the monoanionic double-deckers such as $\text{Li}[\text{RE}(\text{III})(\text{Pc})_2]$ ($\text{RE} = \text{La} - \text{Yb}$ except Ce), $(\text{NBu}_4)[\text{RE}(\text{III})(\text{Pc})_2]$ ($\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Ho}, \text{Lu}$), and $(\text{PNP})[\text{RE}(\text{III})(\text{Pc})_2]$ [$\text{PNP} = \text{bis}(\text{triphenylphosphino})\text{iminium}$; $\text{RE} = \text{La}, \text{Gd}, \text{Tm}$] can also be isolated [60].

4.3.4.1 Homoleptic Bis(phthalocyaninato) Rare Earth Double-Deckers

To date, various crystalline forms of bis(phthalocyaninato) rare earth double-decker complexes including neutral, protonated, and anionic species have been obtained depending on the synthesis procedure [61]. By using the cyclic tetramerization method, Weiss reported the synthesis and crystal structure of both the monomeric phthalocyaninato and bi(phthalocyaninato) lutetium complexes [61a]. Figure 4.36 shows the molecular structure of $\text{LuPc}(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2$. As can be seen, the coordination polyhedron is a slightly distorted square antiprism. The donor atoms consist of four phthalocyanine isoindole nitrogens, two oxygens from the acetylacetonate, and two oxygens of two water molecules. The mean $\text{Lu}-\text{N}$, $\text{Lu}-\text{O}_{\text{OAc}}$, and $\text{Lu}-\text{O}_w$ distances are 0.2345(2), 0.2396, and 0.2331(3) nm, respectively. The perpendicular distance between the lutetium ion and the four isoindole N4 plane of the

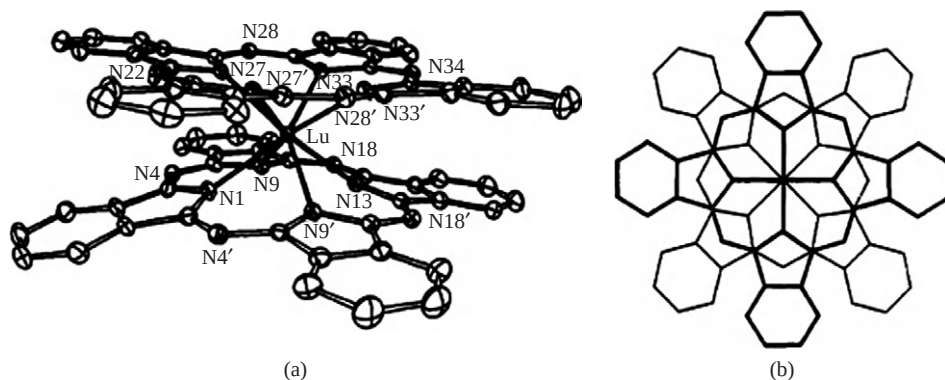


Figure 4.37 The structure of $\text{Lu}(\text{Pc})_2$ [61a]. (Reprinted with permission from J. Fischer, R. Weiss, *et al.*, "Synthesis, structure, and spectroscopic and magnetic properties of lutetium(III) phthalocyanine derivatives: $\text{LuPc}_2 \cdot \text{CH}_2\text{Cl}_2$ and $[\text{LuPc}(\text{OAc})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$," *Inorganic Chemistry*, **24**, no. 20, 3162–3167, 1985. © 1985 American Chemical Society.)

phthalocyanine ring is 0.126 nm. The dihedral angle between the mean plane of the N4 isoindole of phthalocyanine and the mean plane of the four oxygen atoms bonded to lutetium atom is 1.9° .

Similar to the monomeric phthalocyaninato lutetium counterpart, the coordination polyhedron for the bi(phthalocyaninato) lutetium complex $\text{Lu}(\text{Pc})_2$ in the solvated crystal $\text{Lu}(\text{Pc})_2 \cdot \text{CH}_2\text{Cl}_2$ is again a square-antiprism, with the lutetium atom occupying a central position between the two phthalocyanine rings A and B, Figure 4.37 [61a]. As a result, the lutetium ion is eight-coordinate with eight nitrogen atoms from the isoindole nitrogens of the two phthalocyanine rings. The Lu–N bond distance from ring a and b is 0.2381(5), 0.2392(7), 0.2369(5), and 0.2375(4) nm, respectively, with an average of 0.238 nm. The metal atom, the two isoindole nitrogens N1 and N13 of ring a, and the two azamethine nitrogens N22 and N34 of ring b are located in the crystallographic symmetry plane. The two phthalocyanine molecules are saucer-shaped and the skew angle of the two phthalocyanine planes is exactly 45° . The perpendicular distances between the lutetium atom and the four isoindole N4 plane of ring a and ring b are 0.135 and 0.134 nm, respectively, longer than that in the monomeric phthalocyaninato lutetium compound, indicating the stronger repulsion interaction between the adjacent phthalocyanine rings of the double-decker. The separation between the two parallel isoindole N4 planes is 0.269 nm, shorter than the distance of 0.306 nm between the planes through the 24 atoms (C16N8) of the Pc ring framework. This makes the two phthalocyanine rings of whole complex form a biconcave lens structure with a doming degree of 0.2° . The π – π distance, defined between the average planes composed of the four isoindole and the four nitrogen atoms connecting them (C16N8) of the phthalocyanine ring is 0.308 nm.

Interestingly, the single crystal molecular structure for the protonated species $\text{HLu}(\text{Pc})_2$ was also determined by X-ray diffraction analysis [61b]. Figure 4.38 displays the geometry of $\text{HLu}(\text{Pc})_2$ without the acidic hydrogen. The mean Lu–N length and the separation between the two parallel isoindole N4 planes are 0.2371(4) and 0.2676 nm, respectively, a little smaller than those found in its neutral analog $\text{Lu}(\text{Pc})_2 \cdot \text{CH}_2\text{Cl}_2$. It is worth noting that although the crystal structure of complex $\text{HLu}(\text{Pc})_2$ was determined, it did not provide any information concerning the location of the unique proton.

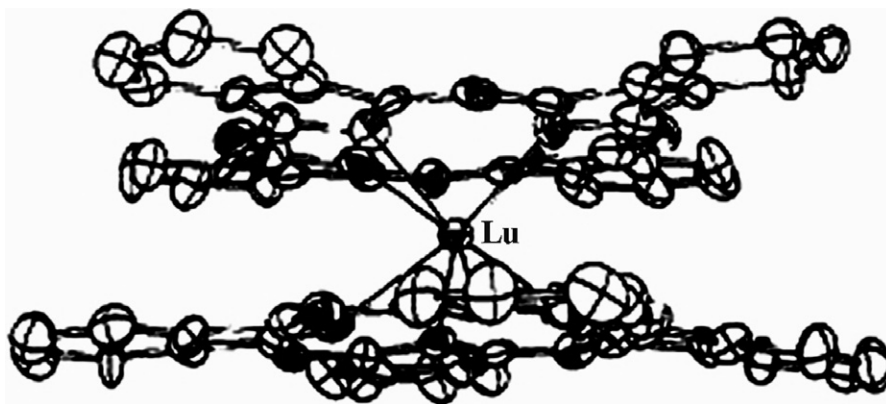


Figure 4.38 The structure of HLu(Pc)_2 [61b]. (Reprinted with permission from J. Fischer, R. Weiss, *et al.*, "Synthesis, structure and spectroscopic properties of the reduced and reduced protonated forms of lutetium diphthalocyanine," *Inorganic Chemistry*, **27**, no. 7, 1287–1291, 1988. © 1988 American Chemical Society.)

On the basis of analysis of many X-ray crystallographic results for bis(phthalocyaninato) rare earth double-decker complexes, there appears to exist a linear relationship between the size of the central rare earth ion and the skew angle. The skew angle increases along with a decrease in the rare earth ion radius. For example, in the tetrabutylammonium salts of bis(phthalocyaninato) complexes with Nd, Gd, Ho, and Lu, the skew angle increases from 6, 34.4, 43.2, to 45° along with the decrease in the rare earth ionic radius in the order of 0.1249, 0.1193, 0.1155, and 0.1117 nm [62]. Usually, the skew angle for almost all the sandwich type bis(phthalocyaninato) rare earth double-decker complexes reported thus far lies between 37 and 45° and the distance between the two mean planes of the 24 atoms (C₁₆N₈) of the Pc ring framework (π – π interaction distance) is in the range of 0.28–0.3 nm. With the decrease in the skew angle, the π – π interaction distance increases and meanwhile the deformation of the macrocyclic phthalocyanine ligands from their normal plane becomes smaller.

4.3.4.2 Monomeric Phthalocyaninato Rare Earth Complex $\text{Sm}_2\mu_2\text{Pc(dpm)}_4$

By reaction between Li_2Pc and RE(III)(dpm)_3 (dpm = 2,2,6,6-tetramethylheptane-3,5-dionato), a series of $\text{RE}_2\mu_2\text{Pc(dpm)}_4$ (RE = Sm–Yb, and Y) have been prepared [63]. For the lutetium ion, the reaction gave only a 1 : 1 complex and for the rare earth ions whose ionic radius is larger than the neodymium ion, the compounds were too unstable to be isolated as analytically pure crystals. The crystal structure of $\text{Sm}_2\mu_2\text{Pc(dpm)}_4$ is shown in Figure 4.39. The crystal belongs to the triclinic crystal system and $P1$ space group with the cell parameters of $a = 1.2941(6)$ (nm), $b = 1.4680(4)$ (nm), $c = 2.1205(4)$ (nm), $\alpha = 88.22(2)^\circ$, $\beta = 86.54(3)^\circ$, $\gamma = 71.32(3)^\circ$, $V = 3.8089$ nm³, and $Z = 2$. The phthalocyanine plane lies between the two samarium atoms, with four nitrogen atoms coordinating to each of the samarium ions. Furthermore, each samarium ion also coordinates to four oxygen atoms from two dpm molecules. In the electronic absorption spectrum, the longest absorption band at about 700 nm in the nonpolar solvent CH_2Cl_2 was found to blue-shift to about 670 nm in the polar solvent DMF, indicating a dissociation equation of the complex owing to the solvation by a polar solvent of the rare earth atoms, Figure 4.40.

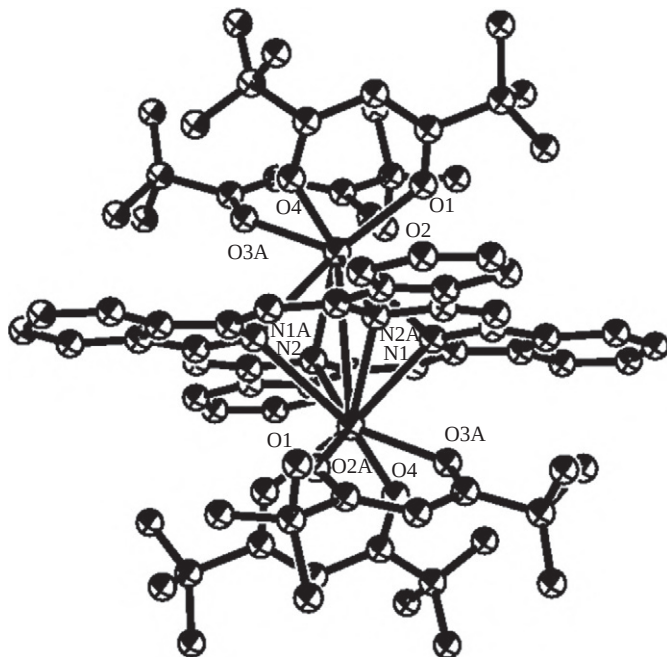


Figure 4.39 The structure of $\text{Sm}_2\mu_2\text{Pc}(\text{dpm})_4$ [63]. (Reproduced from H. Sugimoto *et al.*, "Preparation and X-ray crystal structure (for $\text{Ln} = \text{Sm}$) of $(\mu\text{-phthalocyaninato})\text{bis}[\text{di}(2,2,6,6\text{-tetramethylheptane-3,5-dionato})\text{Ln}^{\text{III}}](\text{Ln} = \text{Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Y})$," *Journal of the Chemical Society, Chemical Communications*, 1234, 1983, by permission of The Royal Society of Chemistry.)

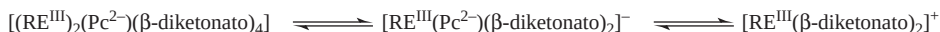


Figure 4.40 Schematic representation of the dissociation equation.

4.3.4.3 Mixed Sandwich-Type Phthalocyaninato and Porphyrinato Rare Earth Double-Decker Complexes

The synthesis of mixed phthalocyaninato and porphyrinato rare earth double-decker complexes is a natural pursuit extending from the homoleptic/heteroleptic phthalocyaninato/porphyrinato rare earth sandwich analogs. Usually, mixed (phthalocyaninato)(porphyrinato) rare earth double-deckers are prepared by $[\text{RE}(\text{III})(\text{Por})(\text{acac})]$ -induced cyclic tetramerization of phthalonitriles or treating metal-free porphyrins with Li_2Pc in the presence of rare earth salts [64]. To date, many mixed (phthalocyaninato)(porphyrinato) rare earth double-deckers including $[\text{La}(\text{III})\text{H}(\text{Pc})(\text{TPP})]$ [65a], $[\text{RE}(\text{III})\text{H}(\text{Pc})(\text{TPyP})]$ ($\text{RE} = \text{Gd, Eu, Y}$) [65b], $\text{Li}[\text{RE}(\text{III})(\text{Pc})(\text{TPyP})]$ ($\text{RE} = \text{Eu, Gd}$) [65c] have been isolated and characterized. Figure 4.41 shows the molecular structure of the neutral nonprotonated and protonated (phthalocyaninato)(porphyrinato) rare earth double-decker complexes, $[\text{Sm}(\text{III})\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ (Figure 4.41a) and $[\text{Sm}(\text{III})\text{H}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ (Figure 4.41b), given as examples to illustrate the molecular structural feature of these complexes [66]. As can be seen, in both

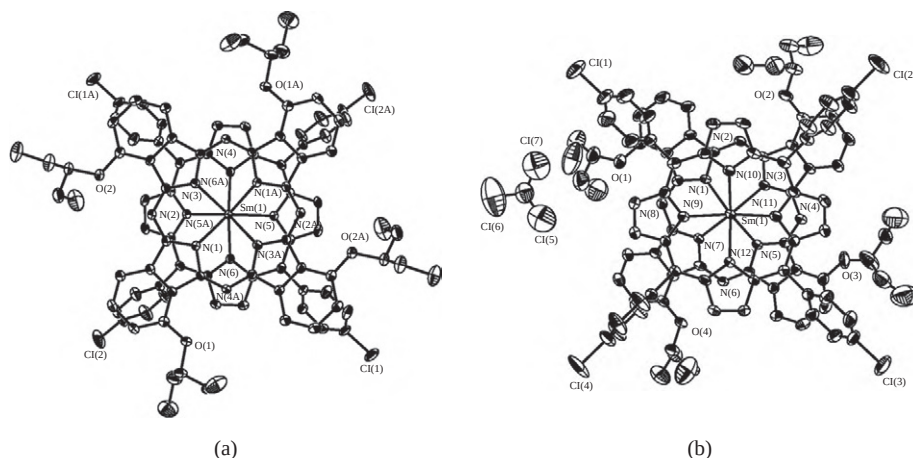


Figure 4.41 The structures of (a) $[\text{Sm(III)}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ and (b) $[\text{Sm(III)}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ [66]. (Reproduced with permission from R. Wang *et al.*, “Controlling the nature of mixed (phthalocyaninato)(porphyrinato) rare-earth(III) double-decker complexes: the effects of non-peripheral alkoxy substitution of the phthalocyanine ligand,” *Chemistry – A European Journal*, 2006, 12, 1475. © Wiley-VCH Verlag GmbH & Co. KGaA.)

compounds the central samarium ion is eight-coordinate with four nitrogen atoms from tetra- α -substituted phthalocyaninato ligands and four nitrogen atoms from porphyrinato ligands. Both coordination polyhedrons adopt a slightly distorted square-antiprismatic structure around the metal center. The average twist angle for $[\text{Sm(III)}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ is 43.8° , larger than that for $[\text{Sm(III)}\text{H}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$, 38.3° . The average Sm–N₄[Pc(α -OC₅H₁₁)₄] plane distance of 0.1557 nm for $[\text{Sm(III)}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ is similar to that of 0.1558 nm for $[\text{Sm(III)}\text{H}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$. However, the distance between the central samarium ion and the N₄ plane of TCIPP is significantly different, 0.1334 nm for $[\text{Sm(III)}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ and 0.1363 nm for $[\text{Sm(III)}\text{H}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$. This evidence, together with other crystal structural parameters for these complexes, clearly indicates the structural difference between the two series of double-deckers.

4.4 Rare Earth Complexes with Schiff Base Type Ligands

Condensation of carbonyl compounds with primary amines is one of the traditional reactions in chemistry, leading to the formation of Schiff base compounds [67]. Owing to their easy preparation and functionalization without too much expense, these Schiff base compounds have been one of the most attractive macrocyclic ligands in coordination and supramolecular chemistry over the past century. Schiff base ligands, representing the most important class of heterocyclic ligands, can coordinate to a metal through the imine nitrogens and other substituted functional groups on the Schiff base ring. As a result, mono-, bi-, and polynuclear Schiff base complexes with transition metals and non-transition metals have been prepared and carefully studied. Because of their wide ranging biological relevance and special applications, a broad variety of Schiff base macrocycles have been utilized as metal-containing liquid crystalline polymers, antiviral agents, in metal biosites modeling, and in asymmetric catalysts.

Compared with transition metal complexes, the rare earth complexes with Schiff base ligands have been studied in relatively recently due to the following three reasons. Firstly, Schiff base ligands exhibit much stronger coordination ability to transition metals in comparison with rare earth ions, the development of transition metal coordination chemistry of Schiff bases has therefore has taken a dominant position in the past few years. Secondly, transition metal elements have been revealed to play important roles in the life science. As a natural consequence, the Schiff base complexes of transition metals were primarily investigated for purposes related to the life sciences. Furthermore, it is well known that the development of rare earth coordination chemistry actually originates from the separation and extraction of the rare earth ions. For this purpose, ligands containing oxygen atoms with a stronger coordination ability to the rare earth metals were usually chosen. The rare earth complexes of Schiff base ligands containing nitrogen coordination atoms have thus been investigated less, due to their weaker coordination ability to rare earth ions. However, inspired by the interesting properties of rare earth complexes with diverse potential applications, the rare earth complexes with Schiff base ligands have attracted increasing research attention in recent years.

Nowadays, Schiff base rare earth complexes have been revealed to exhibit some advantageous properties over their uncoordinated counterparts, which is probably associated with the increased stability of coordinated rare earth ions by the tetradentate Schiff base ligands. Additionally, the high extinction coefficient for absorptions in the near-ultraviolet–visible range of Schiff base rare earth complexes leads to the more effective energy transfer from the ligand to the coordinated rare earth ion center, endowing these complexes with more excellent properties. Briefly summarizing, rare earth complexes with Schiff base ligands have found diverse applications as contrast-enhancing agents in nuclear magnetic resonance imaging, luminescent probes in medicine and biology, radiometal-labeled agents for diagnostic imaging, catalysts, supramolecular assemblies with enhanced physicochemical properties, and even for rare earth separation. In the following section, two types of rare earth complexes in terms of Schiff base ligands, namely salen and imine type, will be introduced.

4.4.1 Rare Earth Complexes with Imine Type Ligands

Imine type Schiff base ligands have been revealed to possess stronger coordination ability, resulting in an emerging interest in rare earth separations using this type of chelating ligand. Thus far, many macrocyclic and macroacyclic imine type Schiff base ligands have been prepared and their single crystal structures reported [68]. Figure 4.42 shows some representative compounds.

It is well known that imine is not a very stable compound and is easy to hydrolyze. For macrocyclic imine type Schiff base ligands, synthesis in the metal-free form with high yield becomes more difficult due to their side polymerization reactions. One effective method to fix this problem involves an *in situ* reaction for adding the rare earth metal in the cyclization process [69]. In other words, the rare earth ions act as a templating ions, directing the condensation preferentially to cyclic rather than polymeric products. Thus far, many macrocyclic imine type Schiff base rare earth complexes have been synthesized. For example, reaction of hydrated rare earth nitrate, 1,2-diaminoethane, and 2,6-diacetylpyridine in the ratio of 1 : 2 : 2 in refluxing methanol for 4–6 hours gave the macrocyclic complex $[\text{RE}(\mathbf{24})(\text{NO}_3)_3]$ (RE = La, Ce) [70]. The compound $[\text{La}(\mathbf{24})(\text{NO}_3)_3]$ crystallizes in a monoclinic system and space group $P2_1/c$ with cell constants $a = 1.6113(5)$ (nm), $b = 0.9782(2)$ (nm), $c = 1.7901(5)$ (nm), $\beta = 95.92(3)^\circ$, and

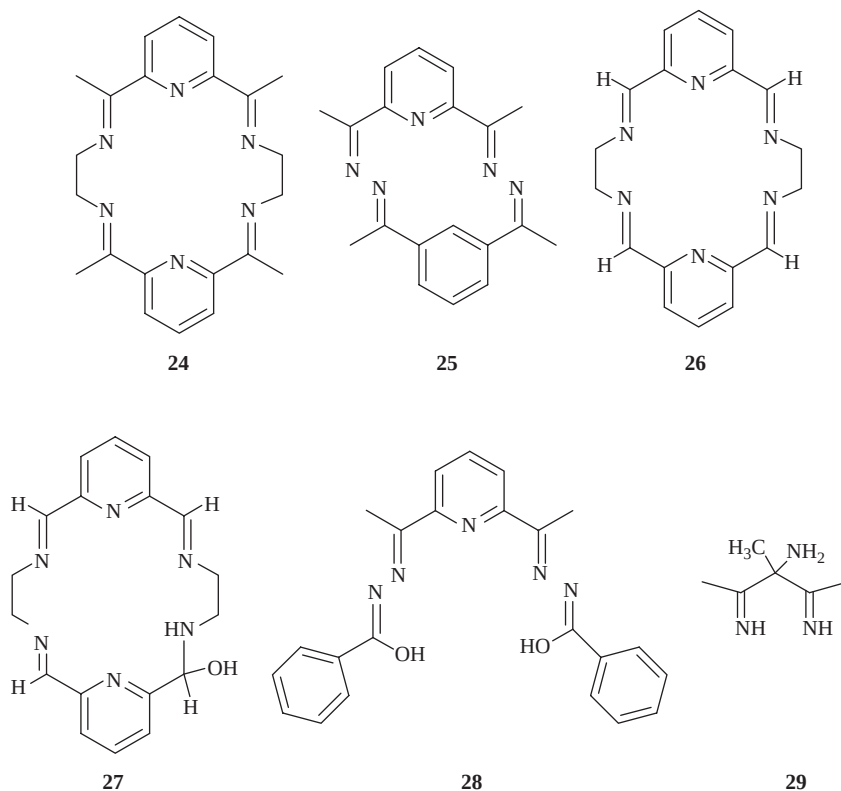


Figure 4.42 Six representative imine type ligands.

$Z = 4$. The crystal structure is shown in the Figure 4.43. The La coordination polyhedron can be depicted as a folded butterfly configuration. Viewed from the two flexible $-\text{CH}_2-\text{CH}_2-$ lateral units, the whole molecule can be divided into two hemispheres, one above and one below the donor atom plane. This structure effectively relaxes the repulsion among the coordination atoms and allows the central metal ion to attain its highest possible coordination number, 12. The donor atoms consist of six nitrogen atoms from one macrocyclic **24** and four nitrogen atoms from two bidentate nitrates on one side of the macrocycle and the other bidentate nitrate on the opposite site.

It must be pointed out that although the rare earth complexes with ligand **24** ($\text{RE} = \text{La}, \text{Ce}$) were successfully prepared, attempts at obtaining analogous complexes of heavier rare earth metals failed. To improve the validity of this method, De Cola and *et al.* optimized the reaction conditions by adopting a more appropriate counterion ClO_4^- instead of NO_3^- , strictly controlling dehydration of the rare earth perchlorate, and adding $\sim 0.1 \text{ M Cl}^-$ [71]. As a total result, a series of rare earth complexes $[\text{RE}(\mathbf{24})(\text{ClO}_4)_2(\text{OH}) \cdot n\text{H}_2\text{O}]$ ($n = 0$ for $\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$, and Er ; $n = 1$ for Eu ; $n = 2$ for $\text{RE} = \text{Gd}$ and Tb) were obtained. The range of rare earth species was further extended to the whole series of rare earth metals except for Pm by using the rare earth acetate, providing $\text{RE}(\mathbf{24})(\text{CH}_3\text{COO})_2\text{Cl} \cdot n\text{H}_2\text{O}$ [72].

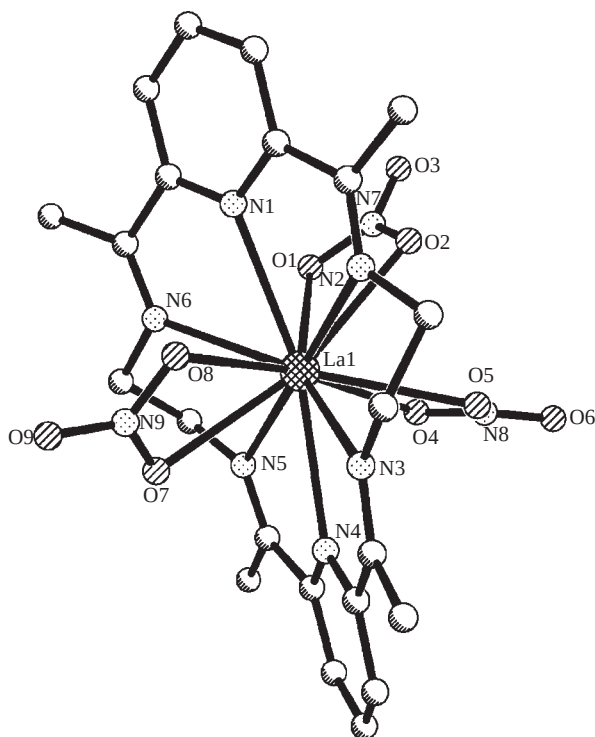


Figure 4.43 The structure of $[\text{La}(\mathbf{24})(\text{NO}_3)_3]$ [70]. (Reproduced from J.D.J Backers-Dirks *et al.*, "Preparation and properties of complexes of lanthanides with a hexadentate nitrogen-donor macrocycle: X-ray crystal structure of the complex $[\text{La}(\text{NO}_3)_3\mathbf{31}]$," *Journal of the Chemical Society, Chemical Communications*, 774, 1979, by permission of The Royal Society of Chemistry.)

The ease and good yield of this reaction was ascribed to the CH_3COO^- counterion, which favors the reaction more than Cl^- or ClO_4^- . It is worth noting that in this series of complexes the IR absorptions for symmetric and antisymmetric stretching of CH_3COO^- , in particular the separation between these two peaks, $\Delta\nu$, can be used to estimate the coordination mode of the CH_3COO^- ligands. The absorptions exhibiting larger $\Delta\nu$ value contribute from the unidentate ionic acetate, whereas those with smaller $\Delta\nu$ value are due to the bidentate chelating acetate. In detail, a strong absorption broadly centered at 1540 cm^{-1} together with shoulders at 1550 and 1530 cm^{-1} , respectively, in the IR spectra of $\text{RE}(\mathbf{24})(\text{CH}_3\text{COO})_2\text{Cl}\cdot n\text{H}_2\text{O}$ is due to the antisymmetric COO^- stretching, and a pair of strong bands observed at 1445 and 1430 cm^{-1} with shoulders at 1443 and 1460 cm^{-1} due to the symmetric COO^- stretching. Accordingly, the vibrations at 1550 and 1430 cm^{-1} with $\Delta\nu = 120\text{ cm}^{-1}$ were assigned to the ionic acetate, whereas those at 1540 and 1455 cm^{-1} with $\Delta\nu = 85\text{ cm}^{-1}$ were assigned to the bidentate chelating acetate. On the basis of this result, these complexes can be further formulated as $[\text{RE}(\mathbf{24})(\text{CH}_3\text{COO})(\text{H}_2\text{O})](\text{CH}_3\text{COO})\text{Cl}\cdot n\text{H}_2\text{O}$, in which the central rare earth ion achieves the usually observed nine-coordinated mode.

By using the template directed cyclization between 2,6-pyridinedicarbaldehyde and ethyldiamine in the presence of rare earth nitrate salts, a series of corresponding complexes

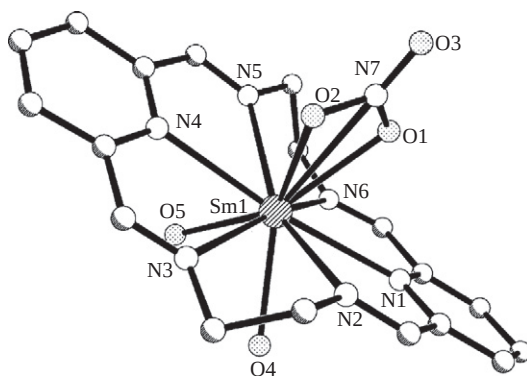


Figure 4.44 Structure of $[\text{Sm}(\mathbf{26})(\text{NO}_3)(\text{OH})(\text{H}_2\text{O})]^+$ [73]. (Reproduced from *Polyhedron*, 23, F.B. Tamboura *et al.*, “Structural studies of bis-(2,6-diacetylpyridine-bis-(phenylhydrazone)) and X-ray structure of its Y(III), Pr(III), Sm(III) and Er(III) complex,” 1191, 2004, with permission from Elsevier.)

formulated as $[\text{RE}(\mathbf{26})(\text{NO}_3)_3] \cdot n\text{H}_2\text{O}$ were provided [73]. The IR spectra of the heavier rare earth (Nd–Lu except for Eu and Pm) complexes are different from those of the lighter rare earth counterparts for $\text{RE} = \text{La–Pr}$ and Eu with respect to the former group exhibiting a distinctive sharp band at *about* 3220 cm^{-1} , assigned to a secondary amine group. Previous research of the transition metal complexes with this ligand indicated that addition of a water molecule across the imine double bond led to the formation of a carbinolamine species, ligand **27**. This induces an increase in the flexibility of the macrocycle, making it capable of accommodating smaller metal cations. Obviously, the IR spectral result for the heavier rare earth complexes proves the existence of ligand **27** in $[\text{RE}(\mathbf{26})(\text{NO}_3)_3] \cdot n\text{H}_2\text{O}$. It is worth noting that carbinolamine complexes might also be proved to be in the solution by ^{13}C and ^1H NMR spectroscopy on the lutetium derivatives. However, significant change occurs in the IR spectrum of the samarium complex with ligand **26** after recrystallization from water. The sharp band appearing at 3210 cm^{-1} assigned to the secondary amine group vanished and a new sharp band attributed to a Sm–OH group was observed at 3560 cm^{-1} . The single crystal molecular structure of this compound shown in Figure 4.44 indicates that this complex consists of a discrete $[\text{Sm}(\mathbf{26})(\text{NO}_3)(\text{OH})(\text{H}_2\text{O})]^+$ cation, NO_3^- anions, and clathrate MeOH molecules. The coordination polyhedron is an irregular antiprism capped on its “square” face by N(1) and N(4). The central samarium ion is ten-coordinate with six nitrogen atoms from one heterocycle, two nitrogen atoms from one bidentate nitrate group, one oxygen atom from the OH^- ion, and one oxygen atom from a water molecule. The Sm–N (pyridine) bond length is 0.266(1) and 0.265(1) nm, significantly longer than that of Sm–N (imine), which is 0.262 nm.

According to the structure determination results, it is presumed that the reversion from the carbinolamine form to the tetraimine one exists probably because of the optimal cation-cavity criteria and the fact that the samarium ion can be accommodated by either form of the two macrocycles. Carbinolamine, acting as the intermediate of the tetraimine Schiff base **27**, is the kinetically favored product. In contrast, the latter species is the thermodynamically favored product. On dissolution and recrystallization in water, a higher temperature is reached than in the original reaction in alcohol, which facilitates completion of the reaction. Furthermore,

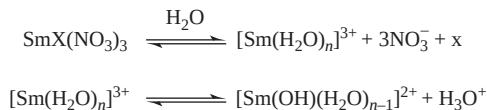


Figure 4.45 Schematic representation of the reaction to form $[\text{Sm}(\mathbf{26})(\text{NO}_3)(\text{OH})(\text{H}_2\text{O})]\text{NO}_3$.

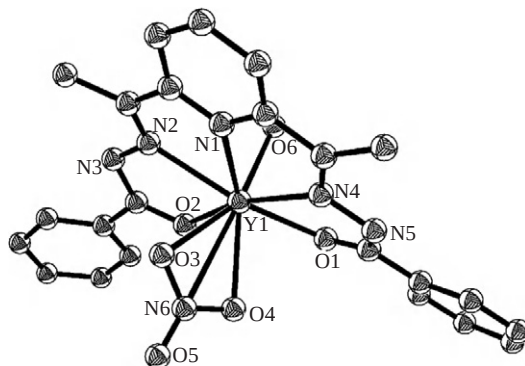


Figure 4.46 The structure of $\text{Y}(\mathbf{28})(\text{H}_2\text{O})(\text{NO}_3)$ [73]. (Reproduced from *Polyhedron*, **23**, F.B. Tamboura *et al.*, "Structural studies of bis-(2,6-diacetylpyridine-bis-(phenylhydrazone)) and X-ray structure of its Y(III), Pr(III), Sm(III) and Er(III) complex," 1191, 2004, with permission from Elsevier.)

$\text{Sm}(\mathbf{26})(\text{NO}_3)_3$ is also hydrolyzed during the recrystallization process to give the compound $[\text{Sm}(\mathbf{26})(\text{NO}_3)(\text{OH})(\text{H}_2\text{O})]\text{NO}_3$. It is plausible that the sequence of the dissociation process for this complex shown in Figure 4.45 occurs.

Associated with the ramifying applications of rare earth elements, a series of rare earth complexes with macrocyclic imine type Schiff bases have been prepared, among which ligands **28** and **29** are two representative compounds.

4.4.1.1 $\text{RE}(\mathbf{28})(\text{H}_2\text{O})(\text{NO}_3)$

Reaction of 2,6-bis(phenylhydrazone)pyridine with $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in alcohol gave $\text{RE}(\mathbf{28})(\text{H}_2\text{O})(\text{NO}_3)$ ($\text{RE} = \text{Y}$ and Er). The crystal structure of $\text{Y}(\mathbf{28})(\text{H}_2\text{O})(\text{NO}_3)$ is shown in Figure 4.46 [73], which belongs to the monoclinic system and crystallizes in a space group $P2_1/n$ with $a = 0.8174(3)$ nm, $b = 1.0099(4)$ nm, $c = 2.9423(6)$ nm, $\beta = 9.023(2)^\circ$, $V = 2.4287(9)$ nm³, and $Z = 4$. The central yttrium ion is eight-coordinate and the donor atoms consist of two oxygen atoms from the iminolic of hydrazone, two nitrogen atoms from the imines of hydrazone, one nitrogen atom from pyridine, two oxygen atoms from the bidentate nitrate group, and one coordinated water molecule. The $\text{Y}-\text{O}(\text{hydrazonic})$ distance is 0.2265(4) and 0.2268(4) nm and that of $\text{Y}-\text{N}(\text{hydrazonic})$ is 0.2418(8) and 0.2450(8) nm. Figure 4.47 shows three isomeric forms of the ligand **28** in solution. Infrared and NMR data proved that in the molecule of 2,6-diacetylpyridine-bis-(benzoylhydrazone), the imine group ($\text{O}=\text{C}-\text{NH}$) is transformed into iminol group ($\text{HO}-\text{C}(=\text{N})$) and the ligand acts with the rare earth ion in the iminol form.

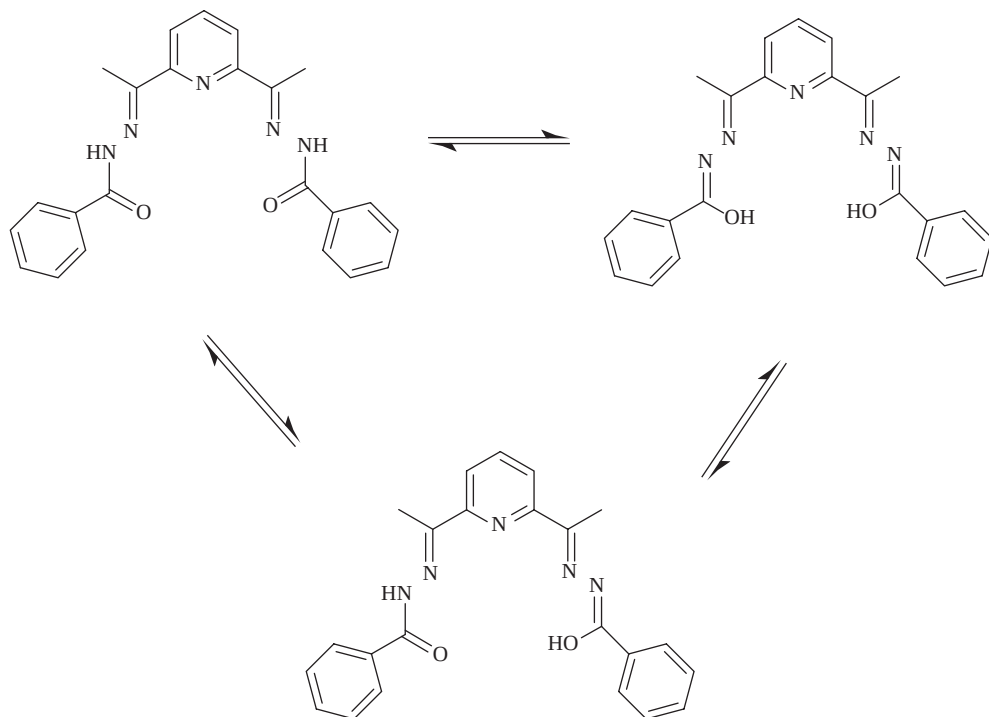


Figure 4.47 Schematic representation of the equilibrium of ligand **28**.

4.4.1.2 $\{(\text{HNdCMe})_2\text{MeCNH}_2\}\text{Dy}(\text{MeCN})_6\text{I}_3$

Reaction of DyI_2 with excess acetonitrile provided a yellow–brown solution [74]. Recrystallization of this solution resulted in the complex $\{(\text{HNdCMe})_2\text{MeCNH}_2\}\text{Dy}(\text{MeCN})_6\text{I}_3$. The crystal was revealed to contain a new type of tridentate ligand, 1,1'-bis(iminoethyl)ethylamine ($\text{HN}=\text{CMe})_2\text{MeCNH}_2$, which is prepared by the C–C coupling reaction of acetonitrile. The complex belongs to the orthorhombic space group $Pnma$ with the cell parameters of $a = 2.03218(3)$ (nm), $b = 1.38313(1)$ (nm), $c = 1.54992(1)$ (nm), $V = 4.35647(8)$ nm³, and $Z = 4$. In the cell unit, four $\{(\text{HNdCMe})_2\text{MeCNH}_2\}\text{Dy}(\text{MeCN})_6\text{I}_3$ cations, 12 I^- anions, and four non-coordinating acetonitrile solvent molecules exist. The coordination polyhedron can be described as a distorted tricapped trigonal prism and the cation shows C_s symmetry (Figure 4.48) with the Dy atom, two of the coordination MeCN molecules, and the central carbon and nitrogen atoms of the 1,1'-bis(iminoethyl)ethylamine ligand located on a crystallographic mirror plane. The central dysprosium ion is nine-coordinate with three nitrogen atoms from 1,1'-bis(iminoethyl)ethylamine and six nitrogen atoms from acetonitrile. The Dy–N_{imino} distance is 0.245 nm, shorter than that of Dy–N_{amino} 0.251 nm. The Dy–N_{acetonitrile} bond length is in the range 0.248–0.253 nm. It is worth noting that due to the presence of heavy rare earth atoms, the hydrogen atoms were not localized experimentally. However, their existence is supported by the IR spectroscopy results, with the appearance of a strong absorption at 3150 cm^{−1}.

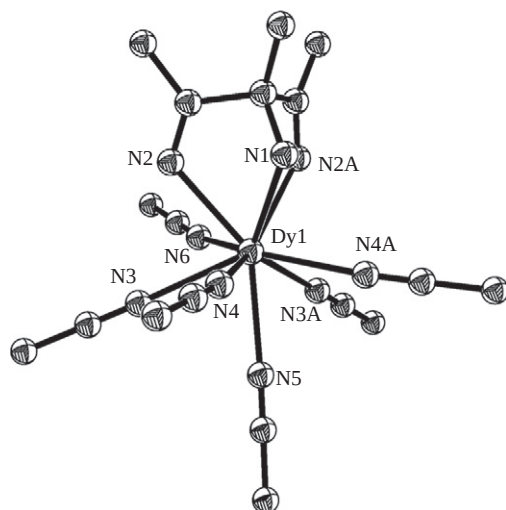


Figure 4.48 The structure of $[(\text{HNdCMe})_2\text{MeCNH}_2]\text{Dy}(\text{MeCN})_6]^{3+}$ [74]. (Reproduced with permission from M.N. Bochkarev, G.V. Khoroshenkov, H. Schumann and S. Dechert, “A novel bis(imino)amine ligand as a result of acetonitrile coupling with the diiodides of Dy(II) and Tm(II),” *Journal of the American Chemical Society*, **125**, 2894, 2003. © 2003 American Chemical Society.)

4.4.2 Rare Earth Complexes with H_2Salen (30) Type Ligands

When a diamine is combined with two equiv of salicylaldehyde, salen ligands come into being. Because of their special structure and advantageous properties when coordinating with rare earth ions, salen type ligands modified with various functional groups have been studied extensively thus far [75]. Figure 4.49 shows some representative salen type ligands.

The research shows that the pH value plays an important role in determining the type of complexes formed during the reaction, as shown in Figure 4.50, as H_2salen is a binary weak acid. When the pH value is between 5 and 6, the ligand does not ionize and mostly adopts the neutral bridging ligand (H_2salen) form to give a chain polymeric complex. In this case, only the oxygen atom of H_2salen coordinates with the rare earth metal without participation of the nitrogen atoms from its $\text{C}=\text{N}$ groups. However, if a base was added into the reaction solution, one or two hydrogen cations of H_2salen would be neutralized, forming a -1 charged Hsalen or a -2 charged salen , which is able to coordinate with the rare earth ions using the naked nitrogen atom(s). Depending on the reaction conditions employed (acidic or alkaline), a number of rare earth salen complexes with different composition have been reported, as exemplified by $\text{Eu}(\text{Hsalen})(\text{salen})$, $\text{RE}(\text{H}_2\text{salen})\text{X}_3 \cdot n\text{H}_2\text{O}$, $\text{RE}_2(\text{salen})_3$, $[\text{RE}_2(\text{H}_2\text{salen})_3(\text{NO}_3)_4](\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{RE}_2(\text{H}_2\text{salen})_3\text{X}_6 \cdot n\text{H}_2\text{O}$, $\text{RE}(\text{H}_2\text{salen})\text{X}_3 \cdot n\text{H}_2\text{O}$, and $\text{RE}(\text{H}_2\text{salen})_3\text{X}_3 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}; n = 0-2$) [76].

4.4.2.1 $[\text{La}(\text{H}_2\text{salen})(\text{NO}_3)_3(\text{MeOH})_2]_n$

Despite reports on the rare earth complexes with H_2salen as early as 1968, their structure was mainly derived according to the corresponding compositions and spectroscopic data. Indeed,

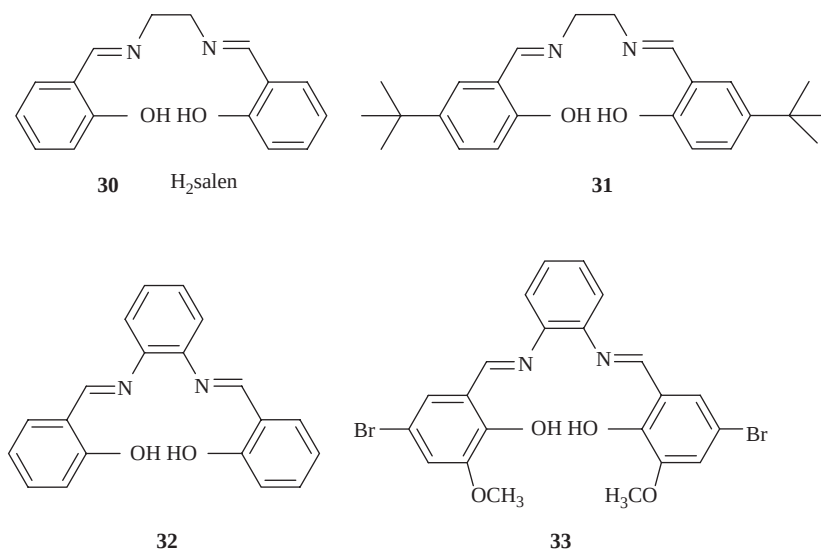


Figure 4.49 Four representative salen type ligands.



Figure 4.50 Schematic representation of the equilibrium of H₂salen.

very little crystallographic evidence was available on the coordination mode of rare earth complexes with Schiff base ligands until recent years. In 1999, Wang and coworkers reported the first X-ray crystal structure of a rare earth complex with the neutral H₂salen ligand [77]. By reacting La(NO₃)₃ hydrate with an equivalent of H₂salen ligand in a mixed solution of methanol and chloroform, crystals of [La(H₂salen)(NO₃)₃(MeOH)₂]_n were obtained. The complex crystallizes in the orthorhombic system with a space group *P*2₁/*n*, with the cell parameters *a* = 0.8605 nm, *b* = 1.5254 nm, *c* = 2.2358 nm, β = 96.31°, *V* = 2.9169 nm³, and *Z* = 4. The skeleton structure of the asymmetric unit of [La(H₂salen)(NO₃)₃(MeOH)₂]_n is shown in Figure 4.51. As can be seen, the central lanthanum ion is ten-coordinate with two phenolic oxygen atoms, three bidentate nitrate ions, and two methanol molecules. Each H₂salen ligand coordinates with two La(III) atoms with its two phenolic oxygen atoms, leading to the formation of a polymeric structural complex, Figure 4.51. It is worth noting that although no coordination bond with lanthanum through the imine nitrogen atom exists in this complex, its structure is still described here to facilitate the comparison with rare earth complexes of Hsalen and the salen ligand. The La–O distance from the methanol ligands is 0.2588(4) and 0.2611(4) nm, respectively. The La–O bond length due to the nitrate ligands is in the range 0.2614(4)–0.2699(4) nm, with an average of 0.2672 nm. The phenolic C–O bond distance is 0.1286(6) and 0.1299(1) nm, respectively, which is notably shorter than that found in the related complexes with salen ligands.

Owing to the relatively close electronegativity between nitrogen and oxygen atoms, the hydrogen atom has two possible positions in the complex: (i) the hydrogen atom residing on the oxygen atom connects with adjacent nitrogen or oxygen atom to form the hydrogen

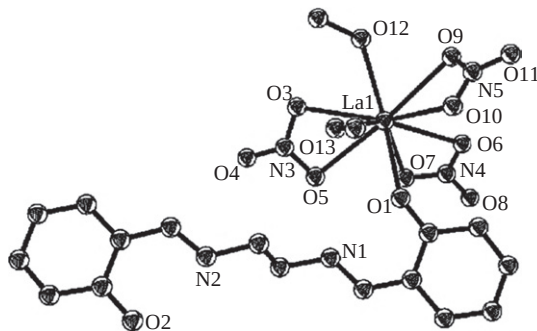


Figure 4.51 The structure of $[\text{La}(\text{H}_2\text{salen})(\text{NO}_3)_3(\text{MeOH})_2]$ [77]. (Reproduced with permission from W. Xie, M. Jane and P.G. Wang, "Formation and crystal structure of a polymeric $\text{La}(\text{H}_2\text{salen})$ complex," *Inorganic Chemistry*, **38**, 2541, 1999. © 1999 American Chemical Society.)



Figure 4.52 Schematic representation of the delocation of the hydrogen atom in H_2salen molecular.

bond ($\text{O}-\text{H}\cdots\text{N}$, $\text{O}-\text{H}\cdots\text{O}$); (ii) the hydrogen atom residing on the nitrogen atom connects with adjacent nitrogen or oxygen atom to form the hydrogen bond ($\text{N}-\text{H}\cdots\text{N}$, $\text{N}-\text{H}\cdots\text{O}$). Because of the much larger distance between the two nitrogen or two oxygen atoms within the framework of H_2salen , it is difficult to form intramolecular hydrogen bonds such as $\text{O}-\text{H}\cdots\text{O}$ or $\text{N}-\text{H}\cdots\text{N}$. As a result, $\text{O}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{O}$ are probably the most likely hydrogen bond formed for this ligand. In fact, equilibrium between the ionized structure (Ia) and the neutral one (Ib) exists in the inner part of the H_2salen molecule, Figure 4.52. As single crystal X-ray diffraction crystallographic data could not give information about the hydrogen atom position, the structure of the ligand form can only be derived according to the IR spectroscopic result. The isolated $\text{O}-\text{H}$ stretching frequency appears around 3590 cm^{-1} . However, if an intramolecule hydrogen bond forms, the $\text{O}-\text{H}$ stretching will red-shift to about 2650 cm^{-1} . Systematic investigation over a series of rare earth complexes with the H_2salen ligands revealed that H_2salen ligand in these compounds exists mainly in the ionized form (Ia). It must be pointed out that to confirm the H_2salen ligand in complexes, the IR spectroscopic result itself is not enough. By comparing the $\text{C}-\text{O}$ (phenolic) bond length in the rare earth complexes containing the neutral H_2salen ligand, Wang also demonstrated the form the H_2salen ligand in $[\text{La}(\text{H}_2\text{salen})(\text{NO}_3)_3(\text{MeOH})_2]_n$ exists in. It has been revealed that the ionized phenolic hydroxyl groups coordinate to the $\text{La}(\text{III})$ ion and, meanwhile, the protons after ionization reside on the imine nitrogen atoms, leaving the whole Schiff base ligand as a neutral molecule.

4.4.2.2 $\text{Eu}(\text{Hsalen})(\text{salen})\cdot\text{H}_2\text{O}$

Huang reported the unique rare earth complex containing two types of ionized ligands (Hsalen and salen) in 1990 [78]. $\text{Eu}(\text{Hsalen})(\text{salen})\cdot\text{H}_2\text{O}$ crystallizes in the monoclinic system with a space group $P2_1/a$ with cell constants $a = 1.6441(2)\text{ nm}$, $b = 2.0599(3)\text{ nm}$, $c = 1.0719(2)\text{ nm}$,

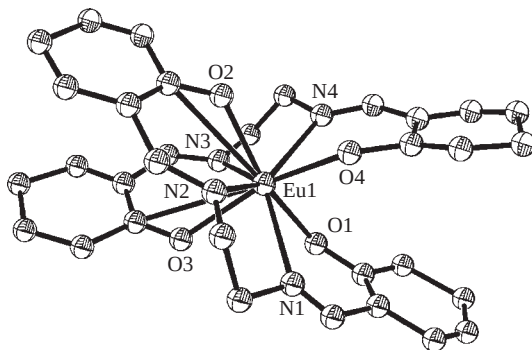


Figure 4.53 Structure of $\text{Eu}(\text{Hsalen})(\text{salen})$ [78]. (Redrawn from L. Huang, C.H. Huang and G.X. Xu, "Synthesis and structure of europium(III) with N,N bis-salicylidene ethylenediamine," *Chinese Journal of Structural Chemistry*, **9**, 100, 1990.)

$\beta = 91.38^\circ$, $V = 3.6115(8) \text{ nm}^3$, and $Z = 4$. The molecular structure of $\text{Eu}(\text{Hsalen})(\text{salen})$ is shown in Figure 4.53. The central europium ion is eight-coordinate with four oxygens from phenolic groups and four nitrogens from $\text{C}=\text{N}$ groups. Two H_2salen ligands in the molecule exist in two forms, namely -1 charged Hsalen and -2 charged salen, to satisfy the charge balance with the central europium ion. This was also supported by the mass spectrometric results with the existence of the protonated complex ion $\text{Eu}(\text{Hsalen})(\text{salen})\text{H}^+$. The average bond length of $\text{Eu}-\text{O}$ is 0.230 nm and the average $\text{Eu}-\text{N}$ distance is 0.252 nm , the latter of which is almost the sum of Eu^{3+} (0.106 nm) and N^{3-} (0.146 nm). In addition, the distance $\text{C}(21)-\text{O}(2)$ (0.1251 nm) is revealed to be close to that of $\text{C}(11)-\text{O}(1)$ (0.1335 nm) in one ligand, while in another ligand the distance $\text{C}(31)-\text{O}(3)$ (0.1134 nm) is significantly different from $\text{C}(41)-\text{O}(4)$ (0.1414 nm). The result indicates that the charge distributes in an equal manner in the former ligand and not equally in the latter, suggesting the salen^{2-} and Hsalen^- nature for the former and latter ligands, respectively. As $\text{Eu}-\text{O}(3)$ shows the longest bond length among all the $\text{Eu}-\text{O}$ bonds, 0.245 nm , the hydrogen ion should situate on the atom of $\text{O}(3)$.

With the exception of cerium(IV) complexes formulated as $\text{Ce}(\text{salen})_2$, the rare earth complexes containing salen type ligands usually have the composition $[\text{RE}_2\text{salen}_3] \cdot (\text{C}_2\text{H}_5\text{OH})_n$ ($n = 0$, $\text{RE} = \text{La}$, Pr , Nd , Er , Yb ; $n = 2$, $\text{RE} = \text{Y}$, Sm , Gd ; $n = 3$, $\text{Ln} = \text{Dy}$). These complexes were prepared by adding $\text{RE}(\text{NO}_3)_3$ to a solution of the ligand in ethanol, methanol, acetone, or DMF at $55\text{--}80^\circ\text{C}$, followed by the addition of a base (ammonia gas, aqueous ammonia, or triethyl amine) [79]. This process was revealed also to be suitable for the ligands of **31** and **32**. The cerium(IV) complexes could be prepared by using either $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ or $\text{Ce}(\text{NO}_3)_3 \cdot (\text{H}_2\text{O})_6$ [80]. Figure 4.54 shows the structure of one salen rare earth complex $\text{Er}(\text{salen})_2(\text{pyridine})$. The central erbium ion was sandwiched between two salen ligands, with all anionic oxygen and neutral nitrogen donor sites coordinating to the metal center, resulting in a formal eight-coordinate erbium complex.

Although numerous rare earth complexes with salen ligands have been reported, few structures of polynuclear rare earth derivatives of salen type ligands are known. In 2005, Yang and Jones described the definitive structural detail of the interaction between the terbium ion and a salen type ligand, $[\text{Tb}_3(\textbf{33})_4(\text{H}_2\text{O})_2]\text{Cl}$ [81]. Reaction of ligand **33** with $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$

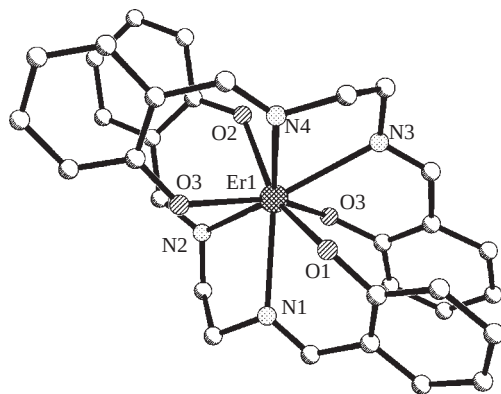


Figure 4.54 Structure of $[\text{Er}(\text{salen})_2]^-$ [79a]. (Reproduced from *Inorganica Chimica Acta*, **155**, S. Mangani, A. Takeuchi, S. Yamada and P. Orioli, "The crystal structure of the eight-coordinated erbium(III) complex with the tetradentate ligand N,N' -ethylene-bis(salicylaldehyde)," **149**, 1989, with permission from Elsevier.)

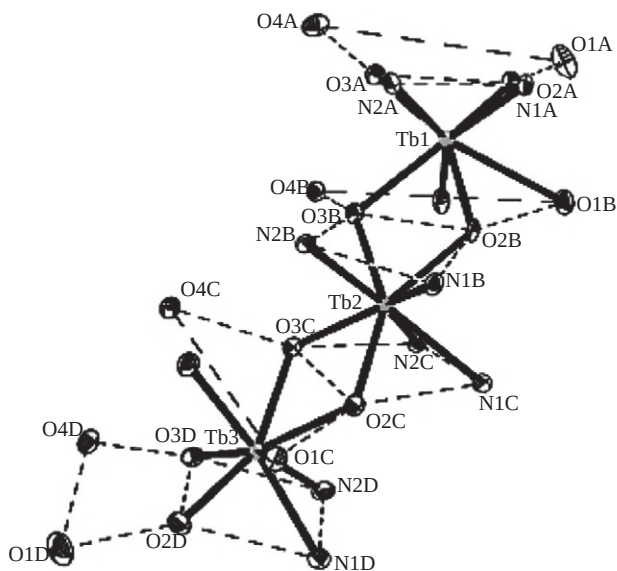


Figure 4.55 Structure of $[\text{Tb}_3(\mathbf{33})_4(\text{H}_2\text{O})_2]$ [81]. (Reprinted with permission from X.P. Yang, X.P. and R.A. Jones, "Anion dependent self-assembly of "tetra-decker" and "triple-decker" luminescent Tb(III) salen complexes," *Journal of the American Chemical Society*, **127**, no. 21, 7686–7687, 2005. © 2005 American Chemical Society.)

(4 : 3) in an acetonitrile/methanol mixed solvent resulted in the formation of the trimetallic tetradecker complex $[\text{Tb}_3(\mathbf{33})_4(\text{H}_2\text{O})_2]\text{Cl}$ in 40% yield. The crystal belongs to the monoclinic system in a space group $P2(1)/c$ with the cell constants $a = 2.2764(5)$ nm, $b = 1.9015(4)$ nm, $c = 2.9285(6)$ nm, $\beta = 104.78(3)^\circ$, $V = 1.2275(4)$ nm³, and $Z = 4$. The cationic structure of complex $[\text{Tb}_3(\mathbf{33})_4(\text{H}_2\text{O})_2]\text{Cl}$ is shown in Figure 4.55. As can be seen, the two outer Tb^{3+} ions,

Tb(1) and Tb(3), have similar nine-coordinate environments consisting of two nitrogen (C=N) atoms and two oxygen (phenolic) atoms from one outer ligand **33**, two oxygen (phenolic) atoms, two oxygen atoms (methoxyl) from one inner ligand, and one water molecule. The central Tb(2) ion is eight-coordinate in a pseudo-square-based antiprismatic geometry formed by two nitrogen (C=N) atoms and two oxygen (phenolic) atom donor sets of the internal ligand **33**. At the same time, the phenolic oxygen atoms of the interior ligand **33** group are bridging, while those of the outer ligand **33** are monodentate. The separation between neighboring terbium atoms is fairly similar, 0.3884 and 0.3872 nm for Tb(1)–Tb(2) and Tb(2)–Tb(3), respectively. To satisfy the charge balance with the central terbium ion, a single uncoordinated Cl[−] anion is present. To coordinate effectively to two Tb³⁺ ions, the inner ligand is planar, while the outer two ligands adopt a twisted configuration. The dihedral angle between these rings is 116.7 and 121.3°, respectively. Furthermore, the presence of an intramolecular π – π stacking interaction between the phenylene units leads to an unusual multi-decker configuration.

4.5 Outlook

In this chapter, we have tried to summarize the synthesis and structural characteristics of N-based rare earth complexes. It is worth noting that despite of the large number of N-based rare earth complexes described here, most of them contain RE–O bonds in addition to RE–N bonds, with few examples solely containing RE–N bonds. Among the N-based rare earth complexes, the most extensively studied ligands are the amide type, N-heterocyclic type, and Schiff-base type ligands. Owing to their different coordination ability to the rare earth ion, synthesis of complexes with various ligands was conducted under different reaction conditions. In comparison with the N-heterocyclic type and Schiff-base type ligands, rare earth complexes with amide type ligands were prepared under much more strictly controlled reaction conditions. Systematic investigation over these complexes revealed that a good control of the inner coordination sphere may lead to a predetermined change in their structure as well as their properties. As a consequence, a wide range of modifications on the nitrogen-containing ligands have been reported for the purpose of preparing rare earth complexes with novel crystal structures and interesting properties.

At the end of this chapter, it should be noted that the research into N-based rare earth complexes is still in its infancy. Much effort is necessary towards the design and synthesis of novel rare earth complexes with novel N-based ligands for practical applications.

List of Abbreviations

acac
acetylacetone
DBU 1,8-diazobicyclo[5.4.0]undec-7-ene
DMF N,N-dimethylformamide
dpm 2,2,6,6-tetramethylheptane-3,5,-dionato
H₂salen Bis-salicylaldehyde o-phenylenediamine
OEP
octaethylporphyrin
Por

porphyrin, porphyrinato
Pc phthalocyanine, phthalocyaninato
TPP
tetraphenylporphyrin
TPyP
tetrapyridineporphyrin
TMPP
tetramethoxylphenylporphyrin
TCB 1,2,4-trichlorobenzene
THF
tetrahydrofuran
4,4'-bpy
4,4'-bipyridine

Acknowledgments

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5

Rare Earth Polyoxometalate Complexes

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The polyoxometalates (POMs) are a large family of metal oxygen clusters, which are composed of edge and corner-shared $\{\text{MO}_6\}$ octahedra with early transition metals in high oxidation states [for example, W(VI), Mo(VI), V(V)] [1]. POMs exhibit not only a wide variety of robust structural motifs with different sizes and topologies, but also diverse physical and chemical properties relevant for applications in material science, catalysis, and medicine. Because of their oxygen-rich compositions, POMs are easily combined with highly oxyphilic rare earth (RE) ions to form a large number of different compounds, which create a new subgroup of POMs, namely RE–POM complexes. The RE–POM complexes display a huge diversity in their structures, including various sized RE–POM clusters, extending structural RE–POM polymers and RE–organocation POM supermolecule complexes. Moreover, RE–POM complexes can combine the intrinsic properties of both constituents. The RE ions can impart useful functionality such as luminescence, magnetic or Lewis acid catalytic centers to POMs, thus extending their range of physical and chemical properties and gaining new potential applications.

5.1 Synthesis

For the preparation of RE–POM complexes, traditional aqueous solution synthesis and hydrothermal synthesis [2] are the two main synthetic methods. In traditional aqueous solution synthesis, reactions are carried out in the temperature range from room temperature to the boiling point of water, and in general start from plenary or lacunary POMs and simple RE salts. Hydrothermal reactions typically proceed in the temperature range 120–200°C under autogenous pressure, and usually use simple metal salts of all the required elements as the starting materials. As different solubility problems are minimized under hydrothermal conditions, the

hydrothermal synthetic method is of more benefit for the preparation of RE–POM complexes containing organic components than the traditional aqueous solution synthetic method. In both methods, the syntheses of RE–POM are governed by the following parameters: concentration and ratio of reagents, pH, temperature, reaction time, counter cations, and ionic strength. Notably, the high reactivity of oxyphilic RE ions with POMs always leads to precipitation instead of crystallization, which makes the elucidation of the structure difficult. Some current efforts indicate that the introduction of organic ligands or solvents during the preparation could stabilize the RE ions somewhat, reduce the reactivity between POMs and RE ions, and improve the solubility of the final products.

5.2 Types and Structure Features

5.2.1 RE-POM Clusters

5.2.1.1 1 : 2, 2 : 2 RE/XM₁₁ Clusters

Keggin polyoxoanion [XM₁₂O₄₀]^{n−} consists of four M₃O₁₃ groups surrounding a central heteroatom in a tetrahedral cavity. Each M₃O₁₃ group is formed by three octahedral sharing edges and has a common oxygen atom that is also shared with the central heteroatom. By removing one M = O unit in the Keggin structure it is possible to obtain the monovacant Keggin anion [XM₁₁O₃₉]^{n−}. This lacunary species may incorporate RE ions resulting in 1 : 2 or 2 : 2 complexes of RE with the XM₁₁ anion (1 : 2 and 2 : 2 representing the stoichiometry of the RE : XM₁₁).

Many 1 : 2 complexes of RE with an α-XM₁₁ anion have been prepared and structurally characterized. They include [Ce(α-SiW₁₁O₃₉)₂]^{13−} [3], [RE(α-PW₁₁O₃₉)₂]^{n−} (RE = Eu(III), *n* = 11 [4] or RE = Ce(IV), *n* = 10 [5]), [Pr(α-GeW₁₁O₃₉)₂]^{13−} [6], [RE(α-PMo₁₁O₃₉)₂]^{n−} (RE = every trivalent lanthanide cation except promethium, *n* = 11 [7] or RE = Ce(IV), *n* = 10 [8]), [Dy(α-SiMo₁₁O₃₉)₂]^{13−} [9]. In the structures, the RE cation is sandwiched between two lacunary [α-XM₁₁O₃₉]^{7−} anions and is coordinated by eight oxygen atoms, four from each of the two [α-XM₁₁O₃₉]^{7−} anions.

1 : 2 complexes of RE with a β₂-XM₁₁ anion, [RE(β₂-SiW₁₁O₃₉)₂]^{13−} (RE = La, Ce, Sm, Eu, Gd, Tb, Yb, Lu), have also been reported, in which an eight-coordinated RE center is sandwiched by two chiral [β₂-SiW₁₁O₃₉]^{8−} units (Figure 5.1) [10].

[{RE(α-SiW₁₁O₃₉)(H₂O)}₂(μ-CH₃COO)₂]^{12−} (RE = Gd, Yb) are 2 : 2 complexes formed by two 1 : 1 [RE(α-SiW₁₁O₃₉)(H₂O)]^{5−} units and two acetate bridges. Each RE ion is eight-coordinate, adopting a distorted Archimedean antiprism geometry (pseudo-*D*_{4d}), with four oxygen atoms from one [RE(α-SiW₁₁O₃₉)(H₂O)]^{5−} anion, one water molecule, and three oxygen atoms from two bridging acetate ligands (Figure 5.2) [11].

5.2.1.2 1 : 1, 1 : 2, 2 : 2 RE/P₂W₁₇ Clusters

Two isomers [α1-P₂W₁₇O₆₁]^{10−} and [α2-P₂W₁₇O₆₁]^{10−} can be derived from the parent Wells–Dawson anion [α-P₂W₁₈O₆₂]^{6−} by removal of a “belt” or “cap” W = O_d unit, respectively. Complexes of RE ions with a lacunary [α-P₂W₁₇O₆₁]^{10−} anion were first reported by Peacock and Weakley in 1971, which is now known as [RE(α2-P₂W₁₇O₆₁)₂]^{n−}. The complex of the α1 isomer, [RE(α1-P₂W₁₇O₆₁)]^{n−}, has also been prepared, although it could not be isolated. Until

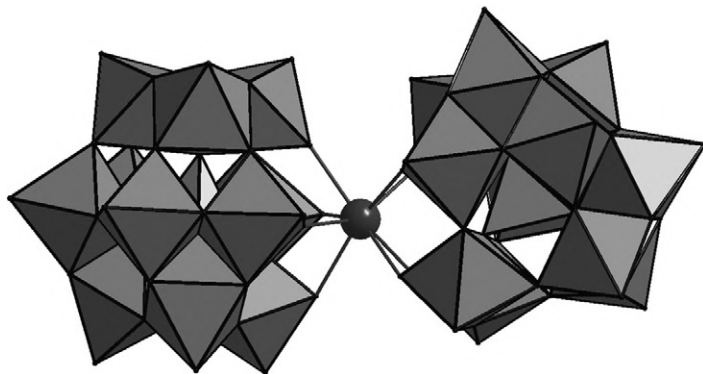


Figure 5.1 The structure of $[\text{La}(\beta\text{-SiW}_{11}\text{O}_{39})_2]^{13-}$ [10]. (Reprinted with permission from B.S. Bassil, *et al.*, "The monolanthanide-containing silicotungstates $[\text{Ln}(\beta\text{-SiW}_{11}\text{O}_{39})_2]^{13-}$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Yb}, \text{Lu}$): A synthetic and structural investigation," *Inorganic Chemistry*, **46**, no. 7, 2452–2458 (Figure 2), 2007. © 2007 American Chemical Society.)

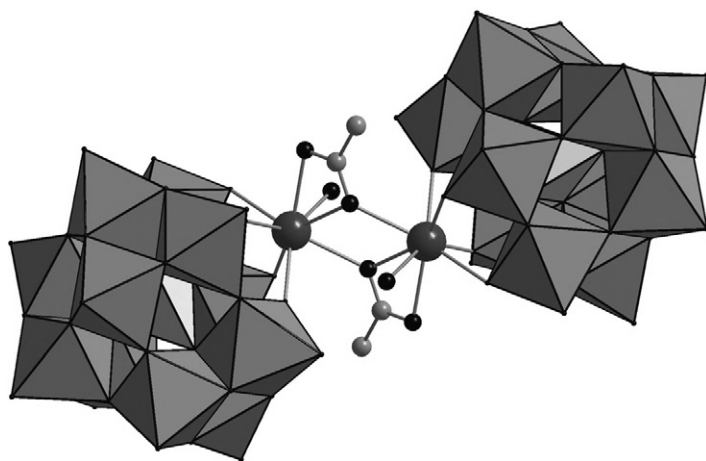


Figure 5.2 The structure of $[\{\text{Yb}(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})\}_2(\mu\text{-CH}_3\text{COO})_2]^{12-}$ [11]. (Reproduced with permission from P. Mialane, *et al.*, "Functionalization of polyoxometalates by a negatively charged bridging ligand: The dimeric $[(\text{SiW}_{11}\text{O}_{39}\text{Ln})_2(\mu\text{-CH}_3\text{COO})_2]^{12-}$ ($\text{Ln} = \text{GdIII}, \text{YbIII}$) complexes," *European Journal of Inorganic Chemistry*, 2004, no. 1, 33–36 (Figure 1). © Wiley-VCH Verlag GmbH & Co. KGaA.)

now, many RE complexes with a lacunary $[\alpha\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ anion have been synthesized and structurally characterized by single-crystal X-ray diffraction. The complexes are denoted as 1 : 1 (monomer), 2 : 2 (dimer) or 1 : 2 indicating the stoichiometry of the RE : $[\alpha\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$.

$[\text{Lu}(\text{H}_2\text{O})_4(\alpha\text{-P}_2\text{W}_{17}\text{O}_{61})]^{7-}$ is an example of 1 : 1 complexes of RE with $[\alpha\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$. In this complex, the lutetium ion is eight-coordinated in a square-antiprism geometry with four oxygen atoms surrounding the vacant site and four water molecules [12].

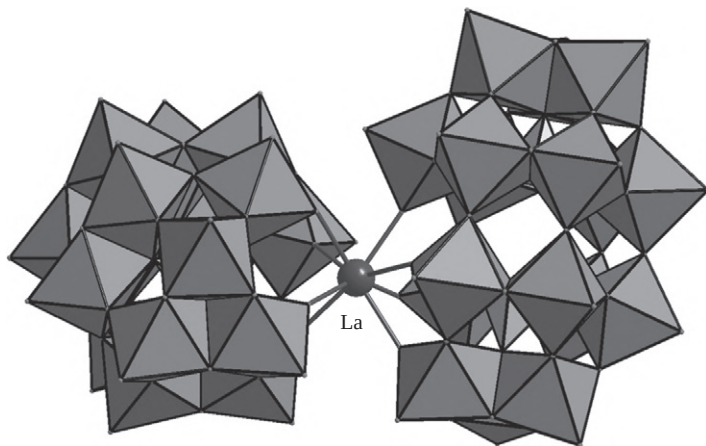


Figure 5.3 The structure of $[\text{La}(\alpha 1\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ [13]. (Reprinted with permission from L. Fieselmann, *et al.*, “Influence of steric and electronic properties of the defect site, lanthanide ionic radii, and solution conditions on the composition of lanthanide(III) $\alpha 1\text{-P}_2\text{W}_{17}\text{O}_{61}^{10-}$ polyoxometalates,” *Inorganic Chemistry*, **44**, no. 10, 3569–3578 (Figure 2), 2005. © 2005 American Chemical Society.)

The reported 1 : 2 species include $[\text{RE}(\alpha 1\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ ($\text{RE} = \text{La}, \text{Nd}, \text{Eu}, \text{Er}$) (Figure 5.3) [13], $[\text{RE}(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ ($\text{RE} = \text{Ce}, \text{Lu}$) [12, 14], and $[\text{Ce}(\alpha 1\text{-P}_2\text{W}_{17}\text{O}_{61})_2(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})]^{17-}$ [14]. In their structures, the RE ions are sandwiched between two $[\alpha\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ anions. The RE ions are coordinated by eight oxygen atoms, four from each of the two $[\alpha\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ anions. In addition, $[\text{H}_4\text{XW}_{18}\text{O}_{62}]^{7-}$ ($\text{X} = \text{P}, \text{As}$) has the same oxometalate skeleton as the Wells–Dawson anions. Reaction of trivalent cerium with lacunary versions of $[\text{H}_4\text{XW}_{18}\text{O}_{62}]^{7-}$ ($\text{X} = \text{P}, \text{As}$) yields the 1 : 2 complexes $[\text{Ce}(\text{H}_4\text{XW}_{17}\text{O}_{61})]^{19-}$ ($\text{X} = \text{P}, \text{As}$) [15]. The structures are similar to that observed for $[\text{RE}(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ ($\text{RE} = \text{Ce}, \text{Lu}$) but with “empty” O_4 tetrahedra that are in positions remote from the cerium ion.

Both of the 2 : 2 complexes $[\{\text{Ce}(\text{H}_2\text{O})_4(\alpha 1\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]^{14-}$ (Figure 5.4) [16] and $[\{\text{La}(\text{H}_2\text{O})_4(\alpha 1\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]^{14-}$ [17] are centrosymmetric dimers built by two $[\text{RE}(\text{H}_2\text{O})_4(\alpha 1\text{-P}_2\text{W}_{17}\text{O}_{61})]^{7-}$ ($\text{RE} = \text{Ce}$ or La) units. They have similar but not identical structures. In both cases, the RE cation is in a distorted monocapped square antiprism geometry, bound to the four oxygen atoms that surround the vacant site of one lacunary anion, to four water molecules, and to a terminal oxygen of the other lacunary anion. The nature of this $\text{W}=\text{O}$ group is distinct in the two complexes, whereas a $\text{W}=\text{O}$ in the belt region of the polyoxoanion is bound to cerium in the former case, a $\text{W}=\text{O}$ in the cap region is bound to lanthanum in the latter case.

$[\{\text{Ce}(\text{H}_2\text{O})_4(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]^{14-}$ [18] and $[\{\text{Eu}(\text{H}_2\text{O})_3(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]^{14-}$ [19] are two examples of 2 : 2 complexes of RE with $[\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$. Although both of them are dimers of the corresponding 1 : 1 units, they have different structures derived from the distinct linkage mode of the two 1 : 1 units. In the former complex, the linkage of the two $[\text{Ce}(\text{H}_2\text{O})_4(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})]^{7-}$ units occurs in a head-on fashion, via two $\text{Ce}-\text{O}-\text{W}$ bridges formed between each cerium ion and one terminal oxygen atom from a cap WO_6 octahedron of the other $[\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ anion (Figure 5.5). However, in the latter case, the linkage of the two $[\text{Eu}(\text{H}_2\text{O})_3(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})]^{7-}$ units occurs in a side-on fashion, via two $\text{Eu}-\text{O}-\text{W}$ bridges

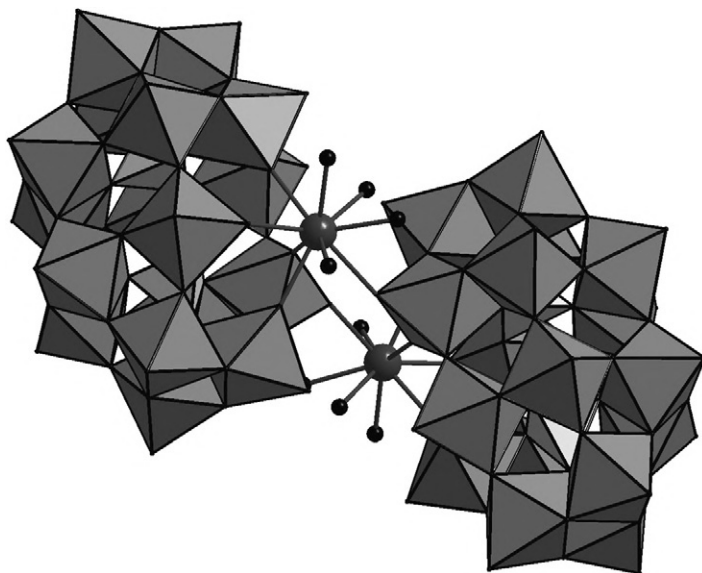


Figure 5.4 The structure of $[\{\text{Ce}(\text{H}_2\text{O})_4(\alpha 1\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]^{14-}$ [16]. (Reprinted with permission from M.H. Dickman, *et al.*, "Chiral polyoxotungstates. 1. Stereoselective interaction of amino acids with enantiomers of $[\text{Ce}^{\text{III}}(\alpha 1\text{-P}_2\text{W}_{17}\text{O}_{61})(\text{H}_2\text{O})_x]^{7-}$. The structure of $\text{DL-}[\text{Ce}_2(\text{H}_2\text{O})_8(\text{P}_2\text{W}_{17}\text{O}_{61})_2]^{14-}$," *Inorganic Chemistry*, **40**, no. 12, 2715–2719 (Figure 1), 2001. © 2001 American Chemical Society.)

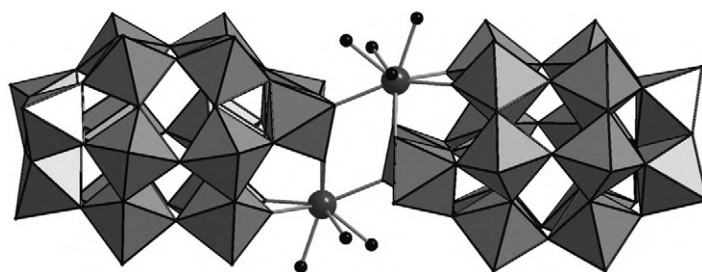


Figure 5.5 The structure of $[\{\text{Ce}(\text{H}_2\text{O})_4(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]^{14-}$ [18]. (Reprinted from M.T. Pope, *et al.*, "Formation of 1:1 and 2:2 complexes of Ce(III) with the heteropolytungstate anion $\alpha 2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$, and their interaction with proline. The structure of $[\text{Ce}_2(\text{P}_2\text{W}_{17}\text{O}_{61})_2(\text{H}_2\text{O})_8]^{14-}$," *Journal of the Chemical Society, Dalton Transactions*, 63–67 (Figure 1), 2002, by permission of The Royal Society of Chemistry.)

formed between each europium ion and one terminal oxygen atom from a belt WO_6 octahedron of the other $[\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ anion. $[\{\text{La}(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]^{16-}$ [20] is another 2 : 2 complex of the RE with $[\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$. It is composed of two 1 : 1 $[\text{La}(\text{H}_2\text{O})_2(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})]^{7-}$ units connected together by two acetate groups, which is different to the above two complexes where 1 : 1 units are linked by RE–O–W bridges. In the structure, each lanthanum ion occupies a distorted monocapped square-antiprism defined by

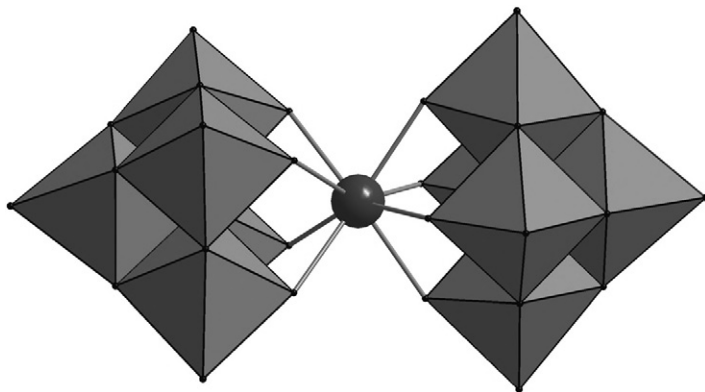


Figure 5.6 The structure of $[\text{La}(\text{W}_5\text{O}_{18})_2]^{9-}$ [21a]. (Reprinted from F.A. Almeida, *et al.*, “A lanthanum(III) complex with a lacunary polyoxotungstate: $\text{Na}_2(\text{NH}_4)_7[\text{La}(\text{W}_5\text{O}_{18})_2] \cdot 16\text{H}_2\text{O}$,” *Acta Crystallographica*, **E61**, i28–i31 (Figure 1), 2005, with permission from International Union of Crystallography (IUCr).)

four oxygen atoms provided by the lacunary anion, three oxygen atoms from two acetate groups, and two water molecules.

5.2.1.3 Sandwich Type RE–POM Clusters

Sandwich type RE–POM clusters, namely the clusters with one or more RE atoms sandwiched between two POM units, have been studied extensively. The aforementioned 1 : 2 complexes $[\text{RE}(\text{P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ are a form of sandwich type RE–POM clusters with one central RE atom. The other sandwich type RE–POM clusters with one central RE atom include a series of $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{n-}$ and $[\text{Ln}(\text{BW}_{11}\text{O}_{39})(\text{W}_5\text{O}_{18})]^{12-}$ clusters in addition to $[\text{La}(\text{Mo}_8\text{O}_{26})_2]^{5-}$ clusters. $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{n-}$ clusters, where $\text{Ln} = \text{La}^{3+}, \text{Ce}^{4+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}$ [21], consist of two $[\text{W}_5\text{O}_{18}]^{6-}$ anions linked together via a central lanthanum cation (Figure 5.6). The $[\text{W}_5\text{O}_{18}]^{6-}$ units can be viewed as monovacant Lindquist anions, which are derived from the Lindquist anion $[\text{W}_6\text{O}_{19}]^{2-}$ by removal of one $\text{W}=\text{O}$ group. Four oxygen atoms formerly bonded to the missing tungsten atom of each of two $[\text{W}_5\text{O}_{18}]^{6-}$ anions are bonded to the RE atom, resulting in the eight-coordinated square-antiprismatic coordination geometry of europium. $[\text{RE}(\text{BW}_{11}\text{O}_{39})(\text{W}_5\text{O}_{18})]^{12-}$ complexes ($\text{RE} = \text{Ce}^{3+}$ and Eu^{3+}) [22] are composed of a monovacant Lindquist anion $[\text{W}_5\text{O}_{18}]^{6-}$ and a monovacant Keggin anion $\alpha\text{-}[\text{BW}_{11}\text{O}_{39}]^{9-}$ bridged by a central RE atom. The RE atom is coordinated by four oxygen atoms from each of the lacunary anions leading to a square-antiprismatic LnO_8 configuration. In the structure of $[\text{La}(\text{Mo}_8\text{O}_{26})_2]^{5-}$, a lanthanum atom is sandwiched between two $[\beta\text{-Mo}_8\text{O}_{26}]^{3-}$ units and achieves eightfold square-antiprismatic coordination defined by two sets of four terminal oxygen atoms from the β -octamolybdate units.

$[(\text{Ce}(\text{IV})\text{O}_3)_3(\text{H}_2\text{O})_2(\text{A-}\alpha\text{-PW}_9\text{O}_{34})_2]^{12-}$ [23] is an example of sandwich type RE–POM clusters with three central RE atoms. The structure is composed of two trivacant Keggin anions $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ and a central belt of three cerium atoms alternating with three oxygen atoms. Three cerium atoms have two types of coordination: one is six-coordinated while

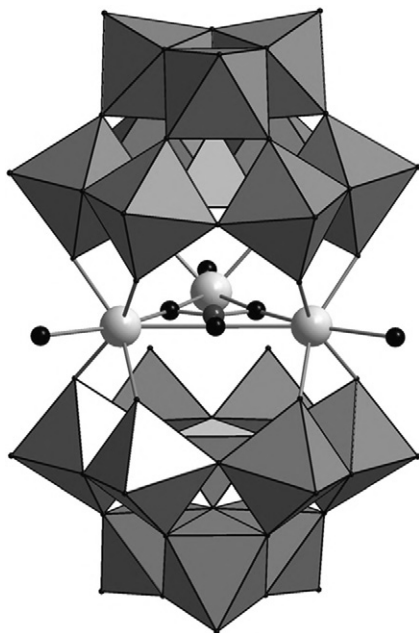


Figure 5.7 The structure of $[(YOH_2)_3(CO_3)(A-\alpha-PW_9O_{34})_2]^{11-}$ [25]. (Reprinted with permission from X.K. Fang, T.M. Anderson, W.A. Neiwert, and C.L. Hill, "Yttrium polyoxometalates. Synthesis and characterization of a carbonate-encapsulated sandwich-type complex," *Inorganic Chemistry*, **42**, no. 26, 8600–8602 (Figure 1), 2003. © 2003 American Chemical Society.)

the other two with external water ligands are seven-coordinated. Another sandwich cluster $[(H_2OCe(IV)O)_3(A-\alpha-AsW_9O_{34})_2]^{12-}$ [24] has a similar structure to $[(Ce(IV)O)_3(H_2O)_2(A-\alpha-PW_9O_{34})_2]^{12-}$, except for some differences in the coordination environments of the cerium atoms. The three cerium atoms in $[(H_2OCe(IV)O)_3(A-\alpha-AsW_9O_{34})_2]^{12-}$ have similar nine-fold tricapped trigonal-prismatic coordination and each cerium atom has an external water ligand. $[(YOH_2)_3(CO_3)(A-\alpha-PW_9O_{34})_2]^{11-}$ [25] is also an example of sandwich type RE–POM clusters with three RE atoms. The RE–POM skeleton of this complex is similar to the above two complexes. However, different from the above two complexes, there is a CO_3^{2-} that is encapsulated in the central $Y(III)_3$ belt and ligated by its oxygen atoms at the midpoints of the sides of the triangle formed by the yttrium ions. In the complex, each yttrium ion adopts an approximate YO_7 capped trigonal prism coordination geometry (Figure 5.7).

$[Yb(H_2O)(H_2OWO)_2(\alpha-As(III)W_9O_{33})_2]^{7-}$ [26] is a unique example of a sandwich type RE–POM cluster, because among the three sandwiched metal atoms only one is an RE atom while the other two are tungsten atoms. In the complex, two $[\alpha-As(III)W_9O_{33}]^{9-}$ fragments are bridged by a V-shaped $[Yb(H_2O)(H_2OWO)_2]$ belt leading to a structure with C_{2v} symmetry. Both tungsten atoms in the central belt of the structure are six-coordinated, whereas the ytterbium atom is seven-coordinated. All three sandwiched atoms have a terminal water ligand.

The structures with four or more RE atoms sandwiched by POM units have also been reported. $[Y_4(\mu_3-OH)_4(H_2O)_8](\alpha-P_2W_{15}O_{56})_2]^{16-}$ and $[Yb_6(\mu_6-O)(\mu_3-OH)_6(H_2O)_6]$

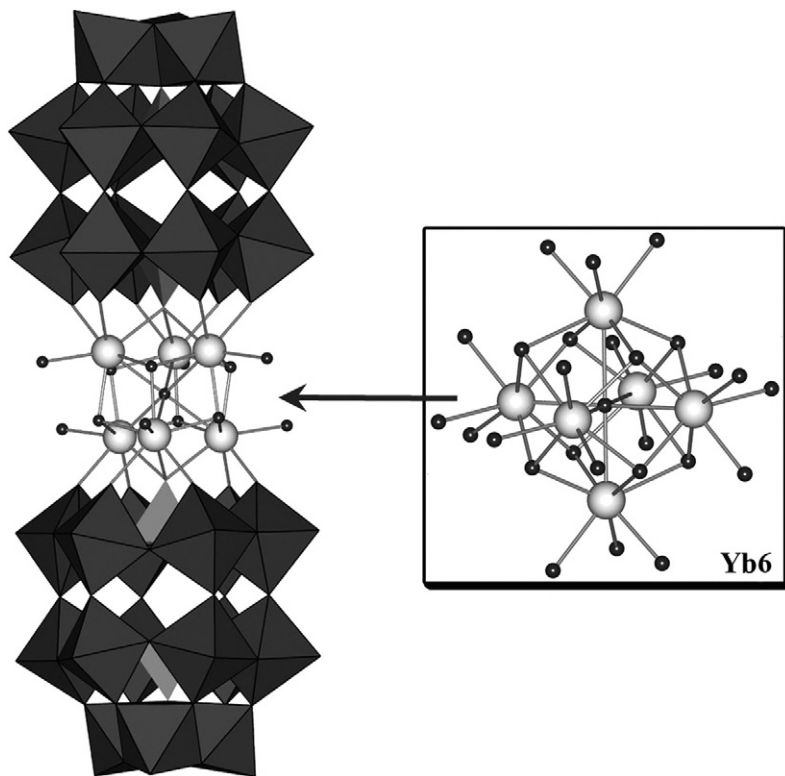


Figure 5.8 The structure of $\{[\text{Yb}_6(\mu_6\text{-O})(\mu_3\text{-OH})_6(\text{H}_2\text{O})_6](\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})_2\}^{14-}$ [27]. (Reproduced with permission from X.K. Fang, *et al.*, “Polyoxometalate-supported Y- and Yb^{III} -hydroxo/oxo clusters from carbonate-assisted hydrolysis,” *Chemistry - A European Journal*, 2005, **11**, no. 2, 712–718 (Figure 3). © Wiley-VCH Verlag GmbH & Co. KGaA.)

$(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})_2]^{14-}$ [27] are two sandwiched type clusters built by two trivacant Wells–Dawson anions $[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ and a central multinuclear RE unit. In the yttrium complex, the central $[\text{Y}_4(\text{OH})_4]^{8+}$ unit is a highly distorted cubane type core constructed by four yttrium ions connected via the $\mu_3\text{-OH}$ bridges. Each yttrium atom adopts a triangularly distorted dodecahedral geometry defined by three $\mu_3\text{-OH}$ groups, two oxygen atoms from two different WO_6 octahedra, one oxygen atom from a PO_4 tetrahedron, and two terminal aqua ligands. While in the ytterbium complex, the central $[\text{Yb}_6(\mu_6\text{-O})(\mu_3\text{-OH})_6(\text{H}_2\text{O})_6]^{10+}$ unit is a hexametallic core centered around a $\mu_6\text{-oxo}$ atom with each $\text{Yb}(\text{III})_3$ triangular face capped by an oxo or a hydroxo group (Figure 5.8).

$[\text{Ce}_4(\text{OH}_2)_9(\text{OH})_2(\text{P}_2\text{W}_{16}\text{O}_{59})_2]^{14-}$ [28] is a cluster with C_{2v} virtual symmetry, in which four cerium ions are sandwiched between two novel lacunary anions $[\text{P}_2\text{W}_{16}\text{O}_{59}]^{16-}$. The $[\text{P}_2\text{W}_{16}\text{O}_{59}]^{16-}$ anion is a divacant derivative of a Wells–Dawson $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ anion, with the lacunae in adjacent belt ($\alpha 1$) sites on either side of the anion’s belt. In the complex, the four central cerium ions are linked by two $\mu_3\text{-OH}(\text{Ce}_3)$, one $\mu_2\text{-H}_2\text{O}(\text{Ce}_2)$, and four $\mu_3\text{-O}(\text{W}, \text{Ce}_2)$. There are two distinct cerium coordination environments. The two cerium atoms

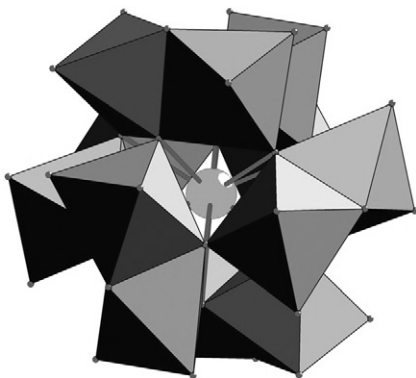


Figure 5.9 The structure of a Silverton type anion [30]. (Reprinted with permission from D.D. Dexter, and J.V. Silverton, "A new structural type for heteropoly anions. The crystal structure of $(\text{NH}_4)_2\text{H}_6(\text{CeMo}_{12}\text{O}_{42}) \cdot 12\text{H}_2\text{O}$," *Journal of the American Chemical Society*, **90**, no. 13, 3589–3590 (Figure 1), 1968. © 1968 American Chemical Society.)

positioned midway between the lacunae of each $[\text{P}_2\text{W}_{16}\text{O}_{59}]^{16-}$ are ten-coordinate and adopt a bicapped cubic geometry. The other cerium atoms positioned between the $[\text{P}_2\text{W}_{16}\text{O}_{59}]^{16-}$ units are nine-coordinate with a tricapped trigonal prism geometry.

5.2.1.4 POM Clusters with RE Ions in the Center

$[\text{GdMo}_6(\text{CH}_3\text{CHOCOO})_6\text{O}_{15}]^{3-}$ is a spherical cluster encapsulating a gadolinium(III) at the center. The structure is composed of six $\{\text{Mo}(\text{CH}_3\text{CHOCOO})\text{O}_{2.5}\}$ units and a nine-coordinate gadolinium atom in D_3 symmetry [29].

The anion $[\text{REMo}_{12}\text{O}_{42}]^{n-}$ ($\text{RE} = \text{Ce}^{3+}$, Ce^{4+}) consists of six Mo_2O_9 units and a 12-coordinate RE atom, which is called a Silverton type anion. In the anion, the Mo_2O_9 units composed of two face-sharing MoO_6 octahedra are linked together by corner sharing (Figure 5.9) [30].

$[\text{REP}_5\text{W}_{30}\text{O}_{110}]^{n-}$ ($\text{RE} = \text{Ce}$, Nd–Lu; $n = 11$ or 12) is derived from the Preyssler anion $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ through the substitution of the central sodium ion by an RE ion. In the anion, five PW_6O_{22} units arrange around a central RE ion leading to a doughnut-shaped cluster [31].

$[\text{Ce(III)(H}_2\text{O)}_5\text{As}_4\text{W}_{40}\text{O}_{140}]^{25-}$ can be viewed as a cyclic cluster $[\text{As}_4\text{W}_{40}\text{O}_{140}]^{28-}$ with a cerium atom in the central site. The structure of $[\text{As}_4\text{W}_{40}\text{O}_{140}]^{28-}$ is constructed by four $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ units linked through four additional WO_6 octahedra. The central cerium atom is nine-coordinate, adopting a monocapped square-antiprism geometry, with four terminal oxygen atoms of the $[\text{As}_4\text{W}_{40}\text{O}_{140}]^{28-}$ anion (one from each of the four bridging WO_6 octahedra) and five water molecules [32].

Different to the above-mentioned compounds with mononuclear RE ion at the center, $[\text{H}_6\text{Ce}_2(\text{H}_2\text{O})\text{Cl}(\text{W}_5\text{O}_{18})_3]^{7-}$ is an example of a polyanion with a central dinuclear RE unit. $[\text{H}_6\text{Ce}_2(\text{H}_2\text{O})\text{Cl}(\text{W}_5\text{O}_{18})_3]^{7-}$ has an approximate C_3 symmetry. The anion consists of a dinuclear cerium unit $\{\text{Ce}_2\text{O}_{13}(\text{H}_2\text{O})\text{Cl}\}$ and 15-membered ring of WO_6 units constructed by three

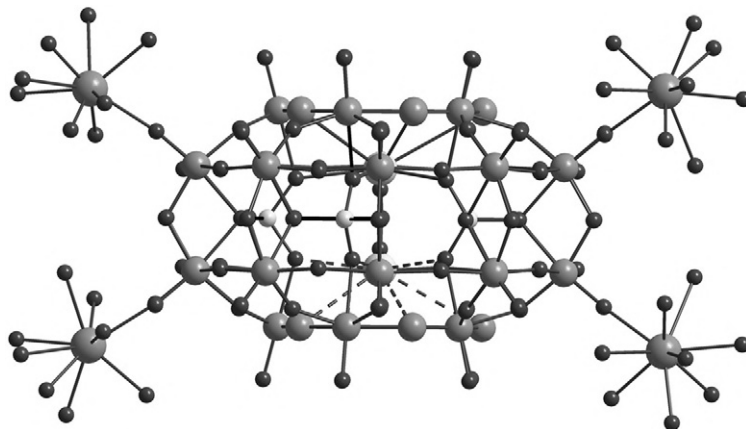


Figure 5.10 The structure of $\{[\text{Ce}(\text{H}_2\text{O})_8]_4\{\text{Na}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}\}\}^{2-}$ cluster [35]. (Reprinted from *Inorganica Chimica Acta*, **360**, no. 6, Y. Lu, Y.G. Li, *et al.*, “A new family of polyoxometalate compounds built up of Preyssler anions and trivalent lanthanide cations,” 2063–2070 (Figure 1), 2007, with permission from Elsevier.)

$\{\text{W}_5\text{O}_{18}\}$ units. The $\{\text{W}_5\text{O}_{18}\}$ unit is built by three edge-sharing WO_6 with two corner-sharing WO_6 octahedra [33].

5.2.1.5 POM Clusters with Capping or Supporting RE Ions

$[\varepsilon\text{-PMo}_{12}\text{O}_{36}(\text{OH})_4\{\text{La}(\text{H}_2\text{O})_4\}_4]^{5+}$ is a cationic cluster composed of a ε -Keggin core $[\varepsilon\text{-PMo}_{12}\text{O}_{36}(\text{OH})_4]^{7-}$ and four $[\text{La}(\text{H}_2\text{O})_4]^{3+}$ capping groups. In the cluster, each lanthanum atom is situated in one of the four faces of the truncated tetrahedron defined by the 12 molybdenum atoms of the ε -Keggin core, which is seven coordinated with three oxygen atoms from ε -Keggin core and four water molecules [34].

The anionic cluster $\{[\text{Ce}(\text{H}_2\text{O})_8]_4\{\text{Na}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}\}\}^{2-}$ consists a Preyssler anion $[\text{Na}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}]^{14-}$ and four $\{\text{Ce}(\text{H}_2\text{O})_8\}^{3+}$ supporting fragments (Figure 5.10). Each cerium atom is coordinated by one oxygen atom from the Preyssler unit and eight water ligands to complete its distorted tricapped trigonal prism coordination environment [35].

The $\{[\text{Nd}(\text{H}_2\text{O})_7]_2\{\text{Nd}(\text{H}_2\text{O})_3(\alpha\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2\}^{8-}$ cluster is composed of a dimeric $[\{\text{Nd}(\text{H}_2\text{O})_3(\alpha\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]^{14-}$ entity and two $\{\text{Nd}(\text{H}_2\text{O})_7\}^{3+}$ supporting groups. The centrosymmetric $[\{\text{Nd}(\text{H}_2\text{O})_3(\alpha\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]^{14-}$ dimer is made of two $[\text{P}_2\text{W}_{17}\text{NdO}_{62}]^{9-}$ subunits connected through two Nd–O–W bridges [36].

5.2.1.6 Large-Sized RE–POM Clusters

RE–POM clusters with a large size are normally composed of several equivalent or nonequivalent POM building units (for example, XW_9 and XW_{10} in a large RE–tungstate cluster, Mo_7 and Mo_8 in a large RE–molybdate cluster) with RE atoms as linkers or decorate groups.

Trivacant Keggin fragments $[\text{B-}\alpha\text{-X(III)W}_9\text{O}_{33}]^{9-}$ ($\text{X} = \text{As, Sb, Bi}$), formed when the heteroatom X possesses a lone pair of electrons, is the most common building unit of large

RE-tungstate clusters. $[\text{B-}\alpha\text{-X(III)W}_9\text{O}_{33}]^{9-}$ is derived from an α -Keggin anion $[\text{XW}_{12}\text{O}_{40}]^{n-}$ by removal of three edge-sharing WO_6 octahedra.

$[\text{As}_3\text{Ln}_2(\text{H}_2\text{O})_7\text{W}_{29}\text{O}_{103}]^{17-}$ ($\text{Ln} = \text{La}, \text{Ce}$) is composed of three $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ units linked by two cerium atoms and two additional tungsten atoms. One cerium has eight-fold square-antiprismatic coordination and the other has ninefold tricapped-trigonal prism coordination [37].

In the structure of $[\text{Eu}_3(\text{H}_2\text{O})_3(\text{Sb(III)W}_9\text{O}_{33})(\text{W}_5\text{O}_{18})_3]^{18-}$, a central $[\text{Eu}_3(\text{H}_2\text{O})_3]^{9+}$ core is linked tetrahedrally by three $[\text{W}_5\text{O}_{18}]^{6-}$ groups and one $[\text{B-}\alpha\text{-Sb(III)W}_9\text{O}_{33}]^{9-}$ group. Each europium atom is eight-coordinated with four oxygen atoms from one W_5O_{18} , two oxygen atoms from one $\text{Sb(III)W}_9\text{O}_{33}$ and two water ligands [38].

$[(\text{H}_2\text{O})_{10}\text{RE(III)(RE(III)}_2\text{OH)(B-}\alpha\text{-AsO}_3\text{W}_9\text{O}_{30})_4(\text{WO}_2)_4]_2^{40-}$ ($\text{RE} = \text{Ce}, \text{Sm}, \text{and Gd}$) exhibits a dimeric structure constructed by two half units of $[(\text{H}_2\text{O})_{10}\text{RE(RE}_2\text{OH)(B-}\alpha\text{-AsO}_3\text{W}_9\text{O}_{30})_4(\text{WO}_2)_4]^{20-}$ linked via W-O-RE bridges. The half unit can be viewed as a cyclic anion $[(\text{B-}\alpha\text{-AsW}_9\text{O}_{33})_4(\text{WO}_2)_4]^{28-}$ ("As₄W₄₀") encapsulating three RE atoms. The $[(\text{B-}\alpha\text{-AsW}_9\text{O}_{33})_4(\text{WO}_2)_4]^{28-}$ anion possesses three types of inner sites (denoted as S1, S2, and S3) available for accommodating external metal ions. In the half unit $[(\text{H}_2\text{O})_{10}\text{RE(RE}_2\text{OH)(B-}\alpha\text{-AsO}_3\text{W}_9\text{O}_{30})_4(\text{WO}_2)_4]^{20-}$, two RE atoms occupy two adjacent S2 sites, which are eight-coordinated in a distorted square-antiprism geometry; while the third RE atom occupies the S3 site, which is nine-coordinated in a monocapped square-antiprism geometry [39].

$[\text{As(III)}_{12}\text{Ce(III)}_{16}(\text{H}_2\text{O})_{36}\text{W}_{148}\text{O}_{524}]^{76-}$ exhibits a folded cyclic structure composed of 12 $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ units connected by WO_6 and $\text{CeO}_{8,9}$ polyhedra and decorated by four $[\text{CeW}_5\text{O}_{18}]^{3-}$ groups (Figure 5.11). In the structure, there are three types of cerium atoms: four of type (a) sandwiched between a $[\text{W}_5\text{O}_{18}]^{6-}$ group and a $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ unit, with eight of type (b) shared between two $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ units, which are eight-coordinated, while four of type (c), bridging three $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ units, are nine-coordinated [40].

$[\text{Ce}_4\text{As}_4\text{W}_{44}\text{O}_{151}(\text{ala})_4(\text{OH})_2(\text{H}_2\text{O})_{10}]^{12-}$ ($\text{ala} = \text{alanine}$) possesses a cryptand type structure based on four $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ building blocks, two $\{\text{WO}_2\}$ segments, two $\{\text{W}_2\text{O}_5(\text{ala})\}$ moieties, two $\{\text{Ce}_2(\text{H}_2\text{O})_5(\text{ala})\}$ linkers, and a linear $\{\text{W}_2\text{O}_5(\text{OH})_2\}$ dimer. In the cluster, two $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ units are linked to each other by an octahedral $\{\text{WO}_2\}$ unit via the corner-sharing mode, leading to a $\{\text{As}_2\text{W}_{19}\}$ segment. Two such $\{\text{As}_2\text{W}_{19}\}$ units are further connected through corner sharing by two $\{\text{W}_2\text{O}_5(\text{ala})\}$ linkers to form a cryptand structure. A linear $\{\text{W}_2\text{O}_5(\text{OH})_2\}$ dimer is situated in the center and four cerium atoms are located in the remnant vacant site at the $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ units of the forming cryptand structure [41].

$[\text{Mn}(\text{H}_2\text{O})_4(\text{Ce}_4\text{As}_4\text{W}_{41}\text{O}_{149})_2]^{46-}$ exhibits a dimeric structure constructed by two $[\text{Ce}_4\text{As}_4\text{W}_{41}\text{O}_{149}]^{24-}$ anions linked via a $[\text{Mn}(\text{H}_2\text{O})_4]^{2+}$ linker. In the structure of the $[\text{Ce}_4\text{As}_4\text{W}_{41}\text{O}_{149}]^{24-}$ anion, four $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ fragments are connected by four cerium atoms forming a cryptand cluster, and five additional tungsten atoms are encapsulated in the cryptand cluster. One tungsten atom is situated in the center of the cryptand cluster and the others are located in the lacunary sites of four $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ fragments [41].

$[\text{K} \subset \{\text{Eu}(\text{H}_2\text{O})_2(\alpha\text{-AsW}_9\text{O}_{33})\}_6]^{35-}$ and $[\text{Cs} \subset \{\text{Eu}(\text{H}_2\text{O})_2(\alpha\text{-AsW}_9\text{O}_{33})\}_4]^{23-}$ are two cyclic clusters that encapsulate an alkali metal cation in the center (Figure 5.12). The former is a potassium ion encapsulated cluster formed by the alternating connection of six $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ units and six europium atoms, whereas the latter is cesium ion encapsulated cluster resulting from the alternating linkage of four $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ units and four europium

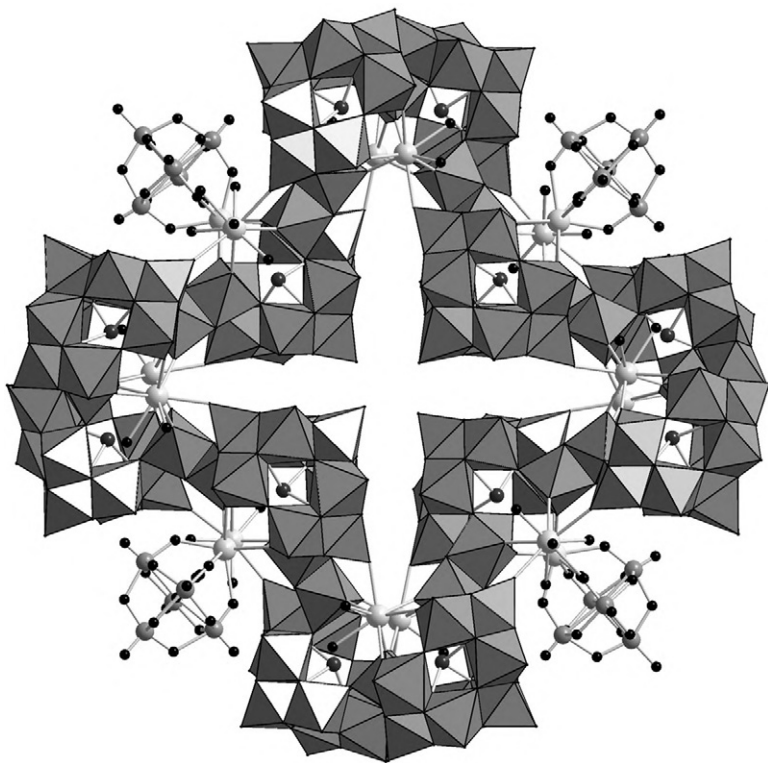


Figure 5.11 The structure of $[\text{As(III)}_{12}\text{Ce(III)}_{16}(\text{H}_2\text{O})_{36}\text{W}_{148}\text{O}_{524}]^{76-}$ cluster [40]. (Reproduced with permission from K. Wassermann, M.H. Dickman, and M.T. Pope, "Self-assembly of supramolecular polyoxometalates: the compact, water-soluble heteropolytungstate anion $[\text{As}_{12}^{\text{III}}\text{Ce}_{16}^{\text{III}}(\text{H}_2\text{O})_{36}\text{W}_{148}\text{O}_{524}]^{76-}$. *Angewandte Chemie (International Edition in English)*, 1997, **36**, 1445–1448. © Wiley-VCH Verlag GmbH & Co. KGaA.)

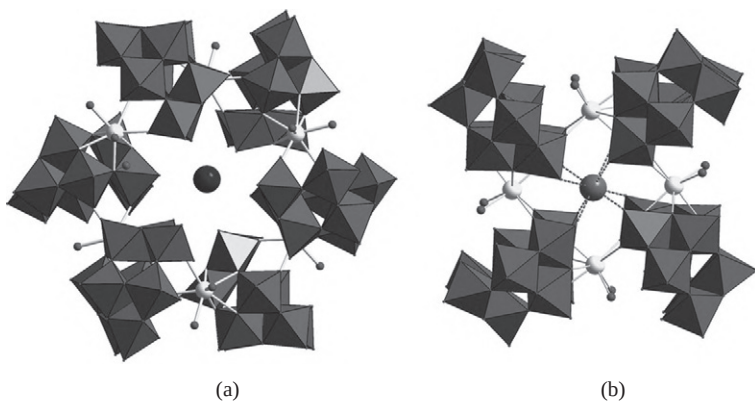


Figure 5.12 The structures of (a) $[\text{K}\{\text{Eu}(\text{H}_2\text{O})_2(\alpha\text{-AsW}_9\text{O}_{33})\}_6]^{35-}$ and (b) $[\text{Cs}\{\text{Eu}(\text{H}_2\text{O})_2(\alpha\text{-AsW}_9\text{O}_{33})\}_4]^{23-}$ [42]. (Reproduced with permission from K. Fukaya, and T. Yamase, "Alkali-metal-controlled self-assembly of crown-shaped ring complexes of lanthanide/ $[\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$: $[\text{K}\{\text{Eu}(\text{H}_2\text{O})_2(\alpha\text{-AsW}_9\text{O}_{33})\}_6]^{35-}$ and $[\text{Cs}\{\text{Eu}(\text{H}_2\text{O})_2(\alpha\text{-AsW}_9\text{O}_{33})\}_4]^{23-}$," *Angewandte Chemie International Edition*, 2003, **42**, no. 6, 654–658 (Figure 1). © Wiley-VCH Verlag GmbH & Co. KGaA.)

atoms. In the two clusters, each europium is eight-coordinated with six oxygen atoms from adjacent two $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ units and two water molecules [42].

$[\{\text{Ce}(\text{IV})_2\text{O}(\text{H}_2\text{O})_5\}\{\text{WO}(\text{H}_2\text{O})\}\{\text{AsW}_9\text{O}_{33}\}_2]^{16-}$ is a dimeric anion composed of two half units $[\{\text{Ce}(\text{IV})_2\text{O}(\text{H}_2\text{O})_5\}\{\text{WO}(\text{H}_2\text{O})\}\{\text{AsW}_9\text{O}_{33}\}_2]^{8-}$ connected via two Ce–O–W bridges. The half unit exhibits a sandwich type structure constructed by two $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ fragments and a central $[\{\text{Ce}_2\text{O}(\text{H}_2\text{O})_5\}\{\text{WO}(\text{H}_2\text{O})\}]^{10+}$ belt. Each tungsten atom in the central belt is coordinated with four oxygen atoms from two $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ fragments, one μ -O atom, and one coordinated water molecule, showing an octahedral coordination geometry. Each cerium center is coordinated with four terminal oxygen atoms from two $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ fragments, one μ -O bridge, one surface oxygen atom from the adjacent half unit, and three coordinated water molecules, possessing a nine-coordination environment [41].

$[\text{Ho}_5(\text{H}_2\text{O})_{16}(\text{OH})_2\text{As}_6\text{W}_{64}\text{O}_{220}]^{25-}$ is a linear cluster composed of six $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ fragments linked by a $[\text{Ho}_5\text{W}_{10}(\text{H}_2\text{O})_{16}(\text{OH})_2\text{O}_{22}]^{29-}$ belt. The five holmium atoms are eight-coordinated with a square-antiprism geometry [43].

$[\text{Ce}(\text{III})_3\text{Sb}_4\text{W}_2\text{O}_8(\text{H}_2\text{O})_{10}(\text{SbW}_9\text{O}_{33})_4]^{19-}$ consists of four $[\text{B-}\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ fragments linked by two additional W atoms, three cerium atoms, and a $\{\text{Sb}_4(\mu_3\text{-O})(\mu_2\text{-O})_3\}^{4+}$ group in a dissymmetrical way. In the structure, three $[\text{B-}\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ fragments are connected by two additional W atoms and one cerium atom leading to a trilobed subunit $[\text{CeW}_2\text{O}_4(\text{H}_2\text{O})_4(\text{SbW}_9\text{O}_{33})_4]^{20-}$. This subunit is linked to the fourth $[\text{B-}\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ fragment through the other two cerium atoms and an antimony cluster $\{\text{Sb}_4(\mu_3\text{-O})(\mu_2\text{-O})_3\}^{4+}$ [32].

The anion $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$, derived from an α -Keggin anion by removal of three corner-shared WO_6 octahedra, can also be used as a building unit to construct large RE–POM clusters. The cluster $[(\text{PRE}_2\text{W}_{10}\text{O}_{38})_4(\text{W}_3\text{O}_{14})]^{30-}$ (RE = Eu, Y) is an assembly of four $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ fragments, eight RE atoms, and seven additional tungsten atoms. In the cluster, each $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ fragment connects with a distorted M_2WO_3 six-membered ring to create a distorted Keggin-like $[\text{PRE}_2\text{W}_{10}\text{O}_{38}]^{5-}$ unit. Four such Keggin-like units are linked together by means of a $[\text{W}_3\text{O}_{14}]^{10-}$ unit [44].

Some large clusters with bivalent Keggin building units have been obtained. The cluster $[\text{Kc}\{\text{FeCe}(\text{AsW}_{10}\text{O}_{38})(\text{H}_2\text{O})_2\}_3]^{15-}$ possesses a cryptand type structure based on three bivalent Keggin units $[\alpha\text{-AsW}_{10}\text{O}_{38}]^{11-}$, three $\{\text{Fe-O}_3\text{-Ce}\}$ linkers, and a potassium ion encapsulated in the center (Figure 5.13). In the cluster, all iron atoms and cerium atoms are located in the lacunas of the three $[\alpha\text{-AsW}_{10}\text{O}_{38}]^{11-}$ units. Each iron center shows a hexa-coordinated octahedral geometry with six oxygen atoms derived from two $[\alpha\text{-AsW}_{10}\text{O}_{38}]^{11-}$ units, whereas each cerium center is coordinated with six oxygen atoms derived from two $[\alpha\text{-AsW}_{10}\text{O}_{38}]^{11-}$ units and two coordinated water molecules, exhibiting an eight-coordinated environment [45].

$[\text{Ce}_{20}\text{Ge}_{10}\text{W}_{100}\text{O}_{376}(\text{OH})_4(\text{H}_2\text{O})_{30}]^{56-}$ can be viewed as a dimeric entity formed by two half units of $[\text{Ce}_{10}\text{Ge}_5\text{W}_{50}\text{O}_{188}(\text{OH})_2(\text{H}_2\text{O})_{15}]^{28-}$ linked through Ce–O–W bridges. Each half unit is composed of five bivalent $[\beta(4,11)\text{-GeW}_{10}\text{O}_{38}]$ units linked asymmetrically by ten cerium atoms situated in the vacant sites of the five $[\beta(4,11)\text{-GeW}_{10}\text{O}_{38}]$ units (Figure 5.14). There are two types coordination number for the ten cerium atoms: two are nine-coordinated and the others are eight-coordinated [46].

$[\text{Ce}(\text{IV})_2(\text{PW}_{10}\text{O}_{38})(\text{PW}_{11}\text{O}_{39})_2]^{17-}$ is a V-shaped cluster composed of one bivalent $[\text{PW}_{10}\text{O}_{38}]^{11-}$ unit, two monovacant $[\text{PW}_{11}\text{O}_{39}]^{7-}$ units, and two cerium atoms. In the cluster, 1,4-bivalent $[\text{PW}_{10}\text{O}_{38}]^{11-}$ unit, located in the middle, connects to two monovacant $[\text{PW}_{11}\text{O}_{39}]^{7-}$ units through the two cerium atoms situated in its lacunas [47].

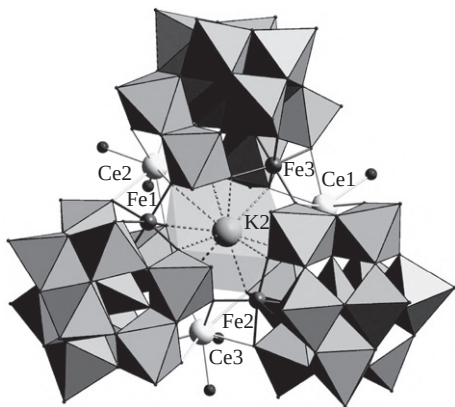


Figure 5.13 The structure of $[\text{K}\{\text{FeCe}(\text{AsW}_{10}\text{O}_{38})(\text{H}_2\text{O})_2\}_3]^{15-}$ cluster [45]. (Reprinted from Chen, W.L. et al., "A new polyoxometalate-based 3d–4f heterometallic aggregate: a model for the design and synthesis of new heterometallic clusters," *Dalton Transactions*, 865–867 (Figure 1), 2008, by permission of The Royal Society of Chemistry.)

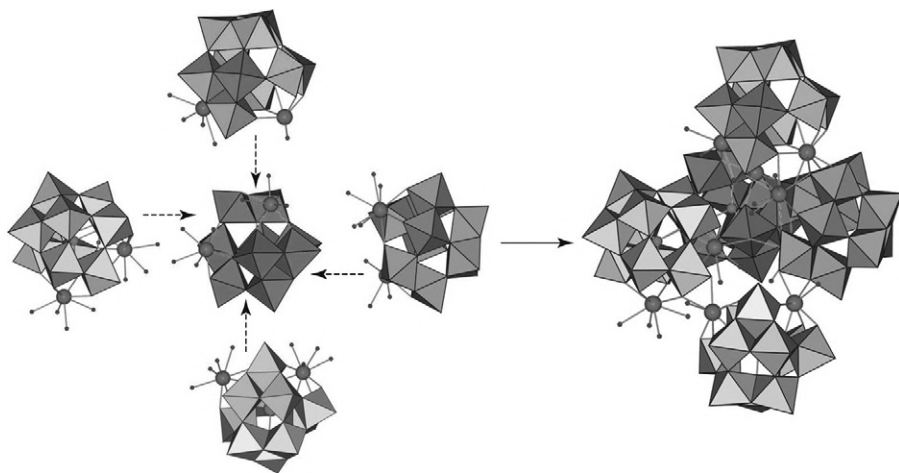


Figure 5.14 The structure of the $[\text{Ce}_{10}\text{Ge}_5\text{W}_{50}\text{O}_{188}(\text{OH})_2(\text{H}_2\text{O})_{15}]^{28-}$ half unit. [46]. (Reproduced with permission from B.S. Bassil, et al., "The tungstogermanate $[\text{Ce}_{20}\text{Ge}_{10}\text{W}_{100}\text{O}_{376}(\text{OH})_4(\text{H}_2\text{O})_{30}]^{56-}$: a polyoxometalate containing 20 cerium(III) atoms," *Angewandte Chemie International Edition*, 2007, 46, no. 32, 6192–6195 (Figure 2). © Wiley-VCH Verlag GmbH & Co. KGaA.)

$[\{\text{Yb}(\text{SiW}_{11}\text{O}_{39})\}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4]^{26-}$ can be viewed as tetrameric entity formed by four $[\text{YbSiW}_{11}\text{O}_{39}]^{5-}$ units bridged through oxalato groups $\text{C}_2\text{O}_4^{2-}$. In the complex, two $[\text{YbSiW}_{11}\text{O}_{39}]^{5-}$ units are linked with each other in a head-on mode through one $\text{C}_2\text{O}_4^{2-}$ group to form a dimeric unit $[(\text{YbSiW}_{11}\text{O}_{39})_2(\text{C}_2\text{O}_4)]^{12-}$, and two such dimers are further connected by another $\text{C}_2\text{O}_4^{2-}$ ligand in a side-on mode to generate a tetrameric cluster. A similar structural cluster $[\{\text{Yb}(\alpha\text{-P}_2\text{W}_{17}\text{O}_{61})\}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4]^{34-}$, formed by exchange of a monovacant

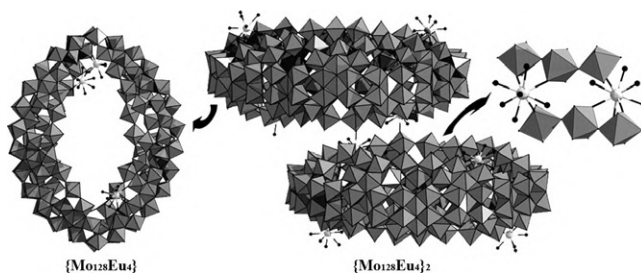


Figure 5.15 The structure of the $[\{Mo_{128}Eu_4O_{388}H_{10}(H_2O)_{81}\}_2]^{20-}$ cluster [52]. (Reproduced with permission from L. Cronin, *et al.*, “Molecular symmetry breakers generating metal-oxide-based nanoobject fragments as synthons for complex structures: $[\{Mo_{128}Eu_4O_{388}H_{10}(H_2O)_{81}\}_2]^{20-}$, a giant-cluster dimer,” *Angewandte Chemie International Edition*, 2002, **41**, no. 15, 2805–2808 (Figure 1). © Wiley-VCH Verlag GmbH & Co. KGaA.)

Keggin anion $[SiW_{11}O_{39}]^{8-}$ by a monovacant Wells–Dawson anion $[\alpha\text{-}P_2W_{17}O_{61}]^{10-}$, has also been reported [48].

Several large RE–molybdate have also been reported. $[Eu_4(H_2O)_{16}(MoO_4)(Mo_7O_{24})_4]^{14-}$ is an RE–molybdate cluster with a D_{2d} symmetry, which is composed of a central $[Eu_4(H_2O)_{16}(MoO_4)]^{10+}$ unit and four $\{Mo_7O_{24}\}$ fragments. In the $[Eu_4(H_2O)_{16}(MoO_4)]^{10+}$ unit, four europium atoms arrange around a central MoO_4 tetrahedron. Each europium atom is nine-coordinate, with one oxygen atom from the MoO_4 tetrahedron, two oxygen atoms from one $\{Mo_7O_{24}\}$ group, and four water ligands [49]. $[Pr_4(MoO_4)(H_2O)_{13}(Mo_7O_{24})_4]_2^{28-}$ is a dimer of $[Pr_4(MoO_4)(H_2O)_{13}(Mo_7O_{24})_4]^{14-}$ entities, which possess similar structure to $[Eu_4(H_2O)_{16}(MoO_4)(Mo_7O_{24})_4]^{14-}$. The two $[Pr_4(MoO_4)(H_2O)_{13}(Mo_7O_{24})_4]^{14-}$ are linked together via Eu–O–W bridges [50].

$[Mo_{120}O_{366}(H_2O)_{48}H_{12}\{Pr(H_2O)_5\}_6]^{6-}$ possesses a wheel-shaped structure constructed from 12 $\{Mo_1\}$, six $\{Mo_2\}$, and 12 $\{Mo_8\}$ building units. In addition, there are six ninefold-coordinated praseodymium atoms that are linked to the inner surface of the wheel-shaped cluster [51].

$[\{Mo_{128}Eu_4O_{388}H_{10}(H_2O)_{81}\}_2]^{20-}$ exhibits a dimeric structure constructed from two $[Mo_{128}Eu_4O_{388}H_{10}(H_2O)_{81}]^{10-}$ anions linked by two Eu–O–Mo bridges (Figure 5.15). Each $[Mo_{128}Eu_4O_{388}H_{10}(H_2O)_{81}]^{10-}$ anion is an ellipsoidal cluster composed of 12 $\{Mo_1\}$, eight $\{Mo_2\}$, four $\{Mo_8\}$, four $\{Mo_7\}$, four $\{Mo_9\}$ and two $\{Mo_2^*\}$ building units, plus four Eu atoms [52].

$[Eu_3O(OH)_3(OH_2)_3]_2Al_2(Nb_6O_{19})_5]^{26-}$ is a rare RE–niobate cluster of large size. In the cluster, five Lindquist anions $[Nb_6O_{19}]^{8-}$ are interconnected by two $\{Eu_3O(OH)_3(OH_2)_3\}^{4+}$ units and two aluminum centers leading to a structure with approximate D_3 symmetry. There are two types of $[Nb_6O_{19}]^{8-}$ units in the structure, two axial ones on the threefold axis, and three equatorial units on the twofold axes. Two $\{Eu_3O(OH)_3(OH_2)_3\}^{4+}$ units arranged in parallel are in the center of the cluster anion, both of which are bound directly to three equatorial $[Nb_6O_{19}]^{8-}$ units via Nb–O–Eu bridges and each of which is linked to one axial $[Nb_6O_{19}]^{8-}$ unit via a bridging aluminum center [53].

At the end of this section, there are two points that should be stated. (i) The RE–POM clusters described here are mainly those with complete structural characterization among a

series of reported analogs with different RE atoms. (ii) The structures of RE–POM clusters described here are determined in the solid state. Several studies have shown some clusters are unstable in aqueous solution and are present as “monomeric” species, such as $[\{\text{Eu}(\text{H}_2\text{O})_3(\alpha\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]^{14-}$ dissociates in solution to form monomeric $[\text{Eu}(\text{H}_2\text{O})_4(\alpha\text{-P}_2\text{W}_{17}\text{O}_{61})]^{7-}$ species [19].

5.2.2 Extending Structural RE–POMs Complexes

Various POM clusters can act as building units and are connected by RE linkers into one-, two-, three-dimensional structural RE–POM complexes. In reported extending structural RE–POMs complexes, various POM building blocks participate in the structural construction as discrete clusters, whereas RE linkers participate in the structural construction as diverse modes, including hydrated RE ions, discrete RE–organo clusters, and one-, two-, three-dimensional structural RE–organopolymers.

5.2.2.1 Anderson Type Anions as Building Units

An Anderson type anion is made up of seven edge-sharing octahedra, six of which are $\{\text{MoO}_6\}$ octahedra arranged hexagonally around the central $\{\text{XO}_6\}$ (A type) or $\{\text{X}(\text{OH})_6\}$ (B type) octahedron.

$[\text{La}(\text{H}_2\text{O})_7\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$ (Figure 5.16) [54], $[\text{La}(\text{H}_2\text{O})_7\text{CrMo}_6\text{H}_6\text{O}_{24}]$ [55], and $[(\text{H}_2\text{O})_6\text{DyCrMo}_6\text{H}_6\text{O}_{24}]$ [56] show one-dimensional chain structure built by B-type Anderson anions and RE cation linkers. In these complexes, each Anderson anions acts as a bidentate ligand coordinating to two RE ions via the terminal oxygen atoms of two interval (in the first complex) or opposite (in the second and third complexes) MoO_6 octahedra. In both of the lanthanum complexes, each lanthanum occupies a tricapped-trigonal prism defined by two terminal oxygen atoms from two Anderson anions and seven water molecules. In the dysprosium complex, each dysprosium is eight-coordinated in a square-antiprismatic geometry with two terminal oxygen atoms of two Anderson anions and six water molecules.

A series of isostructural two-dimensional complexes $[(\text{H}_2\text{O})_4(\text{C}_6\text{NO}_2\text{H}_5)\text{RE}(\text{CrMo}_6\text{H}_6\text{O}_{24})]$ (RE = Ce, Pr, La, and Nd) have been reported. In their structure, B-type Anderson-type anions

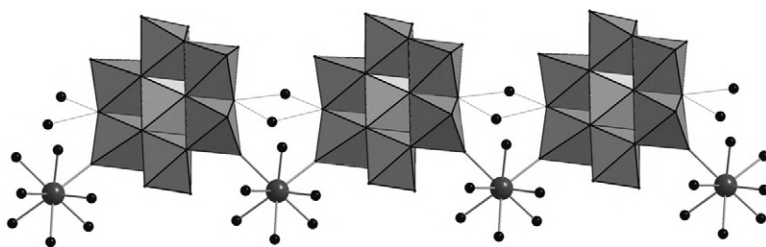


Figure 5.16 The one-dimensional chain structure of $[\text{La}(\text{H}_2\text{O})_7\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$ [54]. (Reprinted from V. Shivaiah, *et al.*, “A novel polyoxometalate chain formed from heteropolyanion building blocks and rare earth metal ion linkers: $[\text{La}(\text{H}_2\text{O})_7\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]_n \cdot 4n\text{H}_2\text{O}$,” *Journal of the Chemical Society, Dalton Transactions*, 3781–3782 (Figure 1), 2002, by permission of The Royal Society of Chemistry.)

are interlinked with each other via RE^{3+} ions to generate a helical $[\text{CrMo}_6(\text{OH})_6\text{O}_{18}\text{RE}]_\infty$ chain, and adjacent same-handed helical chains are further interconnected by pyridine-4-carboxylic acid ligands to generate a two-dimensional chiral layer. The two types of chiral layers, one left-handed and the other right-handed, crystallize in pairs in the space group $C2/c$ with an inversion center, leading to a mesomeric solid state compound [57].

$[\text{RE}(\text{H}_2\text{O})_5(\text{CrMo}_6\text{H}_6\text{O}_{24})]$ ($\text{RE} = \text{Ce}, \text{La}$) displays a three-dimensional structure constructed by B-type Anderson $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ building units and RE cations. In the structure, each $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ unit connects with four RE cations and each RE cation links with four $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ units leading to a 4,4-connected net. Each RE atom resides in a distorted bicapped square-antiprismatic structure, defined by four terminal oxygen atoms from four Anderson units and six water molecules [58].

$[(\text{C}_6\text{H}_5\text{NO}_2)_2\text{RE}(\text{H}_2\text{O})_4]_2[\text{IMo}_6\text{O}_{24}][\text{NO}_3]$ ($\text{RE} = \text{Ce}$ and La) [59] and $[\text{Pr}(\text{H}_2\text{O})_5\text{IMo}_6\text{O}_{24}]^{2-}$ [60] are a series of complexes with extending structure constructed by A-type Anderson anions and RE cation linkers. $[(\text{C}_6\text{H}_5\text{NO}_2)_2\text{RE}(\text{H}_2\text{O})_4]_2[\text{IMo}_6\text{O}_{24}][\text{NO}_3]$ exhibits a two-dimensional layer structure. In the structure, RE atoms are linked by pyridine-4-carboxylic acid ligands to form a cationic one-dimensional chain. Such chains are arranged in parallel and further connected by $[\text{IMo}_6\text{O}_{24}]^{5-}$ anions to form a two-dimensional layer (Figure 5.17). $[\text{Pr}(\text{H}_2\text{O})_5\text{IMo}_6\text{O}_{24}]^{2-}$ displays a three-dimensional structure. In the structure, $[\text{IMo}_6\text{O}_{24}]^{5-}$ units are connected by praseodymium cations to yield a two-dimensional layer. The neighboring layers are further held together by $\text{Pr}-\text{O}-\text{Mo}$ bonds leading to a three-dimensional framework structure.

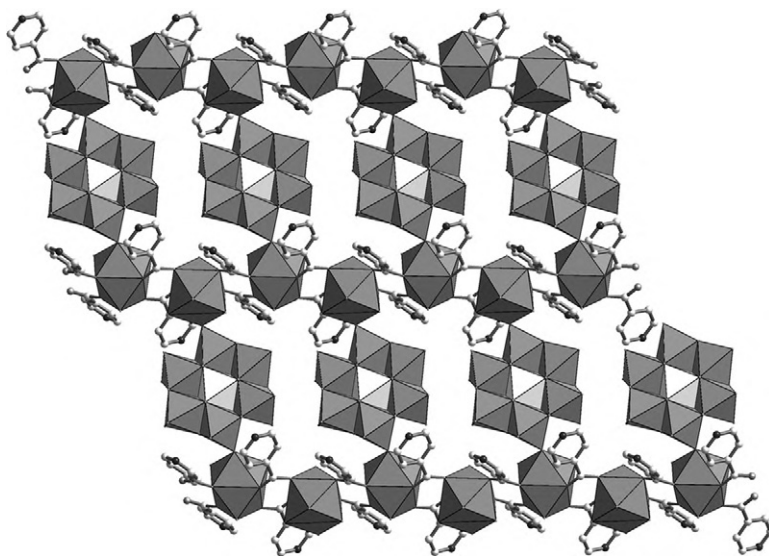


Figure 5.17 The two-dimensional layer in $[(\text{C}_6\text{H}_5\text{NO}_2)_2\text{Ln}(\text{H}_2\text{O})_4]_2[\text{IMo}_6\text{O}_{24}][\text{NO}_3]$ [59]. (Reprinted with permission from H.Y. An, *et al.*, “Self-assembly of extended high-dimensional architectures from Anderson-type polyoxometalate clusters,” *Crystal Growth and Design*, **6**, no. 5, 1107-1112 (Figure 3), 2006. © 2006 American Chemical Society.)

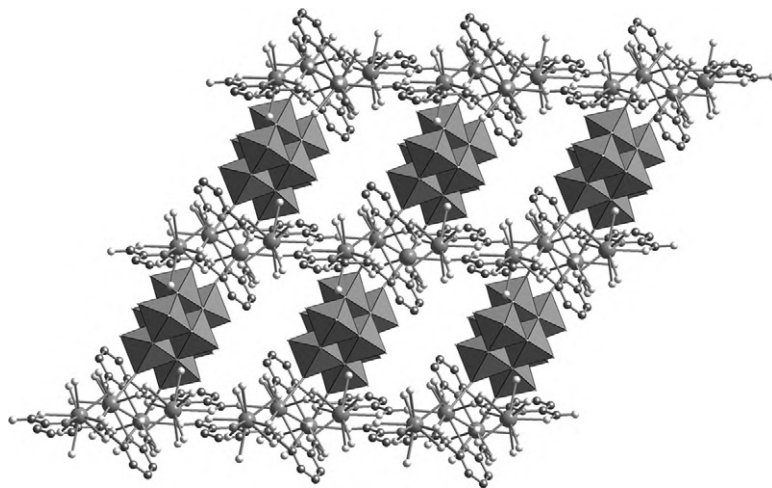


Figure 5.18 The three-dimensional framework of $[\{\text{La}(\text{H}_2\text{O})_5(\text{dipic})\}\{\text{La}(\text{H}_2\text{O})(\text{dipic})\}]_2\{\text{Mo}_8\text{O}_{26}\}$ [61a]. (Reprinted with permission from J. Lü, *et al.*, “A novel pillared-layered organic-inorganic hybrid based on lanthanide polymer and polyoxomolybdate clusters: new opportunity toward the design and synthesis of porous framework,” *Crystal Growth and Design*, 5, no. 1, 65–67 (Figure 3), 2005. © 2005 American Chemical Society.)

5.2.2.2 Octamolybdate Anions as Building Units

$[\{\text{La}(\text{H}_2\text{O})_5(\text{dipic})\}\{\text{La}(\text{H}_2\text{O})(\text{dipic})\}]_2\{\text{Mo}_8\text{O}_{26}\}$ and $\text{Na}_4[\text{Nd}_8(\text{dipic})_{12}(\text{H}_2\text{O})_9][\text{Mo}_8\text{O}_{26}]$ (dipic = pyridinedicarboxylic acid) are two three-dimensional complexes based on the $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ anion and an RE–organic coordination polymer [61]. $[\{\text{La}(\text{H}_2\text{O})_5(\text{dipic})\}\{\text{La}(\text{H}_2\text{O})(\text{dipic})\}]_2\{\text{Mo}_8\text{O}_{26}\}$ shows a pillar–layer structure, which is built by coordinating polymer sheets $[\{\text{La}(\text{H}_2\text{O})_5(\text{dipic})\}\{\text{La}(\text{H}_2\text{O})(\text{dipic})\}]_2^{4+}$ and $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ clusters that are pillared (Figure 5.18). In the structure of $\text{Na}_4[\text{Nd}_8(\text{dipic})_{12}(\text{H}_2\text{O})_9][\text{Mo}_8\text{O}_{26}]$, $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ are covalently incorporated into a three-dimensional alkali metal modified Nd–organic heterometallic framework.

5.2.2.3 Decatungstate $[\text{W}_{10}\text{O}_{32}]^{4-}$ Anions as Building Units

$[\text{W}_{10}\text{O}_{32}]^{4-}$ can be viewed as a dimer composed of two monovacant Lindqvist units $[\text{W}_5\text{O}_{14}]^{2-}$ by sharing of the four oxygen atoms around the vacant sites. $[\text{Ce}(\text{IV})(\text{H}_2\text{O})(\text{DMF})_6(\text{W}_{10}\text{O}_{32})]$ displays a one-dimensional helical chain structure, which is built by the alternating linkage of $[\text{W}_{10}\text{O}_{32}]^{4-}$ anions and $[\text{Ce}(\text{H}_2\text{O})(\text{DMF})_6]^{4+}$ fragments (DMF = dimethylformamide). Each cerium atom adopts a nine-coordinate monocapped square-antiprism geometry, with six oxygen atoms from six DMF ligands, one water molecule, and two terminal oxygen atoms from two adjacent $[\text{W}_{10}\text{O}_{32}]^{4-}$ anions [62].

5.2.2.4 $[\text{H}_2\text{M}_{12}\text{O}_{42}]^{10-}$ Anions as Building Units

A series of complexes $\{\text{RE}(\text{H}_2\text{O})_5\}_2(\text{H}_2\text{M}_{12}\text{O}_{42})^{4-}$ (RE = La, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu; M = W or W/Mo) have been reported. They possess three-dimensional frameworks

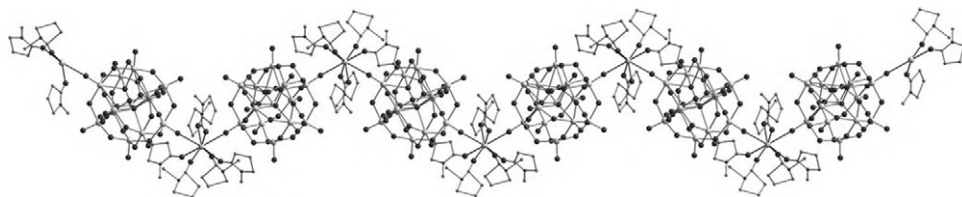


Figure 5.19 The one-dimensional chain structure of $[\text{Ce}(\text{NMP})_6(\text{PMo}_{12}\text{O}_{40})]_n$ [64]. (Reproduced with permission from J.Y. Niu, *et al.*, “1D-polyoxometalate-based composite compounds – design, synthesis, crystal structures, and properties of $[\{\text{Ln}(\text{NMP})_6\}(\text{PMo}_{12}\text{O}_{40})]_n$ (Ln = La, Ce, Pr; NMP = *N*-methyl-2-pyrrolidone),” *European Journal of Inorganic Chemistry*, 2004, no. 1, 160–170 (Figure 4). © Wiley-VCH Verlag GmbH & Co. KGaA.)

assembled from the arrangement of $\text{H}_2\text{M}_{12}\text{O}_{42}^{10-}$ (known as paradodecmetalate-B) and $\text{RE}(\text{H}_2\text{O})_5^{3+}$ with two planes, which are constructed via the unification of $\text{H}_2\text{M}_{12}\text{O}_{42}^{10-}$ and $\text{RE}(\text{H}_2\text{O})_5^{3+}$, along the [100] and [001] directions [63].

5.2.2.5 Keggin Anions as Building Units

$[\text{RE}(\text{NMP})_6(\text{PMo}_{12}\text{O}_{40})]$ (RE = La, Ce, Pr; NMP = *N*-methyl-2-pyrrolidone) are one-dimensional complexes composed of α -Keggin anions $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and $[\text{RE}(\text{NMP})_6]^{3+}$ cationic linkers. In their structures, each RE ion is eight-coordinate, adopting a bicapped trigonal-prism geometry, with six oxygen atoms from the NMP ligands and two oxygen atoms from two adjacent $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anions (Figure 5.19) [64].

$[\text{Nd}(\text{DMF})_4(\text{H}_2\text{O})(\text{BW}_{12}\text{O}_{40})]^{2-}$ exhibits a two-dimensional structure built by α -Keggin anions $[\text{BW}_{12}\text{O}_{40}]^{5-}$ and $[\text{Nd}(\text{DMF})_4(\text{H}_2\text{O})]^{3+}$ linkers. In the layer structure, each $[\text{BW}_{12}\text{O}_{40}]^{5-}$ anion connects with three $[\text{Nd}(\text{DMF})_4(\text{H}_2\text{O})]^{3+}$ linkers, and each $[\text{Nd}(\text{DMF})_4(\text{H}_2\text{O})]^{3+}$ group bridges three $[\text{BW}_{12}\text{O}_{40}]^{5-}$ units [65].

A series of extending structural complexes formed by tetracapped ε -Keggin anions and organic linkers have been obtained [48, 66]. $[\varepsilon\text{-PMo}_{12}\text{O}_{37}(\text{OH})_3\{\text{La}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_6\text{O}_4)_{0.5}\}_4]$ and $[\varepsilon\text{-PMo}_{12}\text{O}_{39}(\text{OH})\{\text{La}(\text{H}_2\text{O})_6\}_2\{\text{La}(\text{H}_2\text{O})_5(\text{C}_4\text{O}_4)_{0.5}\}_2]$ are two one-dimensional chain complexes. In the first complex, tetracapped ε -Keggin $[\varepsilon\text{-PMo}_{12}\text{O}_{37}(\text{OH})_3\{\text{La}(\text{H}_2\text{O})_4\}_4]$ units are linked together by double glutarate ($\text{C}_5\text{H}_6\text{O}_4^{2-}$) bridges into one-dimensional zigzag chains (Figure 5.20). However, in the second complex, tetracapped ε -Keggin $[\varepsilon\text{-PMo}_{12}\text{O}_{39}(\text{OH})\{\text{La}(\text{H}_2\text{O})_6\}_2\{\text{La}(\text{H}_2\text{O})_5\}_2]$ units are connected with each other by a single squarate ($\text{C}_4\text{O}_4^{2-}$) bridge into a straight chain.

$[(\varepsilon\text{-PMo}_{12}\text{O}_{37})(\text{OH})_3\{\text{La}(\text{H}_2\text{O})_4\}_4(\text{C}_{10}\text{H}_2\text{O}_8)]$ and $[(\varepsilon\text{-PMo}_{12}\text{O}_{35})(\text{OH})_5\{\text{La}(\text{H}_2\text{O})_3(\text{C}_9\text{H}_3\text{O}_6)_{0.5}\}_4]$ possess a three-dimensional structure. In the first complex, each pyromellitate ligand $\text{C}_{10}\text{H}_2\text{O}_8^{4-}$ is connected to four lanthanum ions from four distinct tetracapped ε -Keggin units, resulting in a neutral three-dimensional framework. In the second complex, each trimesate anion $\text{C}_9\text{H}_3\text{O}_6^{3-}$ bridges three lanthanum ions from three distinct tetracapped ε -Keggin units, also generating a three-dimensional arrangement.

$[\text{Mo}_{22}\text{O}_{52}(\text{OH})_{18}\{\text{La}(\text{H}_2\text{O})_4\}_2\{\text{La}(\text{CH}_3\text{CO}_2)_2\}_4]^{2-}$ exhibits a two-dimensional structure constructed by $[\text{Mo}_{22}\text{O}_{52}(\text{OH})_{18}\text{La}_4\{\text{La}(\text{H}_2\text{O})_4\}_2]^{6+}$ units and acetate ligands as bridges. $[\text{Mo}_{22}\text{O}_{52}(\text{OH})_{18}\text{La}_4\{\text{La}(\text{H}_2\text{O})_4\}_2]^{6+}$ is a $[\text{Mo}_{22}\text{O}_{52}(\text{OH})_{18}]^{12-}$ cluster with six lanthanum

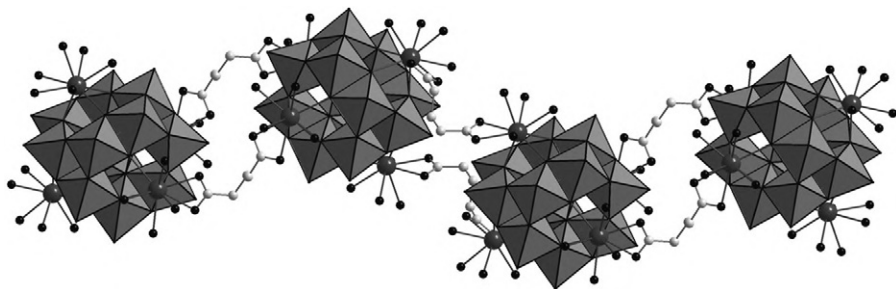


Figure 5.20 The one-dimensional chain structure of $[\epsilon\text{-PMo}_{12}\text{O}_{37}(\text{OH})_3\{\text{La}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_6\text{O}_4)_{0.5}\}_4]$ [66]. (Reproduced with permission from A. Dolbecq, *et al.*, “Hybrid organic-inorganic 1D and 2D frameworks with ϵ -Keggin polyoxomolybdates as building blocks,” *Chemistry – A European Journal*, 2003, **9**, no. 12, 2914–2920 (Figure 1). © Wiley-VCH Verlag GmbH & Co. KGaA.)

caps. Then $[\text{Mo}_{22}\text{O}_{52}(\text{OH})_{18}]^{12-}$ can be viewed as the merging of two $\{\epsilon\text{-Mo}_{12}\text{O}_{40}\}$ units by sharing a Mo(V)–Mo(V) pair. In the complex, $[\text{Mo}_{22}\text{O}_{52}(\text{OH})_{18}\text{La}_4\{\text{La}(\text{H}_2\text{O})_4\}_2]^{6+}$ units connect with acetate ligands through the four lanthanum centers capped at the hexagonal $\{\text{Mo}_2\}_3$ faces of the $[\text{Mo}_{22}\text{O}_{52}(\text{OH})_{18}]^{12-}$ anion, generating a two-dimensional layer.

5.2.2.6 Monovacant Keggin Anions as Building Units

Many one-dimensional chain complexes constructed by monovacant Keggin units $[\alpha\text{-XM}_{11}\text{O}_{39}]^{n-}$ ($\text{X} = \text{Si}, \text{P}, \text{Ge}$; $\text{M} = \text{Mo}, \text{W}$; $n = 4, 5, 6$) and RE linkers have been prepared and structurally characterized. These one-dimensional chain complexes can be separated into two series. The first series include $[\text{Yb}(\text{SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2]^{4-}$, $[\text{Y}(\text{GeW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2]^{5-}$, $[\text{Ce}(\text{H}_2\text{O})_3(\text{SiW}_{11}\text{O}_{39})]^{5-}$, $[\text{Eu}(\text{SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2]^{5-}$, $[\text{Eu}(\text{PW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2]^{4-}$, $[\text{Ce}(\text{BW}_{11}\text{O}_{39})(\text{H}_2\text{O})_3]^{6-}$, and $[\text{La}(\text{H}_2\text{O})_3(\text{SiW}_{11}\text{O}_{39})]^{5-}$ [67]. In these complexes, all RE linkers are situated in the vacant site of $[\text{XM}_{11}\text{O}_{39}]^{n-}$ anions. $[\text{Yb}(\text{SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2]^{4-}$ and $[\text{Y}(\text{GeW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2]^{5-}$ possess similar one-dimensional linear chains, where each RE atom connects with two $[\alpha\text{-XM}_{11}\text{O}_{39}]^{n-}$ anions through four oxygen atoms from the vacant site of one $[\text{XM}_{11}\text{O}_{39}]^{n-}$ anion and one terminal oxygen atom from the other $[\text{XM}_{11}\text{O}_{39}]^{n-}$ anion. $[\text{Ce}(\text{H}_2\text{O})_3(\text{SiW}_{11}\text{O}_{39})]^{5-}$, $[\text{Eu}(\text{SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2]^{5-}$, and $[\text{Eu}(\text{PW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2]^{4-}$ exhibit similar zigzag chain structure, where each RE atom bridges three adjacent $[\text{XM}_{11}\text{O}_{39}]^{n-}$ anions through four oxygen atoms around the vacant site of one $[\text{XM}_{11}\text{O}_{39}]^{n-}$ anion and two terminal oxygen atoms from the other two $[\text{XM}_{11}\text{O}_{39}]^{n-}$ anions (Figure 5.21). $[\text{La}(\text{H}_2\text{O})_3(\text{SiW}_{11}\text{O}_{39})]^{5-}$ also shows a zigzag chain structure. However, in this complex, there are two types of La atoms: one connects with two neighboring $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ anions and the other bridges three $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ anions.

The second series includes $[\text{Nd}_{1.50}(\text{GeW}_{11}\text{O}_{39})(\text{H}_2\text{O})_6]^{3.5-}$ [68], $[\text{RE}_2(\text{SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_{11}]$ ($\text{RE} = \text{La}, \text{Ce}$) [69] and $[\text{Sm}(\text{H}_2\text{O})_7]_{0.5}\text{H}_{0.5}[\text{Sm}_2(\text{GeW}_{11}\text{O}_{39})(\text{DMSO})_3(\text{H}_2\text{O})_6]$ [68]. In these compounds, only part of the RE linkers locate in the vacant sites of $[\text{XM}_{11}\text{O}_{39}]^{n-}$ anions, and the others locate in the surrounding of the $[\text{XM}_{11}\text{O}_{39}]^{n-}$ anions. In the complex $[\text{Nd}_{1.50}(\text{GeW}_{11}\text{O}_{39})(\text{H}_2\text{O})_6]^{3.5-}$, $[\text{GeW}_{11}\text{O}_{39}]^{8-}$ anions are connected into one-dimensional zigzag chains by two types of neodymium cationic linkers. One type of neodymium atom is situated in the vacant sites of one $[\text{GeW}_{11}\text{O}_{39}]^{8-}$ anion and connects to another $[\text{GeW}_{11}\text{O}_{39}]^{8-}$

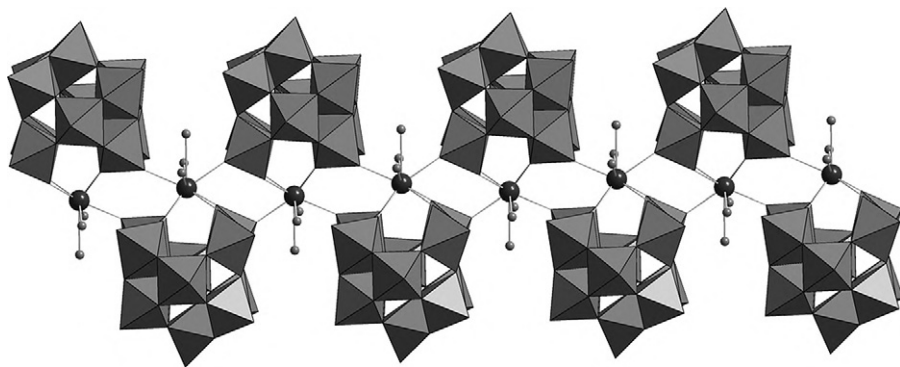


Figure 5.21 The one-dimensional chain in $[\text{Ce}(\text{H}_2\text{O})_3(\text{SiW}_{11}\text{O}_{39})]^{5-}$ [67b]. (Reproduced with permission from M. Sadakane, *et al.*, “Controlled assembly of polyoxometalate chains from lacunary building blocks and lanthanide-cation linkers,” *Angewandte Chemie International Edition*, 2000, **39**, no.16, 2914–2916 (Figure 1). © Wiley-VCH Verlag GmbH & Co. KGaA.)

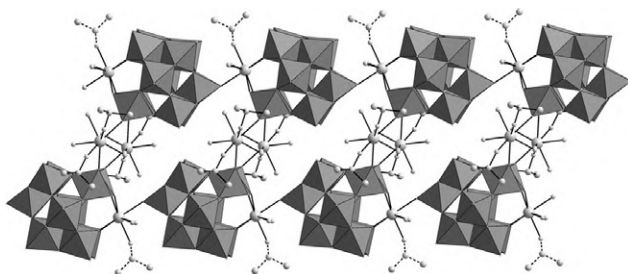


Figure 5.22 The double chain in $[\text{Sm}(\text{H}_2\text{O})_7]_{0.5}\text{H}_{0.5}[\text{Sm}_2(\text{GeW}_{11}\text{O}_{39})(\text{DMSO})_3(\text{H}_2\text{O})_6]$ [68]. (Reprinted with permission from J.P. Wang, *et al.*, “Novel rare earth germanotungstates and organic hybrid derivatives: synthesis and structures of $\text{M}/[\alpha\text{-GeW}_{11}\text{O}_{39}]$ ($\text{M} = \text{Nd}, \text{Sm}, \text{Y}, \text{Yb}$) and $\text{Sm}/[\alpha\text{-GeW}_{11}\text{O}_{39}](\text{DMSO})$,” *Crystal Growth and Design*, **6**, no. 10, 2266–2270 (Figure 5), 2006. © 2006 American Chemical Society.)

anion by a terminal oxygen atom of the $[\text{GeW}_{11}\text{O}_{39}]^{8-}$ anion. The second type of neodymium atom is located between two $[\text{GeW}_{11}\text{O}_{39}]^{8-}$ anions and connects with the two $[\text{GeW}_{11}\text{O}_{39}]^{8-}$ anions by two terminal oxygen atoms from the two anions. In the structure of $[\text{RE}_2(\text{SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_{11}]$ ($\text{RE} = \text{La}, \text{Ce}$), two $\{\text{RE}(\text{SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_4\}$ fragments are connected with each other to form a dimer first, then such dimers are connected by double $\text{RE}(\text{H}_2\text{O})_7$ bridges into a one-dimensional zigzag chain. $[\text{Sm}(\text{H}_2\text{O})_7]_{0.5}\text{H}_{0.5}[\text{Sm}_2(\text{GeW}_{11}\text{O}_{39})(\text{DMSO})_3(\text{H}_2\text{O})_6]$ shows a double chain structure. In the double chain, two parallel chains $\{[\text{Sm}(\text{GeW}_{11}\text{O}_{39})(\text{DMSO})(\text{H}_2\text{O})_2]^{5-}\}_n$, similar to the one-dimensional chain in $[\text{Nd}_{1.50}(\text{GeW}_{11}\text{O}_{39})(\text{H}_2\text{O})_6]^{3.5-}$, are connected together through double $[\text{Sm}(\text{DMSO})_2(\text{H}_2\text{O})_4]^{3+}$ linkers (Figure 5.22).

$\text{Nd}_{0.5}[\text{Nd}_2(\text{SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_{11}]^{0.5-}$ displays a two-dimensional layer structure, which is constructed by $[\text{Nd}_2(\text{SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_{11}]^-$ chains and additional neodymium linkers. The

structure of the $[\text{Nd}_2(\text{SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_{11}]^-$ chain is similar to the one-dimensional chain in $[\text{RE}_2(\text{SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_{11}]$ ($\text{RE} = \text{La}, \text{Ce}$) [67a].

Monovacant α -metatungstate $[\text{H}_2\text{W}_{11}\text{O}_{39}]^{10-}$ possesses a similar structure with monovacant Keggin units $[\alpha\text{-XMO}_{39}]^{n-}$. A three-dimensional complex $[\{\text{Ag}_3(\text{H}_2\text{O})_2\}\{\text{Ce}_2(\text{H}_2\text{O})_{12}\}\text{H}_5 \subset \{\text{H}_2\text{W}_{11}\text{Ce}(\text{H}_2\text{O})_4\text{O}_{39}\}_2]$, constructed by $[\text{H}_2\text{W}_{11}\text{O}_{39}]^{10-}$ anions with cerium and silver linkers, has been reported. In this complex, the dimers constructed by two monosubstituted α -metatungstate $[\text{H}_2\text{W}_{11}\text{Ce}(\text{H}_2\text{O})_4\text{O}_{39}]^{7-}$ units are linked by cerium and silver ions to form two-dimensional layers, and such layers are further connected by $\text{Ag(I)}\text{--Ag(I)}$ bonds to generate a three-dimensional framework [70].

5.2.2.7 Silverton Type Anions as Building Units

$[\text{Gd}(\text{H}_2\text{O})_3]_3[\text{GdMo}_{12}\text{O}_{42}]$ exhibits a three-dimensional structure constructed by Silverton type anions $[\text{GdMo}_{12}\text{O}_{42}]^{9-}$ and gadolinium cationic linkers. In the three-dimensional framework, each $[\text{GdMo}_{12}\text{O}_{42}]^{9-}$ anion acts as an 18-dentate ligand to link with six gadolinium linkers, and each gadolinium ion connects with two $[\text{GdMo}_{12}\text{O}_{42}]^{9-}$ anions. There are two types gadolinium ions in the compound: one is located in the center of the $[\text{GdMo}_{12}\text{O}_{42}]^{9-}$ anion, which adopts 12-coordinate icosahedron geometry; the other is situated at the outer sphere of the $[\text{GdMo}_{12}\text{O}_{42}]^{9-}$ anion, which is nine-coordinate with a distorted tricapped-trigonal prism [71] (Figure 5.23).

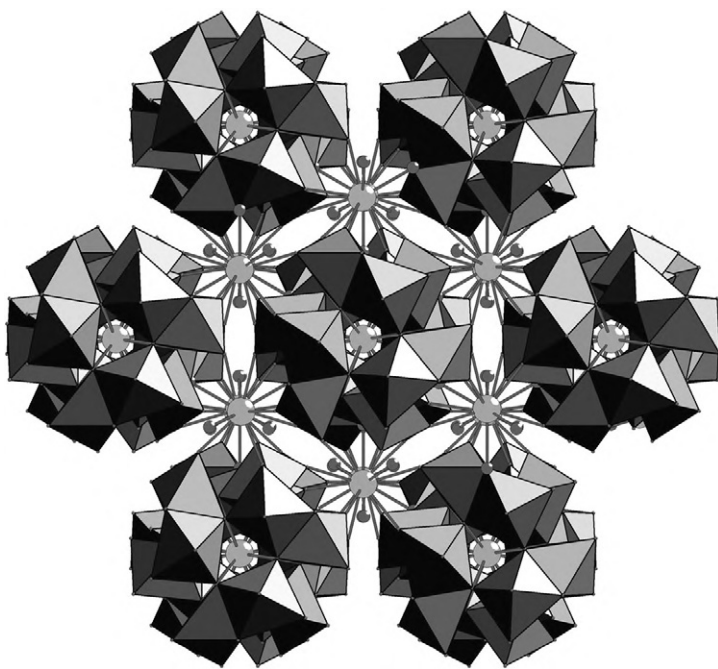


Figure 5.23 The three-dimensional framework of $[\text{Gd}(\text{H}_2\text{O})_3]_3[\text{GdMo}_{12}\text{O}_{42}]$ [71]. (Reprinted with permission from C.D. Wu, *et al.*, “Hydrothermal assembly of a novel three-dimensional framework formed by $[\text{GdMo}_{12}\text{O}_{42}]^{9-}$ anions and nine coordinated Gd^{III} cations,” *Journal of the American Chemical Society*, **124**, no. 15, 3836–3837 (Figure 2), 2002. © 2002 American Chemical Society.)

5.2.2.8 Wells–Dawson Anions as Building Units

$[\text{Sm}(\text{DMF})_6(\text{H}_2\text{O})(\alpha\text{-P}_2\text{W}_{18}\text{O}_{62})]^{2-}$ possesses a one-dimensional zigzag chain structure constructed by the alternate connection of $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ anions and $[\text{Sm}(\text{DMF})_6(\text{H}_2\text{O})]^{3+}$ coordination cations. In $[\text{Sm}(\text{DMF})_6(\text{H}_2\text{O})]^{3+}$ cations, the samarium atom adopts a distorted tricapped-trigonal prismatic geometry defined by six O atoms from six DMF ligands, one water ligand, and two terminal oxygen atoms of two adjacent $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ anions [72].

5.2.2.9 Monovacant Wells–Dawson Anions $[\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ as Building Units

$[\text{Nd}_3(\text{H}_2\text{O})_{17}(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})]^-$ displays a one-dimensional chain structure built up of bisupporting anions $\{[\text{Nd}(\text{H}_2\text{O})_7]_2\{[\text{Nd}(\text{H}_2\text{O})_3(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})]_2\}^{8-}$ and additional neodymium linkers [36]. The structure of the bisupporting anions have similar structures to the above mentioned $\{[\text{Nd}(\text{H}_2\text{O})_7]_2\{[\text{Nd}(\text{H}_2\text{O})_3(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})]_2\}^{8-}$ cluster.

$[\text{RE}_2(\text{H}_2\text{O})_9(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})]^{4-}$ (RE = Nd, La, Eu) shows a two-dimensional layer, constructed of $[\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ linked by RE ions. In the structure, there are two crystallographically distinct RE atoms: RE1 and RE2. The RE1 atoms locate in the vacancies of the $[\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ anions and connect the adjacent $[\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ anions into a one-dimensional chain. The one-dimensional $[\text{RE}(\text{H}_2\text{O})_2(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})]_n^{7n-}$ chain formed is similar to the one-dimensional chain in the $[\text{Eu}(\alpha\text{-SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})_2]^{5-}$ compound. The RE2 atoms are located between the one-dimensional $[\text{RE}(\text{H}_2\text{O})_2(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})]_n^{7n-}$ chains and further link the adjacent chains into a two-dimensional layer (Figure 5.24) [36].

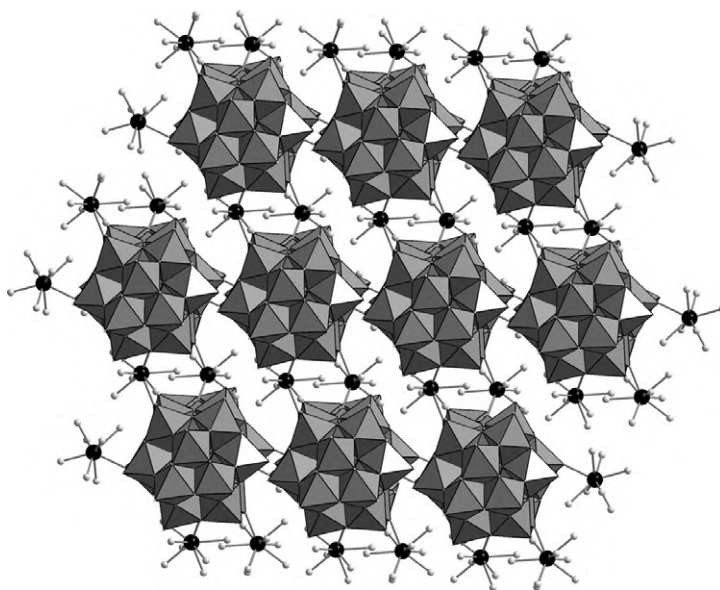


Figure 5.24 The two-dimensional layer structure of $[\text{Ln}_2(\text{H}_2\text{O})_9(\alpha 2\text{-P}_2\text{W}_{17}\text{O}_{61})]^{4-}$ [36]. (Reprinted with permission from Y. Lu, *et al.*, “New polyoxometalate compounds built up of lacunary Wells–Dawson anions and trivalent lanthanide cations,” *Inorganic Chemistry*, **45**, no. 5, 2055–2060 (Figure 3), 2006. © 2006 American Chemical Society.)

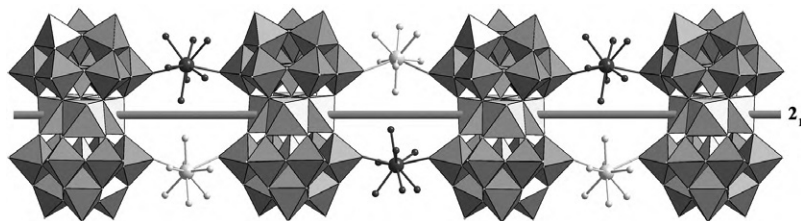


Figure 5.25 The one-dimensional chain in $[\{\text{Ce}(\text{H}_2\text{O})_7\}_2\text{Mn}_4\text{Si}_2\text{W}_{18}\text{O}_{68}(\text{H}_2\text{O})_2]^{6-}$ [73]. (Reproduced with permission from W.L. Chen, *et al.*, “An inorganic aggregate based on a sandwich-type polyoxometalate with lanthanide and potassium cations: from 1D chiral ladder-like chains to a 3D open framework,” *European Journal of Inorganic Chemistry*, 2007, no. 15, 2216–2220 (Figure 2). © Wiley-VCH Verlag GmbH & Co. KGaA.)

5.2.2.10 Sandwich Type $[\text{Mn}_4\text{Si}_2\text{W}_{18}\text{O}_{68}(\text{H}_2\text{O})_2]^{12-}$ Anions as Building Units

$[\{\text{Ce}(\text{H}_2\text{O})_7\}_2\text{Mn}_4\text{Si}_2\text{W}_{18}\text{O}_{68}(\text{H}_2\text{O})_2]^{6-}$ exhibits a chiral chain structure based on sandwich type $[\text{Mn}_4\text{Si}_2\text{W}_{18}\text{O}_{68}(\text{H}_2\text{O})_2]^{12-}$ anions and cerium cationic linkers. In the complex, $[\text{Mn}_4\text{Si}_2\text{W}_{18}\text{O}_{68}(\text{H}_2\text{O})_2]^{12-}$ anions are composed of two trivacant $[\text{B}-\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$ Keggin moieties sandwiching a central symmetric rhombic-like $[\text{Mn}_4\text{O}_{16}(\text{H}_2\text{O})_2]$ segment. The $[\text{Mn}_4\text{Si}_2\text{W}_{18}\text{O}_{68}(\text{H}_2\text{O})_2]^{12-}$ anions are linked by double $[\text{Ce}(\text{H}_2\text{O})_7]^{3+}$ bridges into a ladder-like chain (Figure 5.25) [73].

5.2.2.11 Preyssler Anions as Building Units

$[\text{Nd}_2(\text{H}_2\text{O})_{14}\{\text{Na}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}\}]^{8-}$ shows a one-dimensional chain structure built from Preyssler anions $[\text{Na}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}]^{14-}$ linked by neodymium cations. In the complex, the adjacent $[\text{Na}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}]^{14-}$ clusters are linked to each other about a center of symmetry by two neodymium bridges, leading to a one-dimensional chain [35].

$[\text{Ce}_4(\text{H}_2\text{O})_{16}(\text{HNA})_6\{\text{Na}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}\}]^{2-}$ has a two-dimensional network formed by one-dimensional $[\text{Ce}_2(\text{H}_2\text{O})_{10}\{\text{Na}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}\}]_n^{8n-}$ chains and $\{\text{Ce}_2(\text{H}_2\text{O})_6(\text{HNA})_6\}^{6+}$ linkers. The $[\text{Ce}_2(\text{H}_2\text{O})_{10}\{\text{Na}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}\}]_n^{8n-}$ chain is formed by Preyssler anions $[\text{Na}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}]^{14-}$ double bridged via cerium ions [35].

5.2.2.12 $\{\text{Mo}_{36}(\text{NO})_4\}$ as Building Units

$[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{MoO})_2\text{La}_2(\text{H}_2\text{O})_{28}]$ possesses of a one-dimensional chain structure, in which the $\{\text{Mo}_{36}(\text{NO})_4\}$ units are linked to each other by two parallel lanthanum atoms [74].

$[\{\text{Gd}(\text{H}_2\text{O})_5\}_4\{\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}\}]$ exhibits a two-dimensional network built by $[\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}]^{12-}$ anions and gadolinium cationic linkers. In the network, each $[\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}]^{12-}$ anion connects to eight gadolinium ions, and each gadolinium ion links with two $[\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}]^{12-}$ anions [75].

5.2.2.13 Cyclic $[\text{P}_8\text{W}_{48}\text{O}_{184}]^{40-}$ Anions as Building Units

The $[\text{P}_8\text{W}_{48}\text{O}_{184}]^{40-}$ anion shows a cyclic cluster structure constructed by four $\text{P}_2\text{W}_{12}\text{O}_{48}$ units derived from a Wells–Dawson anion by removal of six adjacent WO_6 octahedra. In the complex $\{\text{RE}_4(\text{H}_2\text{O})_{28}[\text{K}(\text{P}_8\text{W}_{48}\text{O}_{184}(\text{H}_4\text{W}_4\text{O}_{12})_2\text{RE}_2(\text{H}_2\text{O})_{10})]^{13-}$ (RE = La, Ce, Pr,

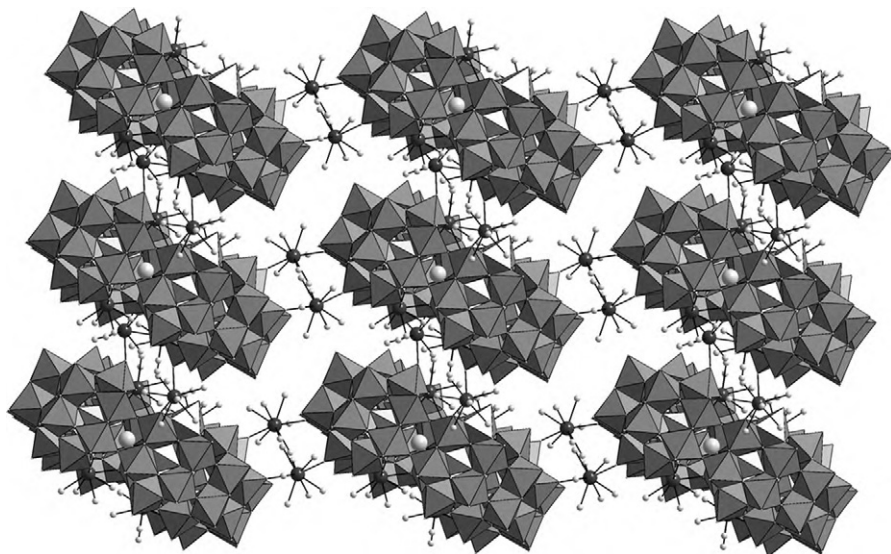


Figure 5.26 The three-dimensional framework of $\{\text{RE}_4(\text{H}_2\text{O})_{28}[\text{KCP}_8\text{W}_{48}\text{O}_{184}(\text{H}_4\text{W}_4\text{O}_{12})_2\text{RE}_2(\text{H}_2\text{O})_{10}]\}^{13-}$ [76]. (Reprinted with permission from M. Zimmermann, *et al.*, “New lanthanide-containing polytungstates derived from the cyclic P_8W_{48} anion: $\{\text{Ln}_4(\text{H}_2\text{O})_{28}[\text{KCP}_8\text{W}_{48}\text{O}_{184}(\text{H}_4\text{W}_4\text{O}_{12})_2\text{Ln}_2(\text{H}_2\text{O})_{10}]\}^{13-}$, $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$,” *Inorganic Chemistry*, **46**, no. 5, 1737–1740 (Figure 3), 2007. © 2007 American Chemical Society.)

Nd), cyclic $[\text{P}_8\text{W}_{48}\text{O}_{184}]^{40-}$ anions, with the central cavity occupied by two additional W_4O_{12} groups and two potassium and four lanthanide cations (each of them has an occupancy of 50%), are linked by additional RE atoms into a three-dimensional framework (Figure 5.26) [76].

5.2.2.14 $[\text{MV}_{13}\text{O}_{38}]^{7-}$ and $[\text{MV}_{12}\text{O}_{38}]^{12-}$ as Building Units

A series of isostructural complexes $[\text{RE}_6(\text{H}_2\text{O})_{25}(\text{MV}_{12}\text{O}_{38})(\text{HMV}_{13}\text{O}_{38})]$ ($\text{M} = \text{Mn}$, $\text{RE} = \text{La}$, Ce , Pr ; $\text{M} = \text{Ni}$, $\text{RE} = \text{La}$, Pr) have been reported, which have two-dimensional structures constructed by $[\text{MV}_{13}\text{O}_{38}]^{7-}$ and $[\text{MV}_{12}\text{O}_{38}]^{12-}$ building units linked through RE ions. In their structures, each $[\text{MV}_{13}\text{O}_{38}]^{7-}$ cluster is connected with three $[\text{MV}_{12}\text{O}_{38}]^{12-}$ clusters by three bridging hydrated RE^{3+} cations. For $[\text{MV}_{12}\text{O}_{38}]^{12-}$ clusters, there are two types of coordination environments. One type of $[\text{MV}_{12}\text{O}_{38}]^{12-}$ cluster is connected with four $[\text{MV}_{13}\text{O}_{38}]^{7-}$ clusters by four bridging hydrated RE^{3+} cations and capped by two additional terminal hydrated RE^{3+} cations. The other type is connected with two $[\text{MV}_{13}\text{O}_{38}]^{7-}$ clusters by two bridging hydrated RE^{3+} cations and capped by four additional terminal hydrated RE^{3+} cations (Figure 5.27) [77].

5.2.3 RE–Organo Cation POM Supermolecule Complexes

$[\text{RE}_2(\text{DNBA})_4(\text{DMF})_8][\text{Mo}_6\text{O}_{19}]$ ($\text{RE} = \text{La}$, Ce , and Eu , $\text{DNBA} = 3,5\text{-dinitrobenzoate}$, $\text{DMF} = \text{dimethylformamide}$) is an example of an RE–organocation POM supermolecule complex. In the complex, two $\text{RE}(\text{III})$ ions are bridged by four 3,5-dinitrobenzoate anions as asymmetrically bridging ligands, leading to dimeric cores, $[\text{RE}_2(\text{DNBA})_4(\text{DMF})_8]^{2+}$; the

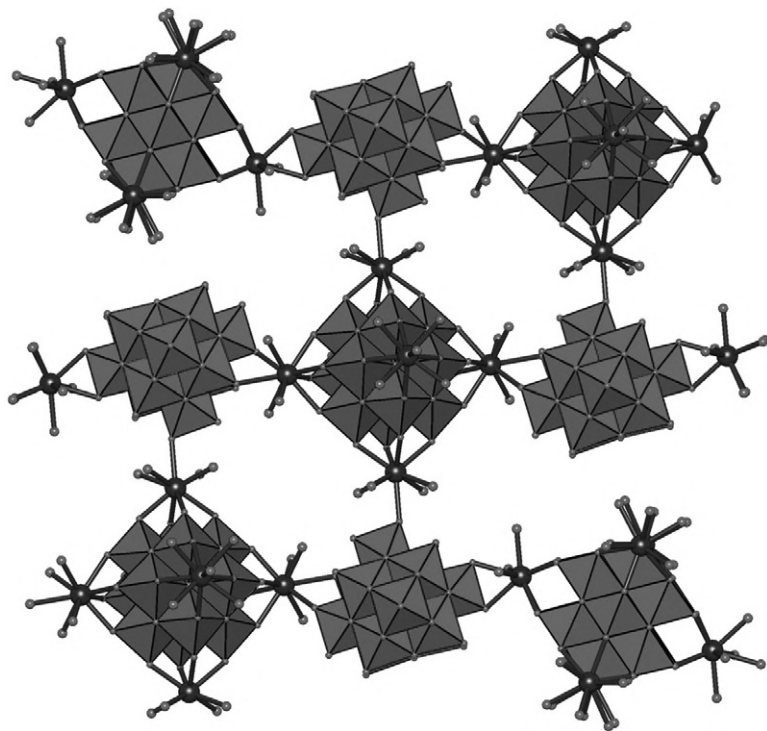


Figure 5.27 The two-dimensional layer in $[\text{Ln}_6(\text{H}_2\text{O})_{25}(\text{MV}_{12}\text{O}_{38})(\text{H}\text{MV}_{13}\text{O}_{38})]$ [77]. (Reprinted with permission from S.X. Liu, *et al.*, “Two-dimensional lanthanide heteropolyvanadates of manganese(IV) and nickel(IV) containing two types of heteropoly anions with 1:13 and 1:12 stoichiometry,” *Inorganic Chemistry*, **45**, no. 20, 8036–8040 (Figure 2), 2006. © 2006 American Chemical Society.)

$[\text{RE}_2(\text{DNBA})_4(\text{DMF})_8]^{2+}$ groups are joined together by π – π stacking interactions between the aromatic groups to form a two-dimensional grid-like network; the two-dimensional supramolecular layers are further extended into three-dimensional supramolecular networks with one-dimensional box-like channels through hydrogen-bonding interactions, in which Lindquist type anions $[\text{Mo}_6\text{O}_{19}]^{2-}$ reside [78].

In the structure of $[\text{RE}(\text{NMP})_4(\text{H}_2\text{O})_4][\text{H}_x\text{GeMo}_{12}\text{O}_{40}]$ ($\text{RE} = \text{Ce(IV)}$, Pr(IV) , $x = 0$; $\text{RE} = \text{Nd(III)}$, $x = 1$; $\text{NMP} = N\text{-methyl-2-pyrrolidone}$), the $[\text{H}_x\text{GeMo}_{12}\text{O}_{40}]^{(4-x)-}$ anions are linked together by $[\text{RE}(\text{NMP})_4(\text{H}_2\text{O})_4]^{4+}$ via the hydrogen-bonding interactions and form a two-dimensional supramolecular network. The RE center exhibits a dodecahedral environment and coordinates to eight oxygen atoms, among which four are from the C=O groups of NMP and the remaining four come from coordinated water molecules [79] (Figure 5.28).

5.3 Applications

5.3.1 Luminescence

The photoexcitation into the oxygen-to-metal ($\text{O} \rightarrow \text{M}$) ligand-to-metal charge transfer (LMCT) bands of polyoxometaloeuropates leads to an intramolecular energy transfer from

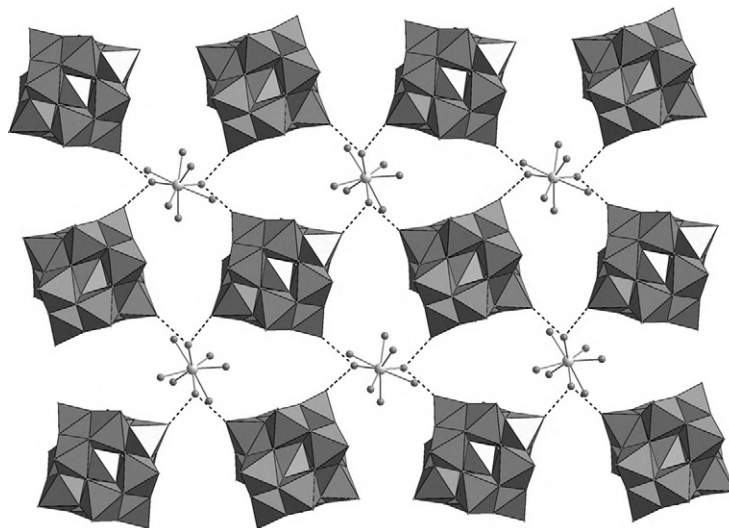


Figure 5.28 The two-dimensional supramolecular network in $[\text{RE}(\text{NMP})_4(\text{H}_2\text{O})_4][\text{H}_x\text{GeMo}_{12}\text{O}_{40}]$ [79]. (Reprinted with permission from H. Zhang, *et al.*, "Synthesis, crystal structure, and photochromism of novel two-dimensional supramolecular networks based on Keggin-type polyoxoanion and lanthanide coordination cations," *Inorganic Chemistry*, **42**, no. 24, 8053–8058 (Figure 3), 2003. © 2003 American Chemical Society.)

POM ligands to trivalent europium. Yamase and coworkers have systematically studied this behavior using a series of polyoxometaloeuropates. Photoexcitation of the $\text{O} \rightarrow \text{M}$ ($\text{M} = \text{Nd}$, Mo , W) LMCT bands of polyoxometaloeuropates leads to a trivalent europium emission with a single exponential decay. The emission originates from both the $^5\text{D}_0$ and $^5\text{D}_1$ excited states of trivalent europium, and the luminescent transitions all terminate in the $J = 0-4$ levels of the $^7\text{F}_J$ ground state (Figure 5.29). The efficiency of the intramolecular energy transfer strongly depends on the structure of the POM ligand. Moreover, they constructed a dispersion type of electroluminescence (EL) cell with a highly photoluminescent $[\text{EuW}_{10}\text{O}_{36}]^{9-}$ system. With AC excitation to the device consisting of the doublet structure of emissive $[\text{EuW}_{10}\text{O}_{36}]^{9-}$ and insulating Mylar film layers, the $[\text{EuW}_{10}\text{O}_{36}]^{9-}$ layer exhibits EL that matches the photoluminescence spectrum of the solid [80].

We have prepared photoluminescent ultrathin multilayer films consisting of the polyoxotungstoeuropate cluster $\text{K}_{12}[\text{EuP}_5\text{W}_{30}\text{O}_{110}]$ ($\text{EuP}_5\text{W}_{30}$) and poly(allylamine hydrochloride) (PAH) using the layer-by-layer self-assembly method. The photoluminescent behavior of the film at room temperature was investigated to show the characteristic trivalent europium emission pattern of $^5\text{D}_0 \rightarrow ^7\text{F}_J$. The fluorescence behavior of the multilayer film is essentially identical to that of $\text{H}_n[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{(12-n)-}$ in a concentrated aqueous solution, except for the relative intensities and peak bandwidths. The occurrence of photoluminescent activity confirms the potential for creating luminescent multilayers with polyoxometalates [81]. Moreover, we successfully transferred PAH/ EuW_{10} bilayers to microcapsules and obtained photoluminescent microcapsules. The fluorescence behavior of the $(\text{PAH}/\text{EuW}_{10})_{10}$ microcapsules is essentially identical to that of the EuW_{10} solid sample we prepared, except for the relative

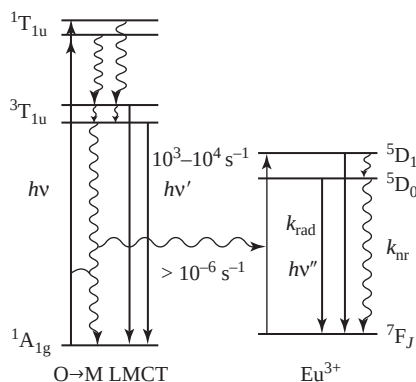


Figure 5.29 A schematic energy diagram of relaxation processes of the O→M LMCT excitation energy in polyoxometaloeuropates lattices [80b]. (Reprinted with permission from T. Yamase, "Photo- and electrochromism of polyoxometalates and related materials," *Chemical Reviews*, **98**, no. 1, 307–326 (Figure 12), 1998. © 1998 American Chemical Society.)

intensities and the bandwidths. The occurrence of photoluminescent activity in microcapsules provides potential for creating luminescent capsules with POMs as a component [82].

Liu *et al.* prepared organic/inorganic hybrid monolayers consisting of $[\text{EuW}_{10}\text{O}_{36}]^{9-}$ clusters with photoluminescence and a series of gemini type amphiphiles through electrostatic interaction at the air/water interface. Typical photoluminescence of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions of $[\text{EuW}_{10}\text{O}_{36}]^{9-}$ was observed in the hybrid films. Interestingly, the relative intensity of the two emission bands varied with the spacer length of the gemini amphiphiles in the films [83].

Green *et al.* observed enhanced emission from $\text{Na}_{13}[\text{Eu}(\text{SiMoW}_{10}\text{O}_{39})_2]$ when attached to amine-rich species, which circumvented problems encountered by water quenching of the rare earth emitting state. The quantum efficiency of $\text{Na}_{13}[\text{Eu}(\text{SiMoW}_{10}\text{O}_{39})_2]$ in a dilute (0.01%) aqueous solution of poly-L-lysine exceeded that of $\text{Na}_{13}[\text{Eu}(\text{SiMoW}_{10}\text{O}_{39})_2]$ in the solid state (quantum efficiency 50%) to a maximum of about 60%, depending upon the ratio of POM : poly-L-lysine and the molecular weight of poly-L-lysine used. They have also immobilized the POMs and the enhancing agent in silica spheres, which confines the POM to the core of the particle while increasing the emission of the material [84].

Akins *et al.* successfully immobilized polyoxometaloeuropates $[(\text{Eu}_2\text{PW}_{10}\text{O}_{38})_4(\text{W}_3\text{O}_8(\text{H}_2\text{O})_2(\text{OH})_4)]^{22-}$ inside the channels of MCM-41 mesoporous molecular sieve material by means of the incipient wetness method. For proper host–guest interactions, amine groups were introduced into the system as a result of an aminosilylation procedure. The photoluminescent behavior of the composite at room temperature indicates a characteristic trivalent europium emission pattern corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions. Such a composite might represent a new material with potential applications as a photoluminescent device or phosphor [85].

Faul and coworkers employed an ionic self-assembly (ISA) route to generate nanostructured organic-inorganic hybrid materials from sandwich type heteropolytungstomolybdate $\text{K}_{13}[\text{Eu}(\text{SiW}_9\text{Mo}_2\text{O}_{39})_2]$ and a series of cationic surfactants. ISA complexes allow the POM tectons to be brought into forms that are useful for materials application and that allow new chemical investigations. Contrary to the parental POM species $\text{K}_{13}[\text{Eu}(\text{SiW}_9\text{Mo}_2\text{O}_{39})_2]$, these nanohybrid materials dissolve in organic solvents and form transparent films and bulk

specimen. The photophysical behavior (fluorescence spectra, fluorescence lifetimes, fluorescence quantum yield) of the complexes differs widely in solid powders, films, and solutions. The cationic surfactants not only play a structural role but also have a strong influence on the photophysical properties of $K_{13}[Eu(SiW_9Mo_2O_{39})_2]$ [86].

Wu *et al.* reported that by using suitable polymerizable surfactant-encapsulated POM clusters, POMs can be encapsulated to form polymerizable SECs (surfactant encapsulated clusters). The SECs can be transferred into an organic monomer solution, and after the subsequent copolymerization, a POM-based hybrid polymer can be obtained. Using this method, they successfully obtained a fluorescent organic glass through incorporating an $[EuW_{10}O_{36}]^{9-}$ cluster into poly(methyl methacrylate) (PMMA). As a result of the synergy between $[EuW_{10}O_{36}]^{9-}$ and PMMA, the resulting fluorescent organic glass (hybrid 1) combines not only the high luminescence of $[EuW_{10}O_{36}]^{9-}$, but also the transparency and processibility of PMMA [87]. Moreover, as an extension of this method, they introduced the $[EuW_{10}O_{36}]^{9-}$ clusters encapsulated with di(11-hydroxyundecyl) dimethylammonium bromide (DOHDA) into the silica matrix through sol-gel reactions. The resulting POM-based material possesses the luminescence of $[EuW_{10}O_{36}]^{9-}$ clusters and the robustness and flexibility of the sol-gel materials [88].

5.3.2 Magnetism

Some of RE-POM complexes have been studied for their magnetic properties provided by the RE ions. POM in generally acts as an antimagnetic building unit in RE-POMs complexes, which can guarantee magnetic insulation of the RE ions incorporated into its structure. Coronado and coworkers studied the magnetic property of the sodium salt of the $[ErW_{10}O_{36}]^{9-}$ polyanion, which exhibits single-molecule magnet (SMM) behavior. Notably, this complex is the first POM displaying SMM behavior. The $[ErW_{10}O_{36}]^{9-}$ anion is formed by two anionic $[W_5O_{18}]^{6-}$ units sandwiching an erbium ion. Each $[W_5O_{18}]^{6-}$ unit is twisted 44.2° with respect to the other. This skew angle is very close to that expected for an ideal D_{4d} symmetry ($\Phi = 45^\circ$). Therefore, the coordination site can be described as slightly distorted square-antiprismatic. This geometry corresponds to an approximate D_{4d} LF symmetry.

Low-temperature AC magnetic susceptibility measurements of this complex reveal the typical features associated with the SMM behavior (Figure 5.30). Thus, both the in-phase (χ'_M) and out-of-phase (χ''_M) signals show strong frequency dependences; χ'_M shows a maximum and starts to decrease in the 5.5–7.5 K range, while χ''_M defines a maximum between 5 (1000 Hz) and 6.2 K (10 000 Hz). Analyses of the frequency dependence of the χ''_M peaks through an Arrhenius plot permit estimation of the magnetization-relaxation parameters in this system. Best fitting ($R = 0.999$) afforded a barrier height (U_{eff}/k_B) of 55.2 K with a pre-exponential factor (τ_0) of 1.6×10^{-8} s [89].

5.3.3 Catalysis

Thorimbert and coworkers have reported the use of complexes $(TBA)_5H_2[\alpha 1-RE(H_2O)_4P_2W_{17}O_{61}]$ (RE = La, Sm, Eu, Yb; TBA = tetrabutylammonium) as Lewis acid catalysts. These complexes are soluble in organic solvents, and the water molecules on the lanthanide ions are labile, thus providing the metal centers with available coordination sites for organic substrates. These catalysts show high chemoselectivity for the competition reactions between

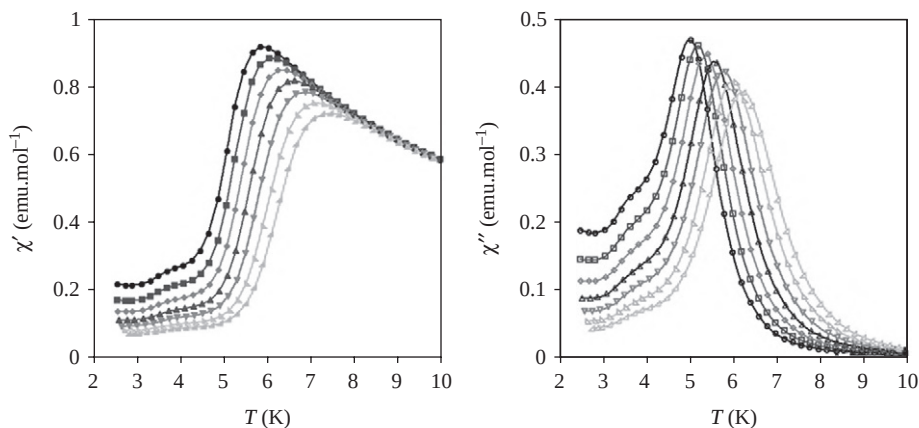


Figure 5.30 In-phase and out-of-phase dynamic susceptibility of $\text{Na}_9[\text{ErW}_{10}\text{O}_{36}] \cdot 35\text{H}_2\text{O}$. From left to right: 1000, 1500, 2200, 3200, 4600, 6800, and 10 000 Hz. Solid lines are eye guides [89]. (Reprinted with permission from M.A. Aldamen, *et al.*, “Mononuclear lanthanide single-molecule magnets based on polyoxometalates,” *Journal of the American Chemical Society*, **130**, no. 28, 8874–8875, 2008. © 2008 American Chemical Society.)

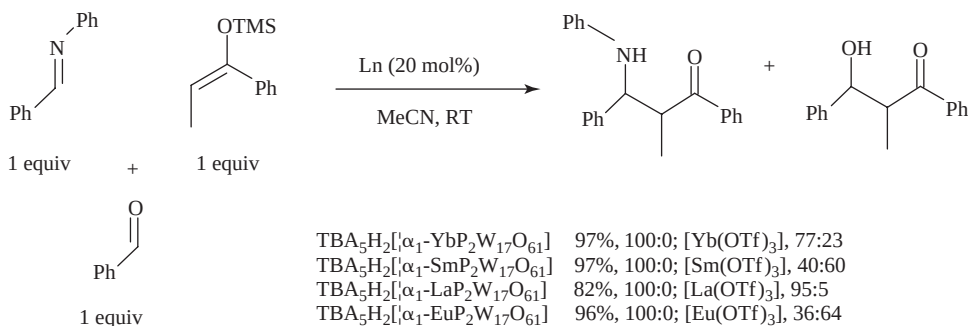


Figure 5.31 Comparison of the chemoselectivity for RE–POM catalysts and RE triflates [90]. (Reproduced with permission from C. Boglio, *et al.*, “Lanthanide complexes of the monovacant Dawson polyoxotungstate $[\alpha_1\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ as selective and recoverable Lewis acid catalysts,” *Angewandte Chemie International Edition*, 2006, **45**, no. 20, 3324–3327. © Wiley-VCH Verlag GmbH & Co. KGaA.)

the benzimine of aniline and benzaldehyde with silyl enol ethers: only the aldime reacted at room temperature. Comparisons of the chemoselectivities for these catalysts and Ln triflates are listed in Figure 5.31. The improved selectivity of these catalysts over $\text{RE}(\text{OTf})_3$ is ascribed to the decreased Lewis acidity of the lanthanides when complexed to the monovacant POM ligand. Moreover, compared with $\text{Yb}(\text{OTf})_3$, $(\text{TBA})_5\text{H}_2[\alpha_1\text{-Yb}(\text{H}_2\text{O})_4\text{P}_2\text{W}_{17}\text{O}_{61}]$ shows an increased stereochemical selectivity for the imino Diels–Alder reactions using bis-aromatic imines as azadienes and cyclic enol ethers as dienophiles. In addition, these catalysts can be easily recovered by the addition of a diethyl ether–ethanol–acetone solution (20 : 1 : 1 by volume) to the reaction mixture, and reused up to ten times with no loss in yield [90].

Hill and coworkers reported the complex $\text{NaH}_3[\text{SiW}_{11}\text{Ce(IV)O}_{39}]$ as a selective and effective catalyst for the aerobic oxidation of formaldehyde to formic acid under very mild (including ambient) conditions. The complex exists as a monomer in solution and as a dimer in the solid state. In the presence of catalytic amounts of $\text{NaH}_3[\text{SiW}_{11}\text{Ce(IV)O}_{39}]$, aqueous solutions of formaldehyde simply exposed to the air are oxidized to formic acid with high selectivity. Optimization of the reaction conditions led to a system that afforded 30 turnovers of $\text{NaH}_3[\text{SiW}_{11}\text{Ce(IV)O}_{39}]$ after 5 hours. Conversions of CH_2O of up to 85% with a 66% yield of HCOOH can be achieved in the presence of small amounts of H_2O_2 [91].

5.3.4 Medicine

Liu *et al.* has reported that the complex $[\text{TbAs}_4\text{W}_{40}\text{O}_{140}]^{25-}$ displays inhibitory action to HL60 (leukemia), B₁₆ (melanoma), H₂₂ (liver cancer cell) cancers, and rectum cancer vivicells as well as breast cancer vivicells [92].

Yamamoto *et al.* have reported that $\text{K}_{13}[\text{Ce}(\text{SiW}_{11}\text{O}_{39})_2]$ shows inhibitory action to the human immunodeficiency virus (HIV) and the simian immunodeficiency virus [93].

Inouye *et al.* have reported $[\text{NH}_4]_{12}\text{H}_2[\text{Eu}_4(\text{MoO}_4)(\text{H}_2\text{O})_{16}(\text{Mo}_7\text{O}_{24})_4] \cdot 13\text{H}_2\text{O}$ displays potent anti-HIV-1 activity [94].

5.4 Outlook

In the large POM family, RE–POM complexes form one of the most interesting subgroups, due to their diverse structures and useful properties for potential applications in material science, catalysis, and medicine. New RE–POM complexes are continuously being prepared and the corresponding property studies have been carried out. However, RE–POM complexes have been experiencing an unparalleled development in the rapid synthesis of new compounds and slow development of RE–POM-based functional materials and devices. How to rationally design and synthesise new RE–POM complexes according to specific application demands and how to transfer rich RE–POM complexes into useful materials are the main problems facing chemists devoted to the field of RE–POMs.

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6

Coordination Chemistry of Rare Earth Alkoxides, Aryloxides, and Hydroxides

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6.1 Introduction

The lanthanides are a unique group of elements. Their f electronic configurations, hard Lewis acid character of their ions, and their large ionic radii render their coordination chemistry distinctly different from that of transition metal elements. Specifically, because of the large ionic size, a high coordination number is required unless sterically bulky ligands are utilized. As an alternative to satisfying this requirement, formation of polynuclear species featuring bridging ligands is a familiar scenario. The insignificant involvement of the f orbitals in chemical bonding means lanthanide–ligand interactions are primarily ionic, leading to generally labile lanthanide complexes with flexible and irregular coordination environments. However, the kinetic lability of a complex can be taken advantage of to promote useful chemical transformations with high turnover numbers. Because of their hard Lewis acid character, lanthanide coordination toward O-based ligands is strongly preferred.

As a class of O-containing ligands, alkoxides and aryloxides occupy an important position in the development of modern coordination chemistry of the lanthanide elements. First known about more than five decades ago and originally prerogatives of academic research, lanthanide alkoxide complexes have become arguably one of the most extensively studied classes of lanthanide-containing compounds [1–4], largely due to the realization that lanthanide alkoxides can be used as molecular precursors for high-purity metal oxide materials [5]. Three decades

of continuous efforts have led to the synthesis of numerous lanthanide alkoxides of various compositions and the production of many useful materials.

Out of the great variety of lanthanide alkoxide complexes stand out two distinct features [6]. First is the frequent observation of polynuclear complexes from reactions actually aiming at the production of the corresponding mononuclear complexes. The formation of such species is in most cases due to serendipity, reflecting the general propensity of the large metal ions to maximize their coordination number and the bridging ability of alkoxide ligands due to their steric and electrical unsaturation. Not surprisingly, the identity of the cluster compounds depends on both the size of the lanthanide ions and the nature of the alkoxide ligands, and cannot be predicted *a priori*. The other distinct feature is the frequent incorporation of small, inorganic entities, most notably, oxo and hydroxo groups, in the structure of many lanthanide alkoxide complexes. These small anionic species are believed to facilitate and template the formation of the resulting complexes and to maintain their structural integrity. They are generally considered to be derived from adventitious hydrolysis of the alkoxide ligands or degradation of ligands or O-containing solvents [for example, THF (tetrahydrofuran), diethyl ether]. These heteroatom-containing species generally display reactivity patterns and properties different from those of homoleptic alkoxides [7].

The chemistry of lanthanide alkoxides is clearly intertwined with that of lanthanide hydroxides. To provide a coherent discussion, the materials in this chapter are organized according to the two distinct ligand types with a selected few alkoxide complexes containing oxo/hydro group(s) in between. As with most lanthanide-containing compounds, the solid-state structures generally differ from those of the solution species, and insights into their structures are often possible through single-crystal X-ray diffraction studies. Thus, particular attention will be paid to the discussion of the salient structural features of the selected examples with an effort to correlate their structures with their properties and possible applications. Interesting properties and chemical reactivities of these two distinct classes of lanthanide complexes are detailed in a separate section toward the respective latter part of their discussions, based on which, useful applications, realized or envisioned, are discussed. This chapter is concluded with a brief summary of the current research status of these two distinct yet closely related research areas of lanthanide coordination chemistry, followed by an account of the challenging issues ahead and suggestions as to toward what directions the chemistries may be heading.

6.2 Lanthanide Alkoxides, Aryloxides, and Macrocyclic Polyaryloxides

Numerous lanthanide alkoxide complexes have been prepared and this family of lanthanide-containing substances continues to attract much interest, both from a synthetic and structural point of view and from the perspective of developing metal oxide-based advanced materials. While the synthetic and structural chemistry of lanthanide alkoxide complexes remains active, creating molecular precursors with tailor-made reactivity and physical properties for advanced materials by employing judiciously designed ligands has enjoyed more recent attention [5, 8–10]. Aliphatic alkoxides, aryloxides, and cyclic polyaryloxides behave rather differently in this regard, due largely to the distinct structural features of the parent ligands. Functionalization of the OR skeletal structure causes not only changes in ligand steric but also coordinating behavior if donor substituents are involved. As compared with aliphatic alkoxides, aryloxido

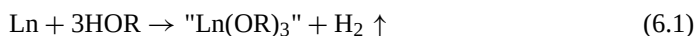
ligands enjoy the ease of functionalization of their aromatic ring. Furthermore, fixing multiple OAr moieties into a macrocyclic setting provides yet another means of controlling the structure and properties of the resulting complexes. Chemistry distinctly different from that of simple aliphatic alkoxides and aryloxides, originating from the constrained and more rigid disposition of the aryloxido moieties, has been observed. Adding more complexity to the situation is the purpose of the functional linking group between the individual aryloxide units within the macrocycle; they may participate in synergetic metal coordination, and thus offering additional opportunities to realize complexes with novel structures and interesting properties.

The discussion below starts with the general synthesis of lanthanide alkoxides, followed by a summary of the OR (R = aliphatic or aryl) coordination modes. Selected examples of complexes will then be presented in order to illustrate the coordination chemistry unique to each class of these ligands (aliphatic alkoxido, aryloxido, and macrocyclic polyaryloxido). Toward the end, catalytic and materials applications of lanthanide alkoxide complexes will be discussed.

6.2.1 Preparative Methods

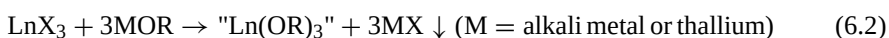
Lanthanide alkoxide complexes can be prepared using a number of methods. The key difference lies in the nature of lanthanide starting materials. These include elemental metals, halides, alkoxides, amides, carboxylates, hydrides, and organometallic species [1–4, 11]. The organic ligands come from aliphatic alcohols, phenols, or their metal salts.

6.2.1.1 Synthesis Starting with Lanthanide Metals



The evolution of H₂ gas serves as a driving force for the reaction. However, lanthanide metals are easily oxidized with the formation of a thin layer of reaction-inhibiting lanthanide oxide. Cleaning and activation of the oxidized metal surface is thus necessary before the reaction can be initiated. This is generally accomplished by treating the metal with Hg(II) catalysts [12–14]. Frequently oxoalkoxides are obtained instead of the targeted alkoxides. One of the best known examples is Ln₅O(OPr^{*i*})₁₃ (Ln = Eu, Nd, Gd, Er, and Yb), isolated from the reaction aiming at the corresponding Ln(OPr^{*i*})₃ [15–21]. The unexpected inclusion of these small anionic entities is generally ascribed to the decomposition of the ligand or solvent molecules, or adventitious hydrolysis if the solvent is not rigorously anhydrous.

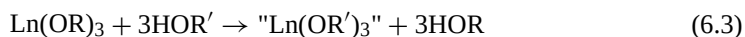
6.2.1.2 Synthesis Starting with Lanthanide Halides



This method makes use of the production of a less soluble metal salt (MX) to drive the reaction to completion. One commonly encountered problem with this route is the low solubility of the starting lanthanide halides. Exposure to anhydrous NH₃ gas helps dissolve lanthanide halides [22]. Following the addition of alkali metal and the appropriate alcohols, the desired alkoxide complexes can be obtained. This reaction is thought to proceed with the formation of a triamide

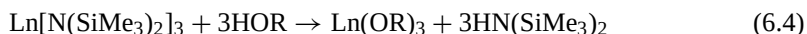
intermediate, similar to the approach starting from lanthanide amides (see below). A major problem is the formation of halide-containing cluster species in addition to the aforementioned inclusion of oxo/hydrox groups when synthesizing aliphatic alkoxide complexes. In fact, this method is generally limited to the synthesis of aryloxide complexes as the steric bulk of the ligand tends to suppress the incorporation of the non-alkoxido groups. In addition, incomplete removal of the MX byproducts presents the other concern, as product mixtures containing both the desired homoleptic complexes and heterometallic complexes are obtained; isolation and purification of products could be difficult, if at all possible.

6.2.1.3 Synthesis Starting with Lanthanide Alkoxides



This method is most useful when the starting lanthanide alkoxides are commercially available. A common issue preventing the extensive application of this methodology is the low solubility of the starting complexes, leading to sluggish reactions and/or incomplete substitution of the alkoxido ligands. Purification and characterization of products thus constitutes a major challenge.

6.2.1.4 Synthesis Starting with Lanthanide Amides



This silylamide route has attracted enormous attention as pure alkoxide complexes may be obtained directly [23]. The success of this reaction hinges upon the volatility of the amine byproduct that drives the reaction to completion [24]. A potential concern is that the amide starting complexes are prepared by the reaction of lanthanide halides with alkali metal amides. High-purity, halide-free amides are thus critical to the success of this synthetic method.

6.2.2 Structural Chemistry of Lanthanide Alkoxide Complexes

An intrinsic feature of the lanthanide coordination chemistry is the tendency of the metal ion to maximize its coordination number. For lanthanide alkoxides, this is readily achieved by bridging interactions via the alkoxido ligands, leading to polynuclear species [25]. The degree of aggregation, that is, the nuclearity of the polynuclear species, depends on the metal size as well as the steric bulk and functionality of the ligands. As the size difference amongst the various lanthanide ions is relatively insignificant due to lanthanide contraction, the ligand dependence of lanthanide alkoxide complexes is expected to be more profound. Indeed, the large number of structurally characterized lanthanide complexes with various alkoxido ligands supports such an analysis.

A number of coordination modes have been observed. Summarized in Figure 6.1, these include monodentate, doubly bridging (μ_2 -OR or μ -OR), triply bridging (μ_3 -OR), and the less common quadruply bridging (μ_5 -OR) modes.

Although it is reasonable to assume that higher-nuclearity complexes generally correspond to the use of less sterically encumbered ligands, the specific structure of a particular complex is uniquely dependent on the nature of its ligand. Thus readers are cautioned that each

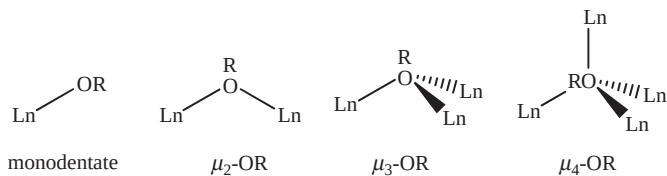


Figure 6.1 Coordination modes of alkoxido ligands observed in lanthanide alkoxide complexes.

example in the following discussion is unique, and should not be treated as general. Adding more complexity to the scenario is the inclusion of the aforementioned small-unit inorganic entities (oxo, hydroxo, hydrido, halo) and coordinating solvent molecules. The outcome of the competition between these different natured ligands is the dauntingly diverse structural patterns of the lanthanide alkoxides.

Using carefully chosen literature examples, specific features of the lanthanide coordination chemistry using aliphatic alkoxido, aryloxido, and macrocyclic polyaryloxido ligands are discussed below. For each ligand type, those bearing simple, spectator-like non-coordinating substituents and those functionalized with donor groups capable of metal coordination will be treated separately.

6.2.2.1 Complexes of Alkoxido Ligands with Non-coordinating Substituents

Some representative alkoxido ligands equipped with non-donor type substituents are shown in Figure 6.2.

Shown in Figure 6.3 is the structure of $\text{Ln}_5(\mu_5\text{-O})(\mu_3\text{-OPr}^i)_4(\mu\text{-OPr}^i)_4(\text{OPr}^i)_5$, prepared by Hg(II)-catalyzed alcoholysis of lanthanide metals [16]. The pentanuclear complex is comprised of a square-pyramid of Ln atoms, each terminally coordinated to one OPr^i ligand. Upon each triangular face of the square-pyramid is a $\mu_3\text{-OPr}^i$, while bridging each edge of the square base is a $\mu\text{-OPr}^i$. An oxo ligand is in the interior of the structure, interacting with all five metal atoms. This structure is shared by a number of rare earth complexes (Ln = Eu, Nd, Gd, Er, Yb).

Reacting NdCl_3 with NaOPr^i in HOPr^i afforded $\text{Nd}_6(\mu_6\text{-Cl})(\mu_3\text{-OPr}^i)_2(\mu\text{-OPr}^i)_9(\text{OPr}^i)_6$ featuring a $\mu_6\text{-Cl}^-$ encapsulated in the trigonal-prism of six Nd atoms (Figure 6.4) [25, 26]. There are 17 OPr^i ligands, six being terminally bound to the metal atoms, nine being edge bridging, and two being capping for the trigonal faces of the prism.

Increasing the ligand steric bulk has significant effects on the complex structure. For example, a trinuclear complex formulated as $[\text{Y}_3(\mu_3\text{-O}^t\text{Bu})(\mu_3\text{-Cl})(\mu\text{-O}^t\text{Bu})_3(\text{O}^t\text{Bu})_3\text{Cl}(\text{THF})_2]$

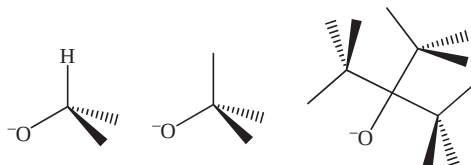


Figure 6.2 Molecular structures of some aliphatic alkoxido ligands for lanthanide complexes.

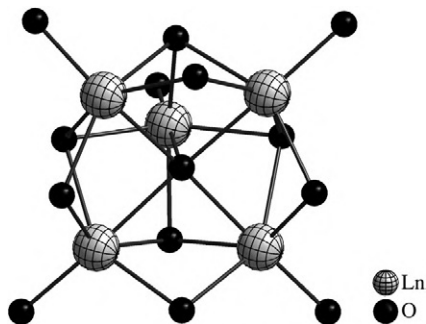


Figure 6.3 The metal–oxygen core structure of $\text{Ln}_5(\mu_5\text{-O})(\mu_3\text{-OPr}^i)_4(\mu\text{-OPr}^i)_4(\text{OPr}^i)_5$. (Ln = Eu, Nd, Gd, Er, Yb) [16]. (Redrawn from W.J. Evans, M.A. Greci and J.W. Ziller, “The utility of N-methylimidazole and acetonitrile as solvents for the direct reaction of europium with alcohols including the first example of acetonitrile as a $\mu - \eta 1:\eta 1$ -bridging ligand,” *Chemical Communications*, 2367–2368, 1998.)

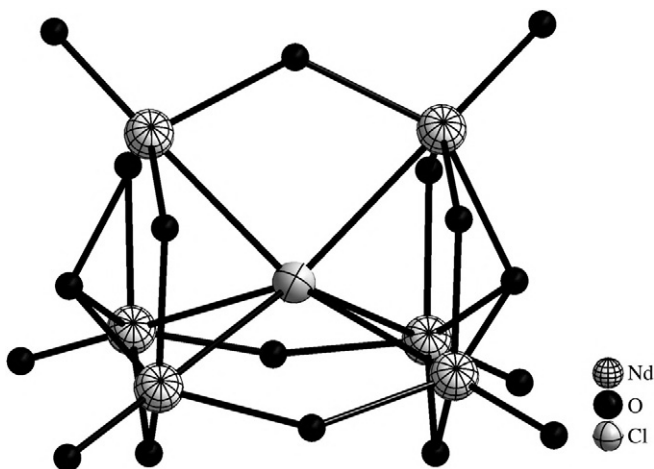


Figure 6.4 Crystal structure of $\text{Nd}_6(\mu_6\text{-Cl})(\mu_3\text{-OPr}^i)_2(\mu\text{-OPr}^i)_9(\text{OPr}^i)_6$ [25]. (Reproduced from Z.P. Zheng, “Cluster compounds of the f-elements,” in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

was obtained from the reaction of YCl_3 with NaOBu^t in THF [25, 27]. The Y atoms form a triangle that has $\mu\text{-OBu}^t$ groups along each edge, a $\mu_3\text{-OBu}^t$ group on one side of the Y_3 plane, and a $\mu_3\text{-Cl}$ ligand on the other side (Figure 6.5). Each of the Y atoms is coordinated to a terminal OBu^t ligand. In addition, one Y atom is additionally coordinated by a chloro ligand, while the other two each features the coordination of one THF molecule.

The coordination of solvent molecules may reflect a compromise between the propensity of the metal to satisfy its coordinative saturation requirement and the inadequate room for the accommodation of an additional alkoxido ligand that is sizably bulkier than a solvent molecule. That is, the relatively small solvent molecules serve to fulfill the metal’s high-coordination need but without interrupting, as a bulkier alkoxido ligand would, the overall structure of the resulting complex.

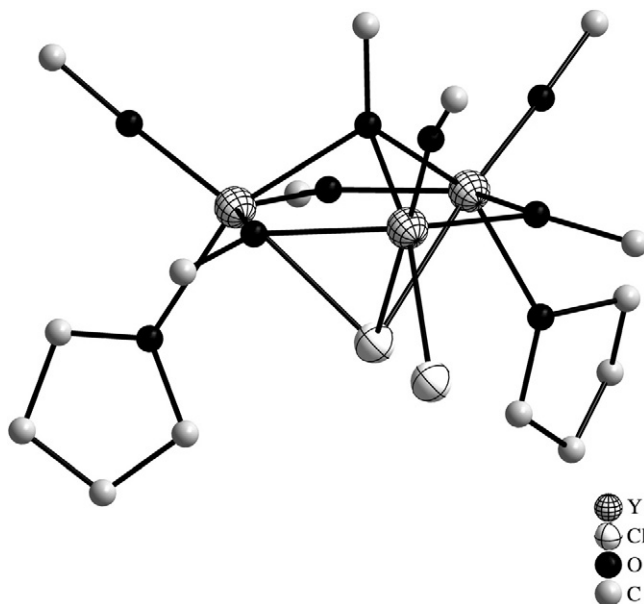


Figure 6.5 Crystal structure of $[Y_3(\mu_3\text{-OBu}^t)(\mu_3\text{-Cl})(\mu\text{-OBu}^t)_3(\text{OBu}^t)_3\text{Cl}(\text{THF})_2]$. [25]. (Reproduced from Z.P. Zheng, "Cluster compounds of the f-elements," in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume **40**, 2010, with permission from Elsevier.)

The presence of solvent ligands offers opportunities for further chemical transformations. Partial desolvation of $[Y_3(\mu_3\text{-OBu}^t)(\mu_3\text{-Cl})(\mu\text{-OBu}^t)_3(\text{OBu}^t)_3\text{Cl}(\text{THF})_2]$ in toluene led to the assembly of a tetradecanuclear $Y_{14}(\text{OBu}^t)_{28}\text{Cl}_{10}\text{O}_2(\text{THF})_2$ composed of four trimetallic units whose structures resemble closely that of the THF-solvated precursor [28]. Inter-unit bridging interactions are provided by $\mu\text{-Cl}^-$, $\mu_4\text{-O}$ ion, and $[(\mu\text{-OBu}^t)_2\text{Y}(\mu\text{-Cl})_2]_2$ groups.

6.2.2.2 Complexes of Donor-Functionalized Alkoxido Ligands

The presence of non-innocent and potentially metal-coordinating donor groups in alkoxido ligands offers the possibility of realizing lanthanide complexes of novel structures and interesting properties. A number of such functionalized ligands are collected in Figure 6.6. The donor groups are responsible for the fine-tuning of the overall electronic and steric structures of the

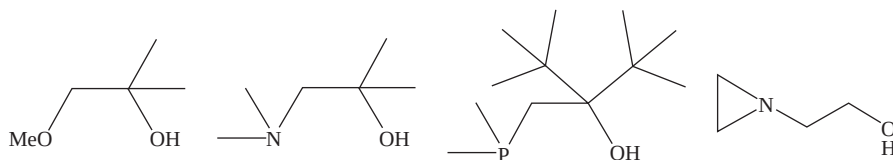


Figure 6.6 Molecular structures of representative donor-functionalized alkoxido ligands.

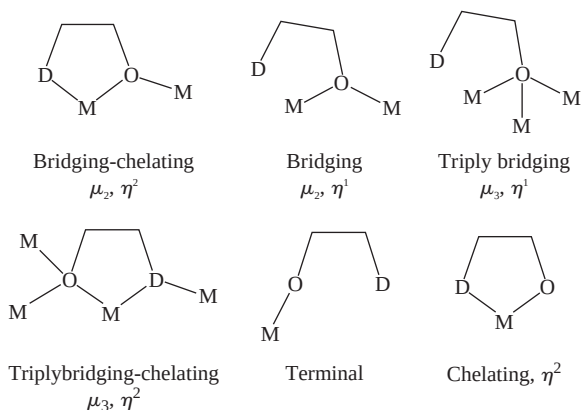


Figure 6.7 Diverse coordination modes achievable with a donor-functionalized alkoxido ligand.

alkoxido ligand via coordination modes unavailable to their unmodified parent, resulting in complexes of novel structures, enhanced stability, and improved processing characteristics in the context of materials preparation [3]. In particular, chelation of metal atoms serves as an efficient way of controlling the degree of oligomerization. It should be noted, however, even with the donor functionality, chelation does not necessarily have to occur. As is clear from the following examples, a number of different coordination modes can coexist in the same complexes, reflecting the necessary compromise between the need of the metal atom for coordination saturation and the lack of enough space for all the ligands to assume the same sterically more demanding modes. The various coordination modes reported for a generic donor-functionalized alkoxido ligand are summarized in Figure 6.7.

Shown in Figure 6.8 is the crystal structure of $[\text{La}_3(\mu_3, \eta^2\text{-mmp})_2(\mu_2, \eta^2\text{-mmp})_3(\text{mmp})_4]$, a trinuclear complex prepared by reacting $[\text{La}\{\text{N}(\text{SiMe}_3)_2\}_3]$ with Hmmp (Hmmp = $\text{HOCMe}_2\text{CH}_2\text{-OMe}$, 1-methoxy-2-methylpropan-2-ol; mmp is the corresponding deprotonated or oxido form) [25, 29]. Each of its three La atoms is bonded to the alkoxide groups of two face-capping and two edge-bridging ligands. Three different coordination modes have been identified, two of which being chelating using both the alkoxido O atom and the MeO donor group. However, one of these chelation interactions utilizes the alkoxido O atom in a triply bridging fashion (μ_3, η^2), whereas the other is doubly bridging (μ_2, η^2). In the third mode, the ligand is monodentate, with the alkoxido O as the only metal-coordinating atom.

A tetranuclear oxo-hydroxo cluster formulated as $\text{Lu}_4(\mu_4\text{-O})(\mu_3\text{-OH})(\mu_3, \eta^2\text{-mmp})(\mu_2, \eta^2\text{-mmp})_3(\mu_2, \eta^1\text{-mmp})(\text{mmp})_6$ was obtained with the same mmp ligand [24, 25], in which a new coordination mode, that is, $\mu_2, \eta^1\text{-mmp}$, not present in the above trinuclear lanthanum complex, is identified (Figure 6.9). The ligand uses only the alkoxido O atom to bridge two Lu atoms. Such a mode is less sterically demanding than $\mu_3, \eta^2\text{-mmp}$ or $\mu_2, \eta^2\text{-mmp}$ as no chelation occurs. The coordination space freed up is compensated by the incorporation of the oxo and hydroxo groups.

Using a highly hindered phosphino-alkoxide ligand, lanthanoid metal complexes $[\text{Ln}(\text{OCBu}_2\text{CH}_2\text{PMe}_2)_3]$ ($\text{Ln} = \text{Y}$ or Nd) have been obtained [30]. These are the first monomeric homoleptic examples of lanthanide alkoxide complexes. The bulky substituents

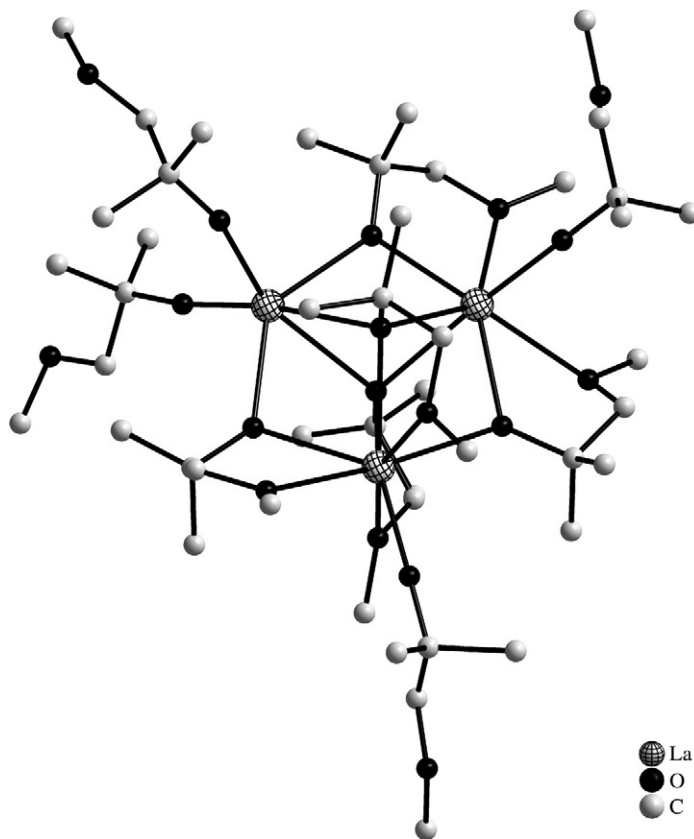


Figure 6.8 Crystal structure of $\text{La}_3(\mu_3, \eta^2\text{-mmp})_2(\mu_2, \eta^2\text{-mmp})_3(\text{mmp})_4$ [25]. (Reproduced from Z.P. Zheng, "Cluster compounds of the f-elements," in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

are certainly responsible for the solubility of the complexes in hydrocarbon solvents and the monomeric nature (Figure 6.10).

Donor-functionalized alkoxido ligands can come in rather unusual forms. H_4L (1,4,7,10-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane), a cyclen type macrocycle functionalized with four pendant hydroxyethyl "arms" was obtained by the cyclooligomerization of aziridineethanol. It has been found to support the assembly of $\{[\text{Nd}(\text{NO}_3)_2]_3[\text{Nd}(\text{L})]_2(\mu_5\text{-OH})\}$ [25, 31], a pentanuclear cluster complex composed of two $[\text{Nd}(\mu_4\text{-L})]^-$ anions, three $[\text{Nd}(\text{NO}_3)_2]^+$ cations, and the $\mu_5\text{-OH}^-$ anion which "glues" these five metal-containing fragments together to form a square pyramidal arrangement of the metal atoms (Figure 6.11).

The macrocyclic ligand is a sophisticated tetraalkoxido ligand functionalized with a 12-membered cyclen. Alternatively, it can be viewed as four amine-functionalized ethyleneoxido ligands being organized into a macrocyclic setting. Two $\text{OCH}_2\text{CH}_2\text{N}$ fragments (μ_2, η^2) of the L ligand each uses its N and O atoms to chelate a Nd in $[\text{Nd}(\mu_4\text{-L})]^-$ while using its alkoxido O atom to bridge one $[\text{Nd}(\text{NO}_3)_2]^+$ cation, whereas the alkoxido O atoms of the other

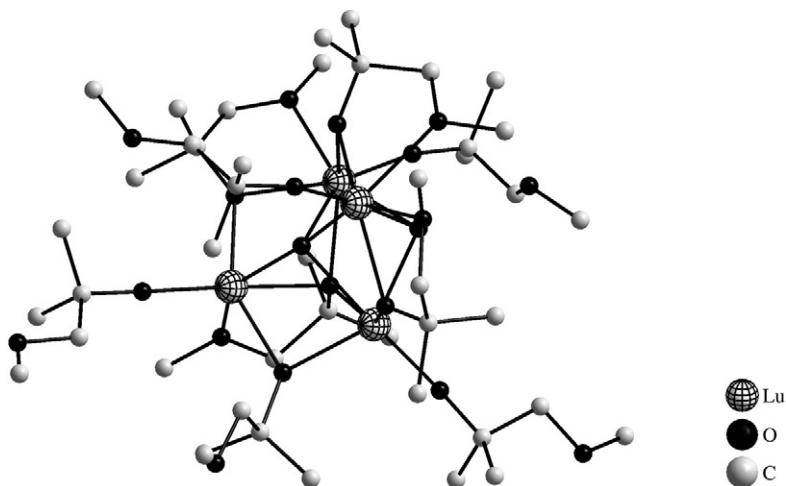


Figure 6.9 Crystal structure of $\text{Lu}_4(\mu_4\text{-O})(\mu_3\text{-OH})(\mu_3, \eta^2\text{-mmp})(\mu_2, \eta^2\text{-mmp})_3(\mu_2, \eta^1\text{-mmp})(\text{mmp})_4$ [25]. (Reproduced from Z.P. Zheng, "Cluster compounds of the f-elements," in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

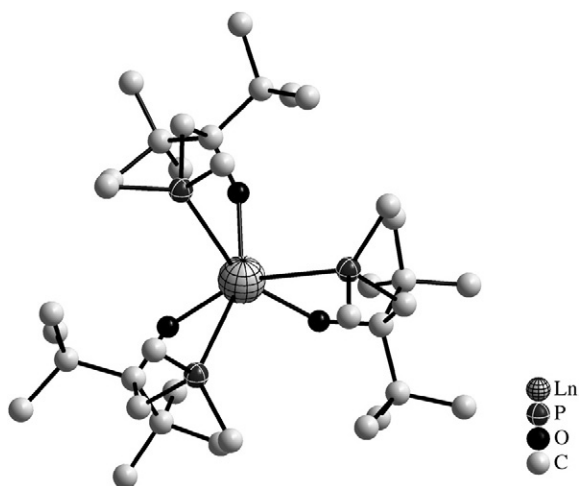


Figure 6.10 Crystal structure of $[\text{Ln}(\eta^2\text{-OCBu}_2\text{CH}_2\text{PMe}_2)_3]$ ($\text{Ln} = \text{Y}, \text{Nd}$) [30]. (Redrawn from P.B. Hitchcock, M.F. Lappert and A.I. MacKinnon, "Use of a highly hindered phosphinoalkoxide ligand in the formation of monomeric homoleptic lanthanoid metal complexes: X-ray structures of $[\text{Ln}(\eta^2\text{-OCBu}_2\text{CH}_2\text{PMe}_2)_3]$ ($\text{Ln} = \text{Y}$ or Nd)," *Journal of the Chemical Society, Chemical Communications*, 1557–1558, 1988.)

two $\text{OCH}_2\text{CH}_2\text{N}$ arms (μ_3, η^2) each is triply bridging, connecting the $[\text{Nd}(\mu_4\text{-L})]^-$ fragment and two units of $[\text{Nd}(\text{NO}_3)_2]^+$.

6.2.2.3 Complexes of Aryloxo Ligands with Non-coordinating Substituents

As with aliphatic alkoxides, aryloxides have also been used extensively for the preparation of lanthanide complexes. Among the many attractive features is the ease of manipulation of the

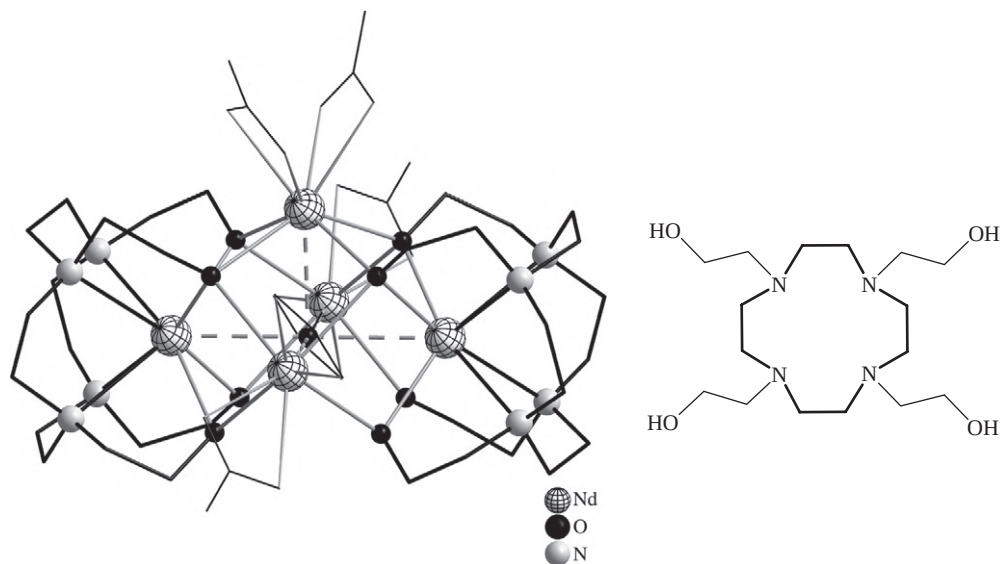


Figure 6.11 Crystal structure of $\{[\text{Nd}(\text{NO}_3)_2]_3[\text{Nd}(\text{L})_2(\mu_5\text{-OH})]\}$ (left), a pentanuclear cluster complex with a donor-functionalized ligand L (right) [25]. (Reproduced from Z.P. Zheng, “Cluster compounds of the f-elements,” in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

steric bulk and introduction of functional groups via chemistry performed on the aromatic ring of these ligands.

Direct reactions of elemental lanthanoids and HOAr ($\text{HOC}_6\text{H}_3\text{Bu}_2^t$ -3,5, 3,5-di-*tert*-butylphenol) followed by crystallization from THF or hexane afforded hydrocarbon-soluble lanthanoid aryloxide cluster complexes $[\text{La}_4(\mu\text{-OAr})_8(\text{OAr})_4(\text{OH}_2)]$ and $[\text{Nd}_3(\mu_3\text{-OAr})_2(\mu\text{-OAr})_3(\text{OAr})_4(\text{THF})_4]\cdot 4\text{THF}$ [25, 32]. The structure of $[\text{La}_4(\mu\text{-OAr})_8(\text{OAr})_4(\text{OH}_2)]$ has its four hexacoordinate La atoms arranged into a square-plane with each edge doubly bridged by two OAr ligands. Each La atom is additionally coordinated by a terminal OAr ligand (Figure 6.12). A single water oxygen atom lies on an inversion center in the middle of the square.

A structural comparison with the trinuclear Nd complex prepared under otherwise the same conditions is revealing. The lower nuclearity is probably due to the smaller size of Nd(III) versus La(III). As such, the metal atoms are brought closer to one another, leading to a somewhat shrunken coordination sphere. A direct consequence is the reduced number of doubly bridging ligands along the edge of the metal triangle, even though the Ln : OAr ratio of 1 : 3 is the same.

6.2.2.4 Complexes of Donor-Functionalized Aryloxido Ligands

Aryloxido ligands can also be functionalized with donor substituents. As compared with the donor-modified aliphatic alkoxido ligands, the present ligands are structurally more rigid, which bears consequence for their coordination of lanthanide ions.

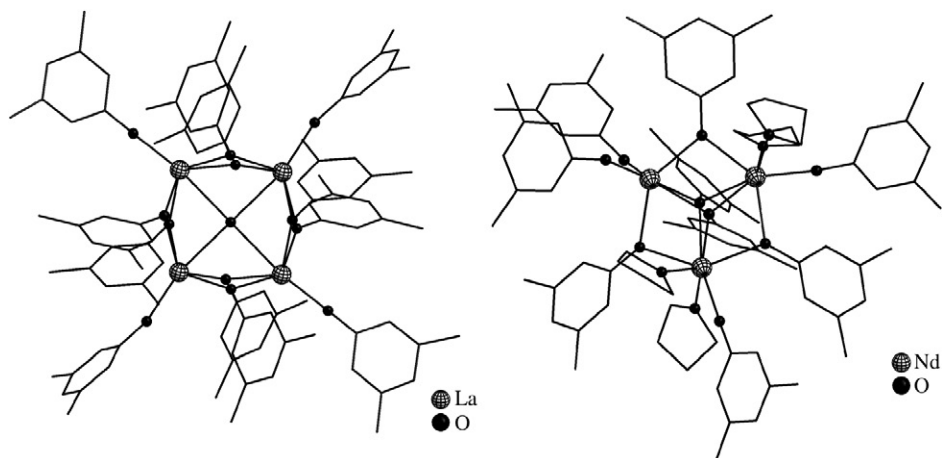


Figure 6.12 Crystal structures of $[\text{La}_4(\mu\text{-OAr})_8(\text{OAr})_4(\mu_4\text{-OH}_2)]$ and $[\text{Nd}_3(\mu_3\text{-OAr})_2(\mu\text{-OAr})_3(\text{OAr})_4(\text{THF})_4]\cdot 4\text{THF}$ [25]. (Reproduced from Z.P. Zheng, “Cluster compounds of the f-elements,” in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

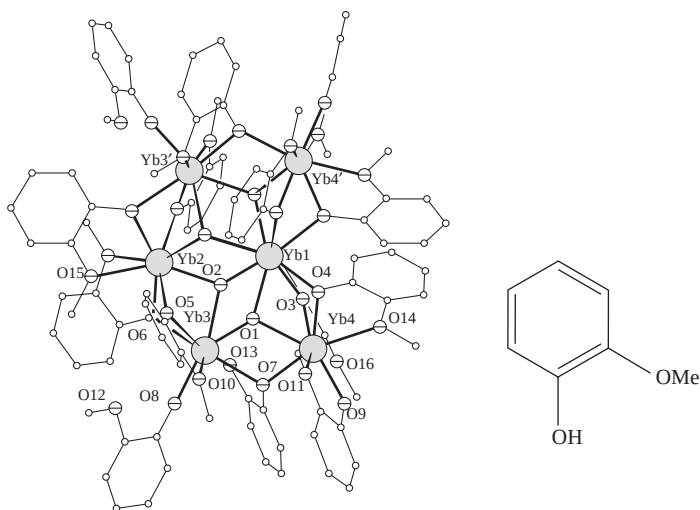


Figure 6.13 Crystal structure of $\text{Yb}_6(\mu_3\text{-OH})_4(\mu, \eta^2\text{-OC}_6\text{H}_4\text{OMe})_{10}(\eta^2\text{-OC}_6\text{H}_4\text{OMe})_2(\text{OC}_6\text{H}_4\text{OMe})_2$ [33]. (Redrawn from J. Carretas *et al.*, “Synthesis and characterization of samarium, europium and ytterbium aryloxides. Crystal structure of $[\text{Yb}_6(\text{OH})_4(\text{OC}_6\text{H}_4\text{OMe})_{14}]\cdot 4\text{THF}$,” *Journal of Alloys and Compounds*, 376, 289–292, 2006.)

A hexanuclear complex $[\text{Yb}_6(\mu_3\text{-OH})_4(\mu, \eta^2\text{-OC}_6\text{H}_4\text{OMe})_{10}(\text{OC}_6\text{H}_4\text{-}\mu\text{-OMe})_2(\text{OC}_6\text{H}_4\text{OMe})_2]\cdot 4\text{THF}$ was obtained by reacting Yb metal with 2-methoxyphenol in liquid NH_3 , followed by recrystallization of the product mixture from THF–pentane [33]. As shown in Figure 6.13, the six Yb atoms form a nearly planar arrangement, joined together by four $\mu_3\text{-OH}$ groups and ten aryloxides in a $\mu, \eta^2\text{-OC}_6\text{H}_4\text{OMe}$ bridging-chelating mode. There are

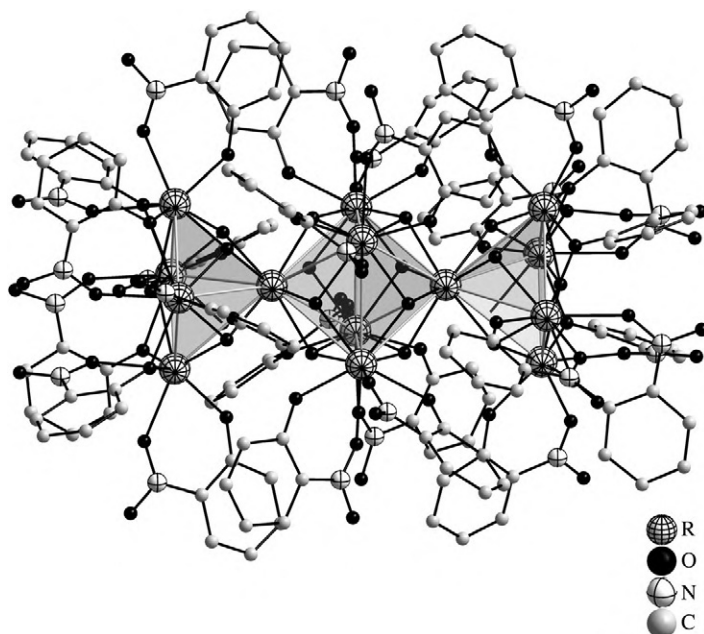


Figure 6.14 Crystal structure of $\text{Ln}_{14}(\mu_4\text{-OH})_2(\mu_3\text{-OH})_{16}(\mu, \eta^2\text{-OC}_6\text{H}_4\text{NO}_2)_8(\eta^2\text{-OC}_6\text{H}_4\text{NO}_2)_{16}$ [25]. (Reproduced from Z.P. Zheng, "Cluster compounds of the f-elements," in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

four more aryloxido ligands, two of them each being chelating ($\eta^2\text{-OC}_6\text{H}_4\text{OMe}$) while the other two each being monodentate using only the phenolato O atom for metal coordination.

Rather unusual tetradecanuclear complexes of the general formula $\text{Ln}_{14}(\mu_4\text{-OH})_2(\mu_3\text{-OH})_{16}(\mu, \eta^2\text{-OC}_6\text{H}_4\text{NO}_2)_8(\eta^2\text{-OC}_6\text{H}_4\text{NO}_2)_{16}$ ($\text{Ln} = \text{Dy}, \text{Er}, \text{Tm}, \text{Yb}$) (Figure 6.14) were obtained with the use of *ortho*-nitrophenolate [25, 34, 35]. The core of $[\text{Ln}_{14}(\mu_4\text{-OH})_2(\mu_3\text{-OH})_{16}]$ can be viewed as a three vertex sharing octahedra of lanthanide atoms with two atoms missing, one from each of the two outer units. Each of the triangular metal faces is capped by a $\mu_3\text{-OH}$ group while each terminal face features one $\mu_4\text{-OH}$ situated in the middle of the square-like arrangement. The 24 nitrophenolato ligands exhibit two distinct coordination modes, one being chelating-bridging ($\mu, \eta^2\text{-OC}_6\text{H}_4\text{NO}_2$) and the other chelating ($\eta^2\text{-OC}_6\text{H}_4\text{NO}_2$) only, both involving the use of the phenolato O atom and one of the two nitro O atoms.

Phenolates modified with other donor groups have also been utilized for the preparation of lanthanide complexes. For example, using 3-methoxysalicylaldehyde or *o*-vanillin – a multidentate ligand whose functional groups include aldehyde, ether, and phenol as ligands, cationic trinuclear Gd and Dy hydroxo clusters, $[\text{L}_3\text{Ln}_3(\mu_3\text{-OH})_2\text{X}_2(\text{H}_2\text{O})_n]^{2+}$ ($\text{L} = 3\text{-methoxysalicylaldehyde}$, $\text{Ln} = \text{Gd}$, $\text{X} = \text{NO}_3^-$, $n = 6$; $\text{Ln} = \text{Dy}$, $\text{X} = \text{Cl}$, $n = 5$), have been obtained [25, 36, 37]. The crystal structure of $[\text{L}_3\text{Dy}_3(\mu_3\text{-OH})_2\text{Cl}_2(\text{H}_2\text{O})_5]^{2+}$, shown in Figure 6.15, displays a trigonal-bipyramid composed of three Dy atoms and two face-capping $\mu_3\text{-OH}$ groups. Using its phenoxo group, each deprotonated *o*-vanillin ligand bridges two

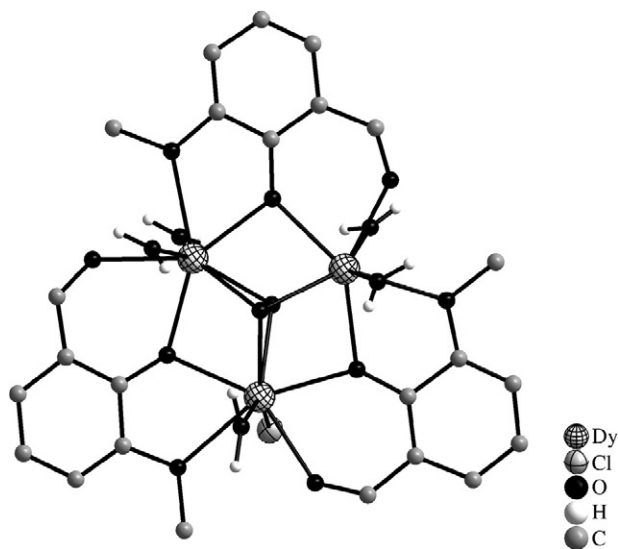


Figure 6.15 Crystal structures of the cationic clusters $[L_3Dy_3(\mu_3-OH)_2Cl_2(H_2O)_5]^{2+}$ ($L = 3$ -methoxysalicylaldehyde) [25]. (Reproduced from Z.P. Zheng, “Cluster compounds of the f-elements,” in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

metal atoms along each side of the triangle. Aldehyde and methoxy groups also coordinate to the metal atoms; each, together with the phenolato O atom, engages in chelation of one particular metal atom. The coordination mode of the ligand can therefore be described as $\mu : (\eta^2, \eta^2)\text{-OC}_6\text{H}_3(3\text{-OMe})(\text{OCH})$.

Schiff base ligands have also been utilized to form lanthanide alkoxide complexes. A $[\text{Sm}_6(\mu_3\text{-OH})_6]^{8+}$ core-containing cluster complex with a double Schiff base (SB) ligand featuring two 3,5-Bu₆ salophen linked by an ethylene group is shown in Figure 6.16 [25, 38]. Each of the SB units uses its phenolato O and the amide N for chelation of one particular metal atom. As such, each ligand contributes six coordination atoms to the hepta-coordinate Sm atom; the other three ligands are $\mu_3\text{-OH}$ groups within the distorted cubane core.

This Sm complex with a double SB ligand provides a unique example of lanthanide coordination with functionalized aryloxides. The coordinating functions are organized in a common ligand framework, and the ligand is expected to show coordination behaviors different from when the same number of coordinating units are independent and can be positioned more freely. Indeed, the formation of the hepta-coordination sphere may be a manifestation of the steric hindrance imposed by the multidentate and somewhat rigid double SB ligand, as the preferred coordination number of Sm(III), a relatively large lanthanide ion, is 8 or 9.

6.2.2.5 Cyclic Polyaryloxo Ligands for Lanthanide Complexation

The foregoing example suggests that with the use of macrocyclic polyaryloxo ligands, different lanthanide coordination chemistry may be anticipated as a result of the constrained

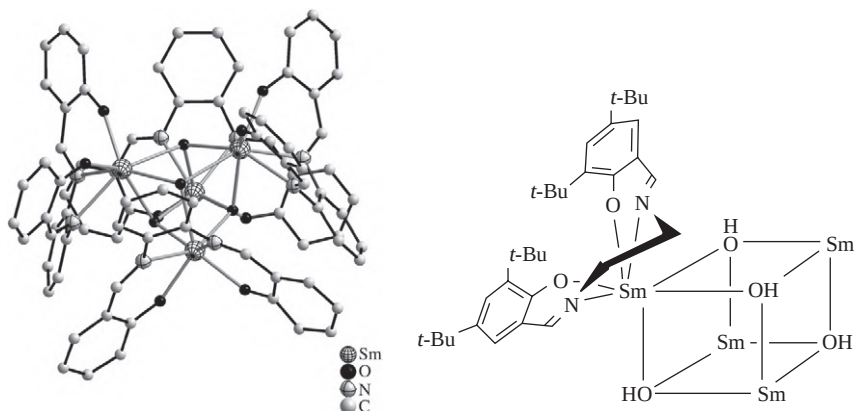


Figure 6.16 Molecular and crystal structure of the $[\text{Sm}_4(\mu_3\text{-OH})_4]^{8+}$ core-containing cluster complex with a Schiff base ligand [25]. (Reproduced from Z.P. Zheng, "Cluster compounds of the f-elements," in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

disposition of the aryloxido moieties. Furthermore, if additional donor groups are present, even more diverse coordination chemistry may be achievable as aryloxides and the donors can participate in synergetic metal coordination.

Calixarenes are macrocyclic ligands featuring n phenol groups connected by n methylene groups to make a ring structure. Using calixarenes as aryloxido ligands, polynuclear lanthanide complexes have been obtained. For example, a tetranuclear cluster assembly, formulated as $[(\mu_3\text{-OH})_2(\mu_3 : \eta^2, \eta^2\text{-CO}_3)\text{Eu}_4(p\text{-Bu}^t\text{-calix[7]arene-4H})_2(\text{DMSO})_6]$ (DMSO = dimethyl sulfoxide) was obtained from a mixture of $\text{Eu}(\text{ClO}_4)_3$, $p\text{-Bu}^t\text{-calix[7]arene}$, and Et_3N [25, 39]. Its solid-state structure (Figure 6.17, left) may be viewed as a pair of binuclear units bridged by carbonate and adventitious hydroxide, each incompletely enveloped by a calix[7]arene (not shown) whose deprotonated phenol units display both terminal and bridging coordination modes. With the use of $p\text{-Bu}^t\text{-calix[9]arene}$, a larger oligonuclear assembly $[(\mu_3\text{-OH})_9(\text{H}_2\text{O})_2\text{Eu}_7(p\text{-Bu}^t\text{-calix[9]arene-6H})_2(\text{DMSO})_6]$ results, featuring a core of two corner-sharing cubanes (Figure 6.17, right) encapsulated by the bulky ligands. It should be noted that not all the phenol groups are deprotonated, as mandated by the charge balancing requirement.

6.2.2.6 Macrocyclic Polyaryloxido Ligands with Coordinating Bridging Groups

Donor groups present in a calixarene framework offer an additional means of increasing structural sophistication of their complexes. This has been illustrated in $[\text{Nd}_4(\mu_4\text{-OH})(p\text{-Bu}^t\text{-tetrathiacalix[4]arene-4H})_2(\text{DMF})_8(\text{DMSO})_2](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ [25, 40], the first crystallographically characterized lanthanide complex with thiacalixarene, a heteroatom-containing calixarene ligand. The four Nd atoms of the cationic complex are bridged by a $\mu_4\text{-OH}$ group into a square arrangement, encapsulated by two cone-shaped calixarene units (Figure 6.18). The coordination geometry of Nd can be described as a tricapped trigonal-prism formed by four

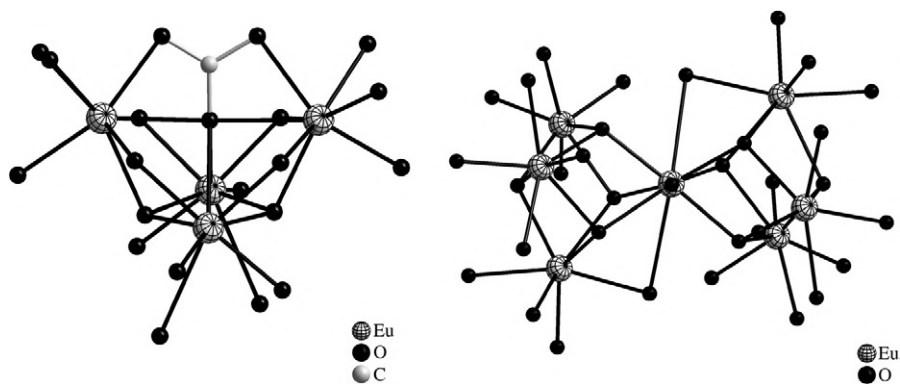


Figure 6.17 Crystal structures of $[(\mu_3\text{-OH})_2(\mu_3 : \eta^2, \eta^2\text{-CO}_3)\text{Eu}_6(p\text{-Bu}^t\text{-calix[7]arene-4H})_2(\text{DMSO})_6]$ (left) and $[(\mu_3\text{-OH})_9(\text{H}_2\text{O})_2\text{Eu}_7(p\text{-Bu}^t\text{-calix[9]arene-6H})_2(\text{DMSO})_6]$ (right). Only their core structures are shown [25]. (Reproduced from Z.P. Zheng, “Cluster compounds of the f-elements,” in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

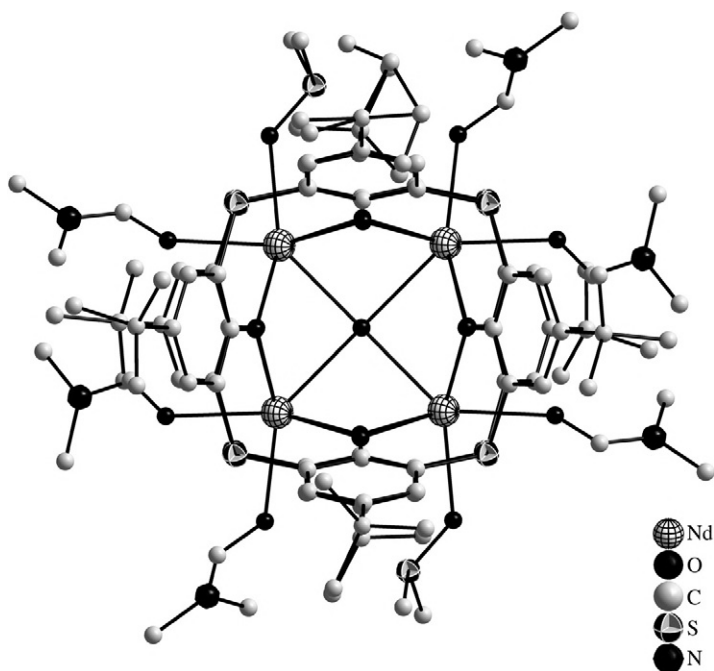


Figure 6.18 Crystal structure of the cationic cluster $[\text{Nd}_4(\mu_4\text{-OH})(p\text{-Bu}^t\text{-tetrathiacalix[4]arene-4H})_2(\text{DMF})_8(\text{DMSO})_2]^{3+}$ [25]. (Reproduced from Z.P. Zheng, “Cluster compounds of the f-elements,” in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

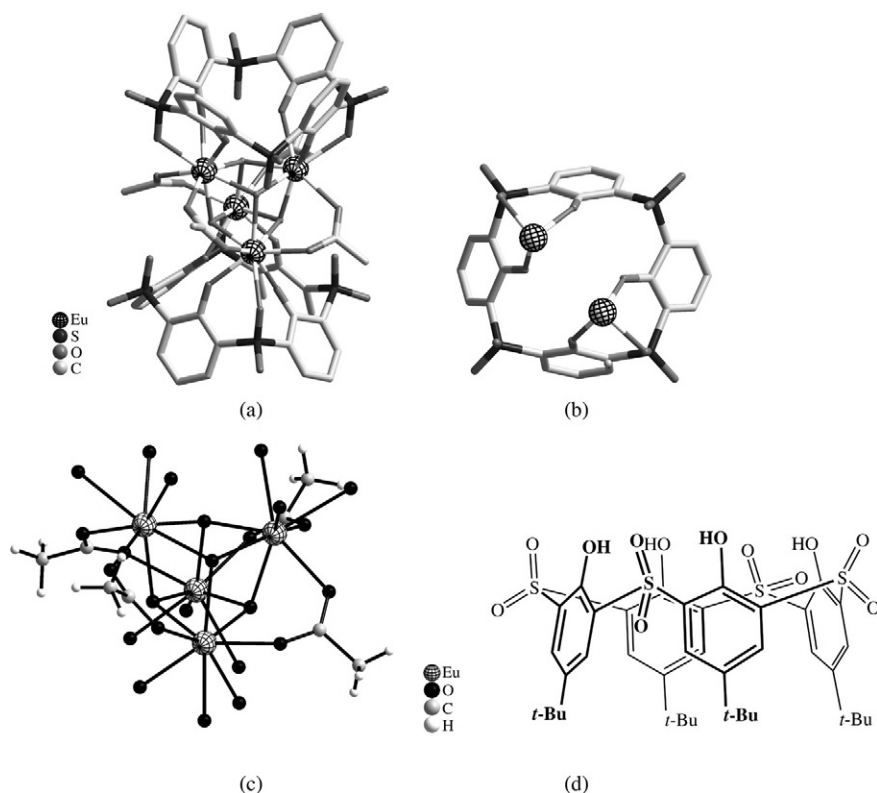


Figure 6.19 (a) Crystal structure of $[\text{Eu}_4(\text{SO}_2\text{calix[4]arene})_2(\mu_3\text{-OH})_4(\text{AcO})_4]^{4-}$; (b) the structure of one of its dinuclear building units; and (c) the hydroxo bridged tetranuclear cluster core; (d) the molecular structure of the ligand in its neutral form is shown [25]. (Reproduced from Z.P. Zheng, “Cluster compounds of the f-elements,” in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

bridging calixarene phenoxide and two solvent (DMF or DMSO) oxygen atoms; the capping groups are the $\mu_4\text{-OH}$ and two S atoms.

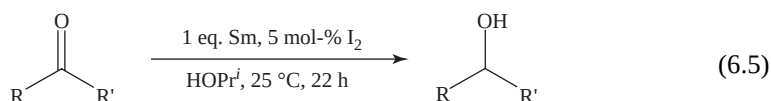
In addition to providing extra coordination atoms and therefore generating novel complex structures, the use of donor-functionalized ligands may also lead to improved materials properties. For example, reacting *p*-Bu^t-tetrasulfonyl[4]arene ($\text{SO}_2\text{calix[4]arene}$) with $\text{Ln}(\text{AcO})_3 \cdot n\text{H}_2\text{O}$ in the presence of Bu_4^tNOH afforded tetranuclear complexes of the general formula $(\text{Bu}_4^t\text{N})_4[\text{Ln}_4(\text{SO}_2\text{calix[4]arene})_2(\mu_3\text{-OH})_4(\text{AcO})_4]$ ($\text{Ln} = \text{Gd}, \text{Eu}, \text{and Tb}$). Because of the π -conjugated system over the entire molecule, this ligand exhibits enhanced antenna effects over a regular calixarene (its component phenol groups in a regular calixarene are isolated by methylene groups) for the UV excitation of coordinated lanthanide ions in luminescence studies. The crystal structure of its Eu(III) complex is shown in Figure 6.19, in which a conical $\text{SO}_2\text{calix[4]arene}$ behaved as a bis-tridentate ligand, coordinating each lanthanide ion via two phenoxo and one sulfonyl O atoms [25, 41, 42].

6.2.3 Applications of Lanthanide Alkoxides

Lanthanide alkoxide complexes are of fundamental interest because of the associated synthetic challenges and the great variety of their structures. They are also an important class of materials, either as catalysts to promote useful but otherwise difficult chemical transformations or as molecular precursors for the realization of high-quality metal oxide-based advanced materials. Selected examples illustrating these applications are discussed below.

6.2.3.1 Chemical Applications, Stoichiometric and Catalytic Synthesis

Lanthanide alkoxide complexes have been shown to promote a number of useful chemical reactions, whereby the complex is used catalytically or applied in stoichiometric amount. One such reactions is the Meerwein–Ponndorf–Verley reduction (MPV) or the Oppenauer oxidation, depending on which component is the desired product (Equation 6.5). If the alcohol is the desired product, the reaction is viewed as Meerwein–Ponndorf–Verley Reduction [43].



This reaction is believed to proceed via a hydride shift from the α -carbon of an alcohol component to the carbonyl carbon of a second component, which proceeds via a six-membered transition state involving the metal center of the catalyst (Figure 6.20). Isopropanol has been frequently used as the hydride donor because the resulting acetone can be continuously removed from a reaction mixture by distillation.

Shibasaki and Groger developed lanthanide/alkali binaphthoxide-based Lewis acid–Brønsted base bifunctional catalysts [44]. One such example, the (*R,R*)-Ln-M-linked BINOL complex,

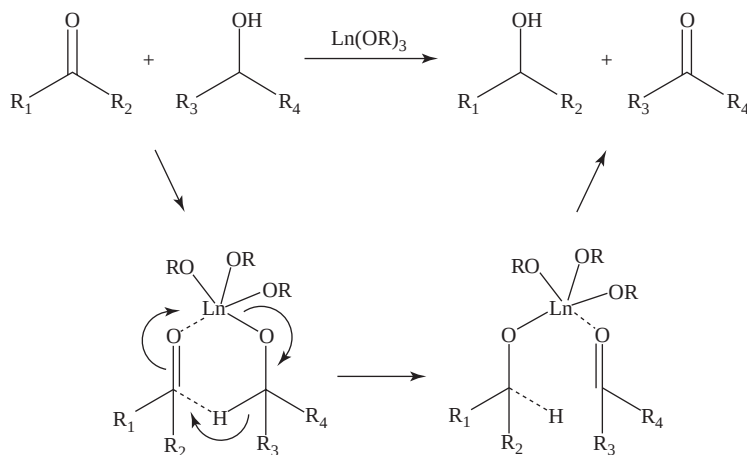


Figure 6.20 Schematic illustration of a generic Meerwein–Ponndorf–Verley reduction catalyzed by a lanthanide alkoxide complex.

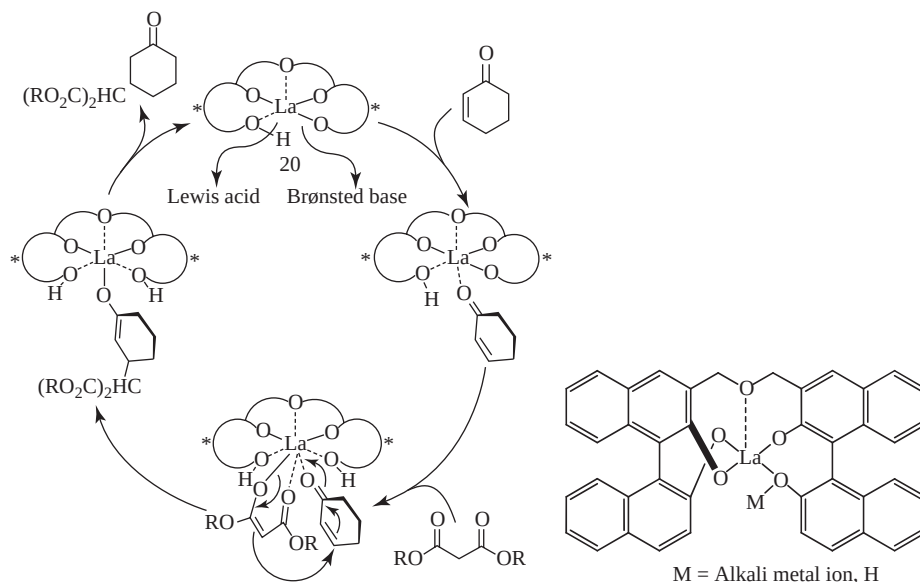


Figure 6.21 The proposed mechanism of Michael reaction of enones with malonates catalyzed by (R,R) -Ln-M-linked BINOL complex, a bifunctional asymmetric catalyst developed by Shibasaki.

is shown in Figure 6.21, together with the proposed mechanism of a Michael reaction of enones with malonates catalyzed by this complex [45]. With these bifunctional asymmetric catalysts, many important asymmetric C–C bond-forming reactions, for example, Dies–Alder reactions and Michael addition, among others, can proceed through simple proton transfer. As such, reaction complexity is markedly reduced, so are the byproduct wastes.

Lanthanide alkoxide complexes have also been used to catalyze the ring-opening polymerization of lactones [46–48]. For example, ϵ -caprolactone is a cyclic ester with a ring size of seven. It is a monomer used in the production of various polymers including synthetic fibers, polyurethane elastomers, plastics, adhesive fabrics, and coatings. The ring-opening polymerization can be catalyzed by a lanthanide alkoxide complex as schematically shown in Figure 6.22. The first step involves the coordination of the lactone carbonyl group by the lanthanide atom. Intramolecular nucleophilic addition of an alkoxido ligand to the lactone and the accompanying lactone C–O bond cleavage lead to the opening of the ring and a new Ln–alkoxide complex. Propagation proceeds with this newly formed alkoxide species acting as a catalyst for the ring-opening of a second molecule of lactone.

6.2.3.2 Materials Applications

Creating metal oxide based advanced materials using lanthanide alkoxide complexes as molecular precursors is another area where the lanthanide alkoxide chemistry has found significant applications [5, 7–10]. A technique heavily used in the semiconductor industry for the growth of metal oxides materials is the process of metal-organic vapor chemical vapor deposition

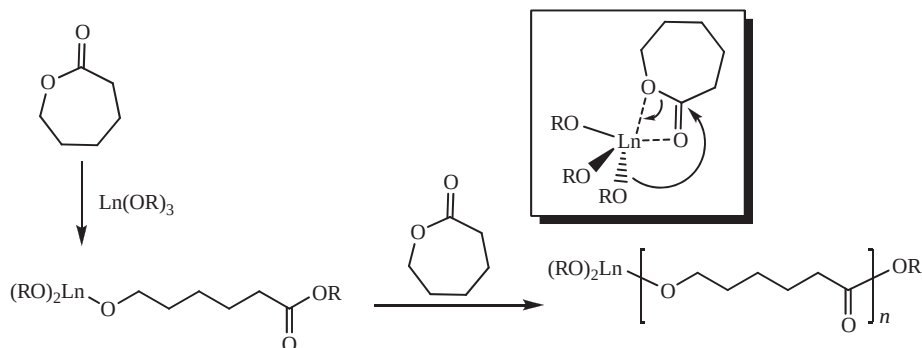


Figure 6.22 Schematic presentation of the ring-opening polymerization of ϵ -caprolactone catalyzed by a lanthanide alkoxide complex.

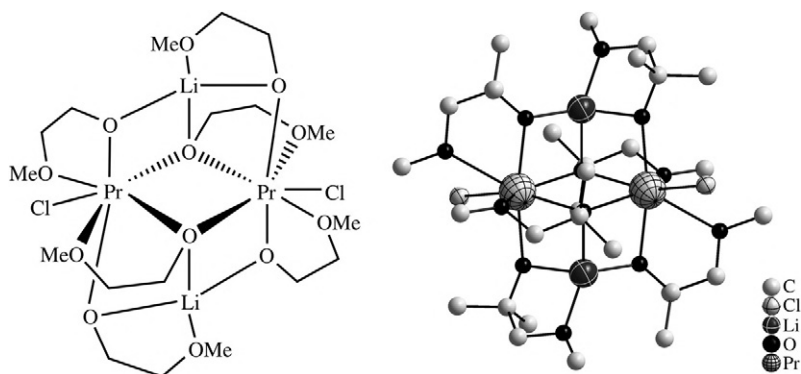


Figure 6.23 The molecular (left) and crystal (right) structures of $[\text{Pr}(\text{mmp})_3\text{LiCl}]_2$. For clarity, the ligand methyl groups are omitted from the molecular structure [49]. (Redrawn from J.M. Gaskell *et al.*, “Deposition of Pr- and Nd-aluminate by liquid injection MOCVD and ALD using single-source heterometallic alkoxide precursors,” *Chemistry of Materials*, **19**, 4796–4803, 2007.)

(MOCVD). Key to its success is the availability of precursors with desired physical properties, volatility, and low melting point, for example. Additional desirable characteristics include the precursor’s thermal stability, non-toxicity, and a high-temperature decomposition pathway that leads to zero ligand incorporation into the growing film at the heated substrate interface. Many lanthanide alkoxide complexes meet these stringent requirements as they can be made mononuclear by using sterically cumbersome ligands, in particular with the use of fluorinated ligands to reduce the intermolecular interactions and to enhance volatility.

Using tetraglyme stabilized $[\text{Ln}(\text{mmp})_3]$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Gd}$) as precursors [29], the growth of lanthanide oxides Ln_2O_3 by the MOCVD process has been achieved. The molecular and crystal structures of one such precursor molecule, $[\text{Pr}(\text{mmp})_3\text{LiCl}]_2$ [49], crystallized out from a solution containing $[\text{Pr}(\text{mmp})_3]$ and LiCl are shown in Figure 6.23.

Lanthanide aluminates (LnAlO_x) are of interest as buffer layers in controlling the overgrowth of various perovskite films and as alternative gate dielectrics to SiO_2 . Using the “single-source” heterometallic lanthanide aluminum isopropoxide precursors $[\text{LnAl}(\text{OPr}^i)_6(\text{HOPr}^i)]_2$

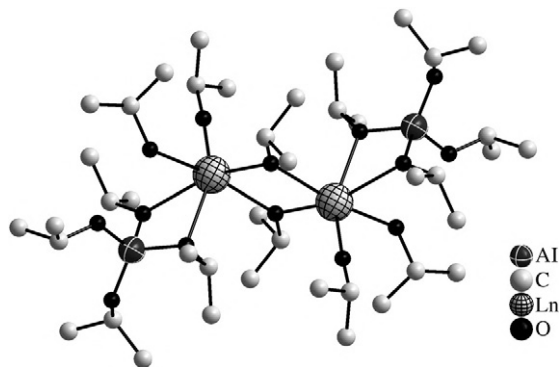


Figure 6.24 The crystal structure of $[\text{LnAl}(\text{OPr}^i)_6(\text{HOPr}^i)_2]$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$), a single-source precursor to corresponding lanthanide aluminates (LnAlO_x) [50]. (Redrawn from T.D. Manning *et al.*, “Deposition of LaAlO_3 films by liquid injection MOCVD using a new $[\text{La-Al}]$ single source alkoxide precursor,” *Journal of Materials Chemistry*, **15**, 3384–3387, 2005.)

($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$), whose structure is shown in Figure 6.24, stoichiometric, amorphous LnAlO_3 can be deposited at 450–500°C by liquid injection MOCVD [50, 51].

Lanthanide alkoxide complexes can also be used as precursors for materials synthesis by the sol–gel process. Dissolving a high-purity alkoxide precursor in a suitable solvent, usually the parent alcohol, a homogeneous solution of the precursor can be obtained. Hydrolysis can then be initiated by altering the pH conditions of the solution. Condensation of the hydrolysis products/intermediates leads to the production of a gel containing the hydrated metal oxide. Drying and calcinating the wet gel eventually affords oxide-based ceramic or glassy materials. The high purity of the metal alkoxide precursors, the homogeneity of the components at the molecular level, and the low processing temperature all contribute to the eventual realization of high-quality advanced materials.

A heterometallic alkoxide complex $[\text{GdFe}(\text{OPr}^i)_6(\text{HOPr}^i)_2]$, isostructural to $[\text{LnAl}(\text{OPr}^i)_6(\text{HOPr}^i)_2]$, the lanthanide aluminate precursor described, has been used for the preparation of metastable rare earth iron perovskites of the general formula LnFeO_3 [52]. These materials are of interest for magneto-optical data storage because of their unique magnetic properties, such as high coercivity and Farady rotation [53, 54]. Previous synthesis using a mixture of Ln^{3+} and Fe^{3+} constituents suffered from the production of a mixture containing garnet ($\text{Ln}_3\text{Fe}_5\text{O}_{12}$) and magnetite (Fe_3O_4), both favored thermodynamically [55]. A major breakthrough in the synthesis of orthiferrite films and particles has now been achieved by using a controlled hydrolysis of $[\text{GdFe}(\text{OPr}^i)_6(\text{HOPr}^i)_2]$. The key to such success clearly lies in the required cation ratio being present in $[\text{GdFe}(\text{OPr}^i)_6(\text{HOPr}^i)_2]$ with preformed Ln-O-Fe bonds.

6.3 Lanthanide Hydroxide Complexes

The large number of lanthanide alkoxide complexes featuring the inclusion of oxo or hydroxo groups unmistakably suggests that the coordination chemistry of lanthanide hydroxide is intimately associated with that of the alkoxides. Arguably the simplest and most ubiquitous O-containing ligand, the water molecule, occupies a special position in the development of lanthanide coordination chemistry. Upon coordination to the Lewis acidic lanthanide ion, an

aqua ligand is activated, and there is a natural propensity for its deprotonation and the concomitant formation of corresponding hydroxo species. With the hydroxo ligand being unsaturated, both coordinatively and electrically, an ololation reaction, that is, the aggregation of individual mononuclear hydroxo species via bridging interactions, is expected, leading to polynuclear hydroxo-bridged species [56, 57]. If this hydrolytic process proceeds naturally without any control, intractable gel-like mixtures composed of mainly lanthanide oxides or hydroxides of various degrees of aggregation will eventually be obtained. It is because of this uncertainty in lanthanide hydrolysis that the chemistry of lanthanide hydroxide complexes has traditionally been considered uninteresting and limited in scope. However, stimulated by the recurring appearance of a number of well defined, cluster-like lanthanide-hydroxo core motifs [38, 58–65] and the structural and functional resemblance of some of these species [58–63] to the naturally occurring nucleases (metalloenzymes capable of catalyzing the hydrolytic cleavage of DNA and RNA) [66–68], systematic efforts have been made for about the last decade in the search for rational synthetic methods for these otherwise elusive lanthanide-containing species. A large number of lanthanide hydroxide complexes, frequently polynuclear in nature and characterized with cluster-like core structures, have since been prepared. In addition, their interesting physical properties and chemical reactivity have been studied. In fact, the coordination chemistry of lanthanide hydroxide complexes has now evolved into an exciting area in lanthanide research. It is as extensive and accessible as the polymetallic chemistry that had been dominated by lanthanide alkoxides.

6.3.1 Rational Synthetic Methodologies for Lanthanide Hydroxide Complexes

The most successful synthetic approach to structurally well defined lanthanide hydroxide complexes is the “ligand-controlled hydrolysis” approach [69–71]. The essence of this methodology is schematically shown in Figure 6.25. It makes use of the high propensity of lanthanide ions toward hydrolysis, but controlled and limited by certain supporting ligands. The scheme starts with a lanthanide complex whose coordination sphere constitutes both organic and aqua

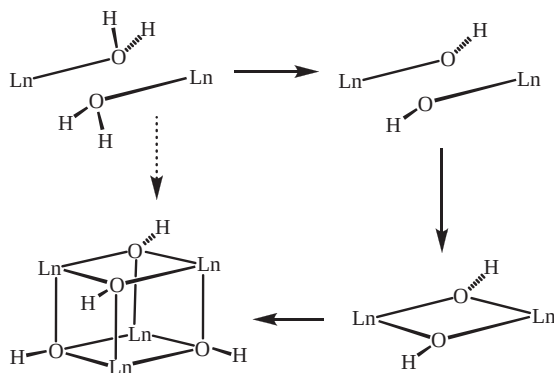


Figure 6.25 Schematic illustration of ligand-controlled hydrolytic approach to polynuclear lanthanide hydroxide complexes.

ligands. Upon deliberate pH enhancement, the aqua ligands, bound to, and hence activated by, the metal ion, undergo deprotonation, affording the corresponding hydroxo species. To fulfill its coordinative and electrical unsaturation, the hydroxo group is expected to seek its coordination to other lanthanide ions, resulting in the aggregation of a number of such lanthanide–hydroxo units and the assembly of polynuclear lanthanide hydroxide complexes. It is the preoccupation of the coordination sphere by the supporting ligands that controls the number of sites available for aqua coordination, and, in turn, the degree of hydrolysis and the structure of the cluster eventually assembled.

This hydrolysis followed by the aggregation process is analogous to the one underlying the sol–gel chemistry, although condensation rather than olation occurs in the latter process. The key difference is that for the rational synthesis of hydroxide complexes, multidentate ancillary ligands are employed to limit the degree of hydrolysis and aggregation, leading eventually to finite-sized and structurally well defined clusters rather than the less well defined, gel-like materials by the conventional sol–gel process. The degree of olation (and therefore the nuclearity of the resulting polynuclear complex) depends on a number of factors. These include the steric bulk of the organic ligands, the metal ion (size and Lewis acidity), and the number of aqua ligands present in the low-pH complexes.

A great variety of organic ligands have been successfully applied in this capacity. These include α -amino acids [56, 72–74], polyaminopolycarboxylates [69–71], functionalized carboxylates [65, 75–77], β -diketonates [66, 78–89], Schiff bases [38], and some other less commonly used ligands [90–93]. Hydroxide complexes have also been prepared by direct hydrolysis of simple lanthanide salts, such as iodide [94], nitrate [95–98], OTf[−] (OTf = triflate) [99], and perchlorate [98]. In these cases, the anions may serve to limit the degree of lanthanide hydrolysis, especially in the case of strongly coordinating nitrate ions [95–98]. However, it is not surprising that in general the complexes so assembled are not nearly as stable as those obtained with the use of organic, multidentate supporting ligands [97, 98].

6.3.2 Coordination Modes of Hydroxo Ligands and Key Lanthanide–Hydroxo Motifs

The hydroxo ligand displays a number of coordination modes, collected in Figure 6.26. Although there are only three lone pairs of electrons on one OH[−] group, it can accommodate more than three lanthanide atoms in its coordination sphere, as a result of the primarily ionic nature of the bonding of the lanthanide ions.

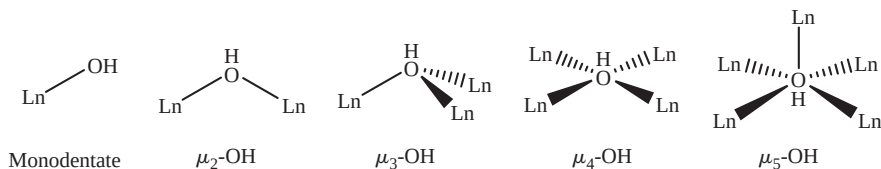


Figure 6.26 Coordination modes displayed by hydroxo ligand in its lanthanide complexes.

There exists only one example of a lanthanide complex where a hydroxo ligand is terminally coordinated [100]. The crystal structure of $\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OH})$ [Tp^{Me_2} = tris(dimethylpyrazolyl)borate] is shown in Figure 6.27, from which it is clear that the two extremely bulky Tp^{Me_2} ligands offer perfect steric protection of the metal atom. The complex formed with the sterically hindered calixarene, $[\text{Nd}_4(\mu_4\text{-OH})(p\text{-Bu}^t\text{-tetrathiocalix[4]arene-4H})_2(\text{DMF})_8(\text{DMSO})_2](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ (Figure 6.18) represents one rare example of discrete tetranuclear species possessing a quadruply bridging hydroxo group [60]. In comparison, the coordination of lanthanide ions with doubly or triply bridging hydroxo ligands is a common phenomenon. The two latter coordination modes are largely responsible for the great varieties of polynuclear lanthanide hydroxide complexes known. Many higher-nuclearity cores can be formally constructed using smaller well defined $\text{Ln}\text{-OH}$ building blocks. The most frequently encountered building blocks are depicted in Figure 6.28.

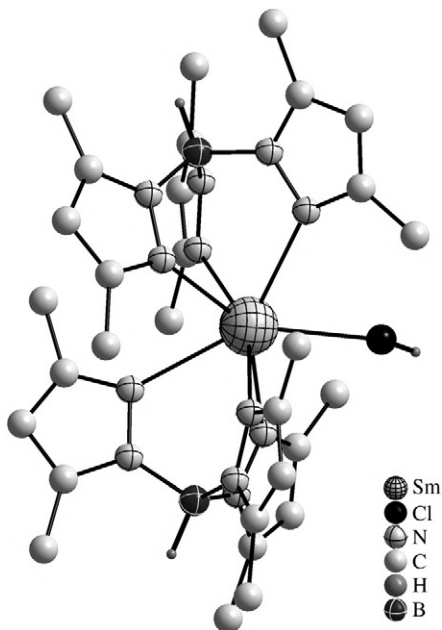


Figure 6.27 The crystal structure of $\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OH})$ where Tp^{Me_2} is tris(dimethylpyrazolyl)borate, a sterically cumbersome ligand [100]. (Redrawn from N. Marques, A. Sella and J. Takats, "Chemistry of the lanthanides using pyrazolylborate ligands," *Chemical Reviews*, **102**, 2137–2160, 2002.)

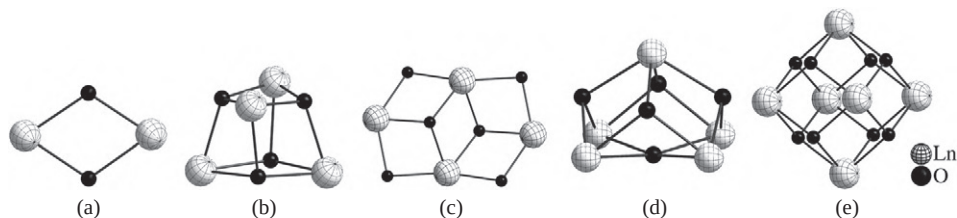


Figure 6.28 Commonly observed lanthanide-hydroxo coordination building blocks with which higher-nuclearity cluster complexes may be assembled.

6.3.2.1 Dinuclear Complexes

A large number of lanthanide hydroxide complexes featuring a diamond-shaped dinuclear core doubly bridged by two μ_2 -OH groups have been reported [58–63]. This dinuclear core structurally resembles the active site of many naturally occurring nucleases. Shown in Figure 6.29 is a recently reported dinuclear complex $[\text{Eu}_2\text{L}_2(\mu\text{-OH})_2]$ ($\text{L} = 1,7\text{-diaz-4,10,13-trioxacyclopentadecane-}N,N'\text{-diacetic acid}$) [66]. It has been shown that this dinuclear hydroxo complex and its kinetic equivalents are capable of cleaving phosphodiester 2-hydroxypropyl-6-nitrophenyl phosphate, a simple RNA analog.

It should be noted that most structurally characterized dinuclear complexes are products of adventitious lanthanide hydrolysis, and are not reproducible. With the ligand-controlled hydrolytic approach, they can now be rationally synthesized starting from a mononuclear aqua complex. Shown in Figure 6.30 is the synthesis of $[(\text{EDTA})\text{Er}(\mu\text{-OH})_2\text{Er}(\text{EDTA})]^{4-}$ ($\text{EDTA} = \text{ethylenediaminetetraacetate}$); the dinuclear core doubly bridged by the $\mu\text{-OH}$ groups is encapsulated by two hexadentate EDTA ligands, one on each metal atom [69].

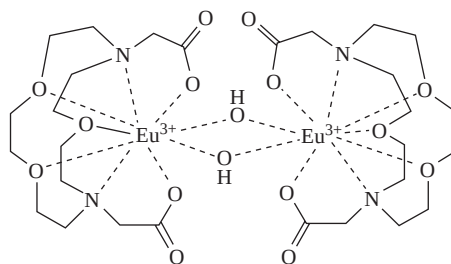


Figure 6.29 The molecular structure of dinuclear complex $[\text{Eu}_2\text{L}_2(\mu\text{-OH})_2]$ ($\text{L} = 1,7\text{-diaz-4,10,13-trioxacyclopentadecane-}N,N'\text{-diacetic acid}$.)

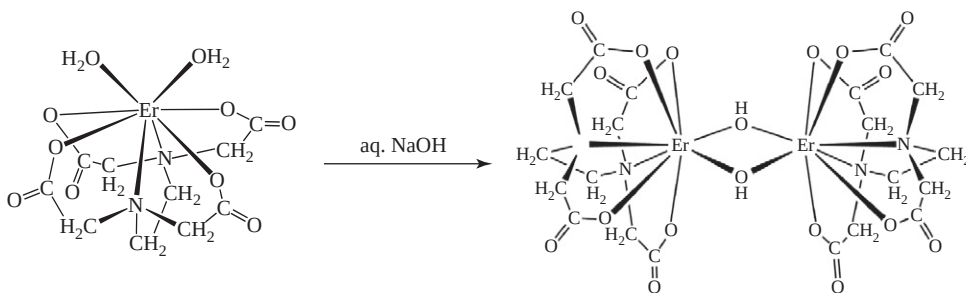


Figure 6.30 Synthesis of the dinuclear hydroxide complex $[(\text{EDTA})\text{Er}(\mu\text{-OH})_2\text{Er}(\text{EDTA})]^{4-}$ by deliberately hydrolyzing $[(\text{EDTA})\text{Er}(\text{H}_2\text{O})_2]^-$ with aqueous NaOH.

6.3.2.2 Trinuclear Complexes

The number of trinuclear lanthanide hydroxide complexes is relatively small in comparison with dinuclear or tetranuclear complexes. The first example to be structurally characterized was reported by Evans and coworkers, based on which the insightful suggestion of extensive and accessible chemistry of lanthanide hydroxides was made [63]. Later examples include species of the general formula $[\text{L}_3\text{Ln}_3(\mu_3\text{-OH})_2\text{X}_2(\text{H}_2\text{O})_n]^{2+}$ ($\text{L} = 3\text{-methoxysalicylaldehyde}$, $\text{Ln} = \text{Gd}$, $\text{X} = \text{NO}_3^-$, $n = 4$; $\text{Ln} = \text{Dy}$, $\text{X} = \text{Cl}$, $n = 5$); the complexes display a common triangular arrangement of the metal atoms face-capped by one or two $\mu_3\text{-OH}$ ligands, as shown in Figure 6.15 [36, 37].

6.3.2.3 Tetranuclear Complexes

Tetranuclear complexes are the most abundant amongst all reported lanthanide hydroxides. Three distinct core motifs have been identified, namely the cubane, the rhombus, and the square.

The distorted cubane features four metal atoms and four $\mu_3\text{-OH}$ groups occupying the alternate vertices of the cube. This motif was identified as early as 1968 in the crystal structure of rare earth Faujasite-type zeolites [101]. Its prevalence has subsequently been suggested by a number of unexpected cluster complexes isolated under markedly different reaction conditions [38, 64, 65]. The large number of complexes bearing such a core structure, from the extensive work by Zheng and coworkers, clearly establish its ubiquity [69–71].

The prevalence of this cubane-like motif is also reflected by the many higher-nuclearity cluster complexes where the presence of the cubane units is conspicuous. By sharing one vertex, a heptanuclear cluster core is achieved. Two such examples are $[(\mu_3\text{-OH})_9(\text{H}_2\text{O})_2\text{Eu}_7(p\text{-Bu}^t\text{-calix[9]arene-6H})_2(\text{DMSO})_6]$ (Figure 6.17) [39] and $[\text{Ln}_7(\mu_3\text{-OH})_8(1,4\text{-NDA})_6(\text{OH})_{0.5}(\text{Ac})_{0.5}(\text{H}_2\text{O})_7]$ ($\text{Ln} = \text{Ho}$, Yb) $[\text{Yb}_7(\mu_3\text{-OH})_8]^{13+}$ (1,4-NDA = 1,4-naphthalenedicarboxylate) [75].

With four, five, and six vertex-sharing cubanes, wheel-like cyclic structures have also been obtained (Figure 6.31) [72, 73, 102]. Small anionic entities including halide and carbonate ions have been found to assist in or template the assembly of these multi-cubane clusters. Utilizing squares and hexagons of the cubanes, clusters featuring 24 vertex-sharing cubanes organized into a giant cage of the well known sodalite structure have been realized [102].

Individual cubane units can also be linked by bridging ligands. Shown in Figure 6.32 is the crystal structure of the cationic cluster complex $\{[\text{Eu}_4(\mu_3\text{-OH})_4(\text{nic})_6(\text{H}_2\text{O})_8]_2\}^{4+}$ (nic = nicotinate) [57]. This octanuclear complex is a dimer of $[\text{Eu}_4(\mu_3\text{-OH})_4(\text{nic})_6(\text{H}_2\text{O})_8]^{2+}$, each encapsulated by six nicotinate ligands. These ligands display three different coordination modes, four of which using only their carboxylate groups to bridge two lanthanide ions, one being monodentate using its carboxylate O atom, and the sixth one bridging the two cluster units, using its carboxylate group for two lanthanide ions of one of the cubanes while using its pyridyl N atom to coordinate a lanthanide ion within the other tetranuclear cluster core.

Using glutamic [25, 56] and aspartic acids [74], two amino acids equipped with a side-chain carboxylate group as bridging ligands, polymeric arrays of the cubanes have also been obtained. Each edge of the Ln_6 tetrahedron is bridged by a carboxylate group. With the presence of carboxylate groups in both the amino acid backbone and its side-chain, individual cubane units are linked into an extended porous structure, as shown in Figure 6.33.

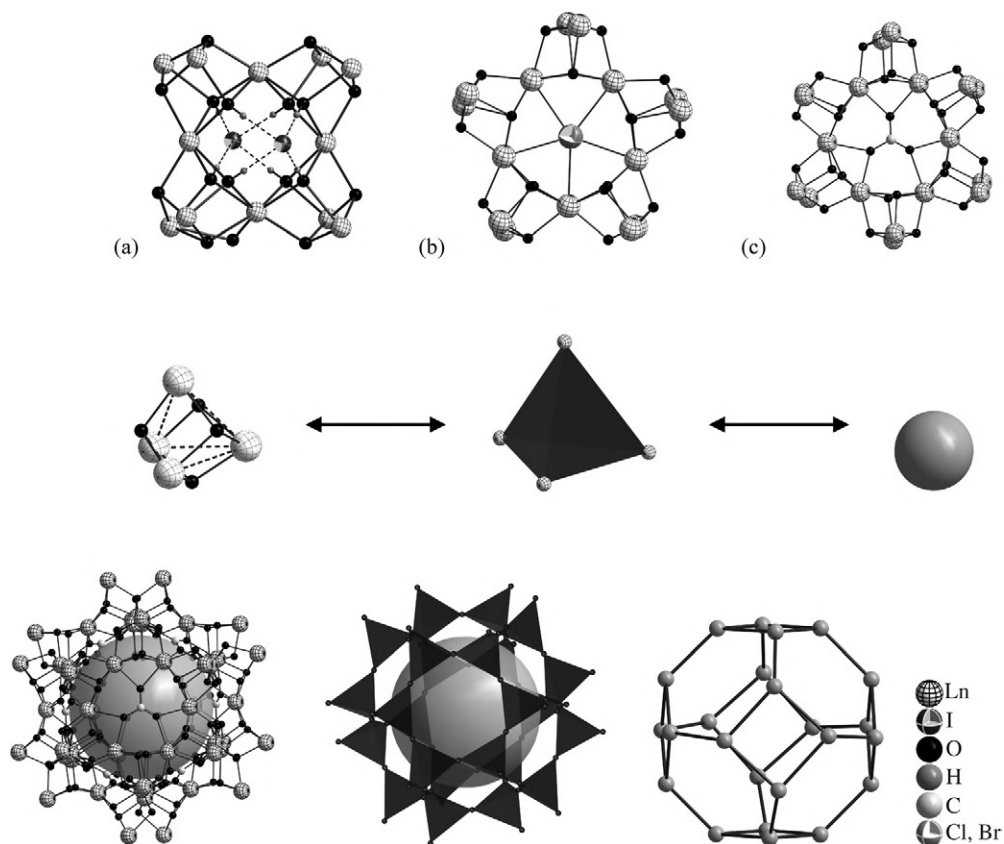


Figure 6.31 The structures of (a) dodeca-, (b) pentadeca-, and (c) octadeca-nuclear clusters templated by two $\mu_4\text{-I}^-$ ions, a $\mu_5\text{-X}^-$ ($\text{X} = \text{Cl}, \text{Br}$) ion, and $\mu_6:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1\text{CO}_3^{2-}$, respectively. Formal assembly of a 60-metal hydroxide complex featuring 26 vertex-sharing $[\text{Ln}_4(\mu_3\text{-OH})_4]$ cubane units. These cubane building blocks form six dodecanuclear squares and eight octadecanuclear hexagons [102]. (Redrawn from X. Kong *et al.*, “A chiral 60-metal sodalite cage featuring 26 vertex-sharing $[\text{Er}_4(\mu_3\text{-OH})_4]$ cubanes,” *Journal of the American Chemical Society*, **131**, 6918–6919, 2009.)

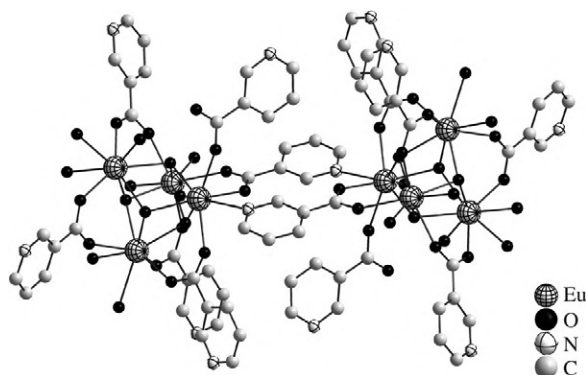


Figure 6.32 Structure of the cationic cluster complex $\{[\text{Eu}_4(\mu_3\text{-OH})_4(\text{nic})_6(\text{H}_2\text{O})_8]_2\}^{4+}$ (nic = nicotinate). Hydrogen atoms are removed for clarity [57]. (Redrawn from X. Kong *et al.*, “Hydrolytic synthesis and structural characterization of lanthanide hydroxide clusters supported by nicotinic acid,” *Inorganic Chemistry*, **48**, 3268–3273, 2009.)

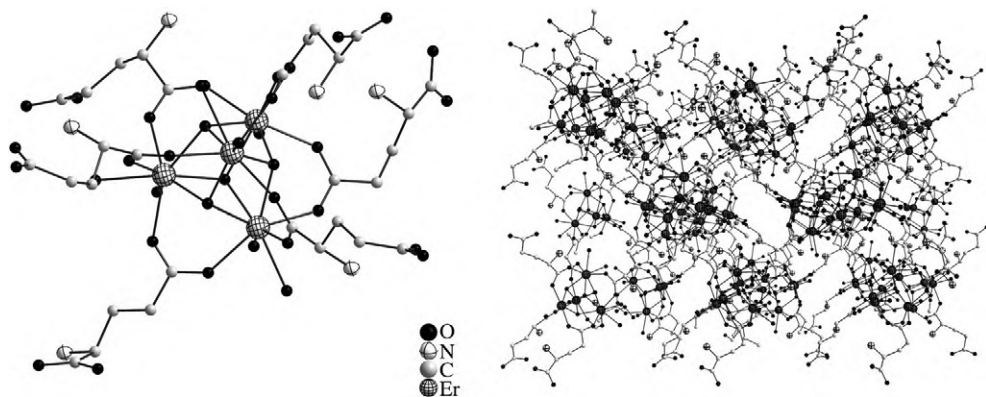


Figure 6.33 Presentation of an extended porous structure featuring glutamate-bridged cuboid $[\text{Er}_4(\mu_3\text{-OH})_4]^{8+}$ building blocks. The channel dimension is approximately $4.4 \times 9.1 \text{ \AA}$ [25]. (Reproduced from Z.P. Zheng, "Cluster compounds of the f-elements," in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

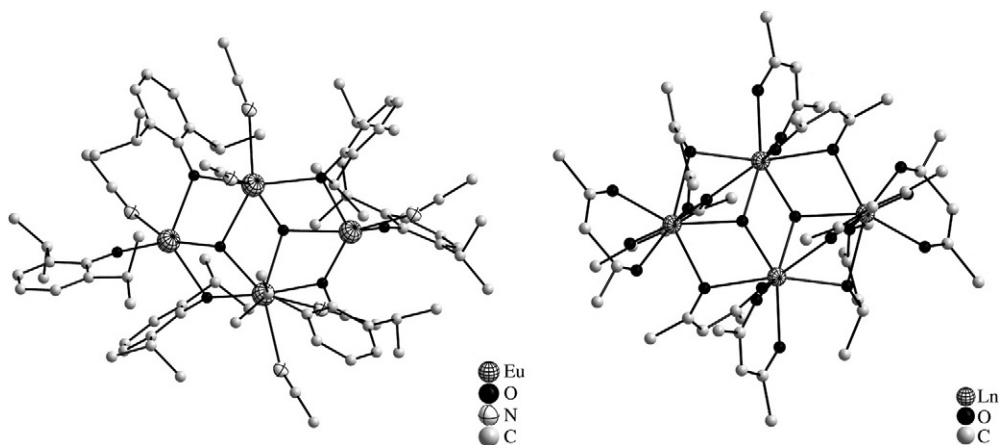


Figure 6.34 Crystal structures of $\{\text{Eu}_4(\mu_3\text{-OH})_2[\mu\text{-O}(2,6\text{-Pr}_2\text{-C}_6\text{H}_3)]_4[\text{O}(2,6\text{-Pr}_2\text{-C}_6\text{H}_3)]_2(\text{NCMe})_6\}$ and $\text{Ln}_4(\mu_3\text{-OH})_2(\mu, \eta^2\text{-acac})_6(\eta^2\text{-acac})_4$ ($\text{Ln} = \text{Y}, \text{Nd}$) [25]. (Reproduced from Z.P. Zheng, "Cluster compounds of the f-elements," in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

Although not nearly as prevalent as the cuboidal structure, the rhombus-shaped tetranuclear core (Figure 6.28c) is featured in a number of lanthanide hydroxide complexes, in particular with the use of β -diketonato or alkoxido ligands. Such an arrangement can also be viewed as two edge-sharing equilateral triangles, each being face-capped by a $\mu_3\text{-OH}$ group, one above and the other below the tetrametallic plane. Shown in Figure 6.34 are the crystal structures

of $\{\text{Eu}_4(\mu_3\text{-OH})_2[\mu\text{-O}(2,6\text{-Pr}_2^i\text{-C}_6\text{H}_3)]_4[\text{O}(2,6\text{-Pr}_2^i\text{-C}_6\text{H}_3)]_2(\text{NCMe})_6\}$ [25, 103] and $\text{Ln}_4(\mu_3\text{-OH})_2(\mu, \eta^2\text{-acac})_6(\eta^2\text{-acac})_4$ ($\text{Ln} = \text{Y}, \text{Nd}$; acac = acetylacetonate) [25, 78, 79]. Both possess a common rhombus-like tetranuclear core of $\text{Ln}_4(\mu_3\text{-OH})_2$.

6.3.2.4 Pentanuclear Complexes

Capping the square-like motif of $[\text{Ln}_4(\mu_4\text{-OH})]$ with a fifth metal atom results in a square-pyramidal unit of $\text{Ln}_5(\mu_4\text{-OH})$, a pentanuclear building block frequently observed in lanthanide hydroxide complexes with diketonate ligands. One such example is $[\text{Dy}_5(\mu_4\text{-OH})(\mu_3\text{-OH})_4(\mu, \eta^2\text{-Ph}_2\text{acac})_4(\eta^2\text{-Ph}_2\text{acac})_6]$ (Ph = phenyl) whose structure is shown in Figure 6.35 [25, 80].

Vertex-sharing by two such pentanuclear units results in a nonanuclear complex. Examples include $[\text{Ln}_9(\mu_4\text{-OH})_2(\mu_3\text{-OH})_8(\text{acac})_{16}]^+[\text{Mo}_2(\text{CO})_{10}(\mu\text{-H})]^-$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Yb}$) and $[\text{Sm}_9(\mu_4\text{-OH})_2(\mu_3\text{-OH})_8(\text{acac})_{16}]^+[\text{CrW}(\text{CO})_{10}(\mu\text{-H})]^-$, obtained by the hydrolysis of $\text{Ln}(\text{acac})_3 \cdot 2\text{H}_2\text{O}$ promoted by homo or heterodinuclear decacarbonyl hydrides [25, 82–84]. The crystal structure of the nonanuclear cluster cation is shown in Figure 6.36.

Cluster complexes featuring an almost identical core structure and of the general formula $[\text{Ln}_9(\mu_4\text{-O})_2(\mu_3\text{-OH})_8\text{L}_{16}]^-$ [$\text{Ln} = \text{Y}$; $\text{L} = \text{MeC}(\text{O})\text{CHC}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ or $\text{MeC}(\text{O})\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3$ [85]; $\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Er}$; $\text{L} = \text{C}_6\text{H}_5\text{C}(\text{O})\text{CHC}(\text{O})\text{CH}_3$] [86] have also been reported. However, in these complexes the end-capping units are assigned to be $\mu_4\text{-O}$ rather than $\mu_4\text{-OH}$ groups. This assignment is consistent with the number of counter ions and is supported by the noticeably different $\text{Ln}\text{-O}$ distances. That two different forms of the O-based ligands are present in closely related cluster core structures indicates the subtlety of this class of lanthanide-containing compounds and the coordination chemistry of lanthanide hydroxides in general.

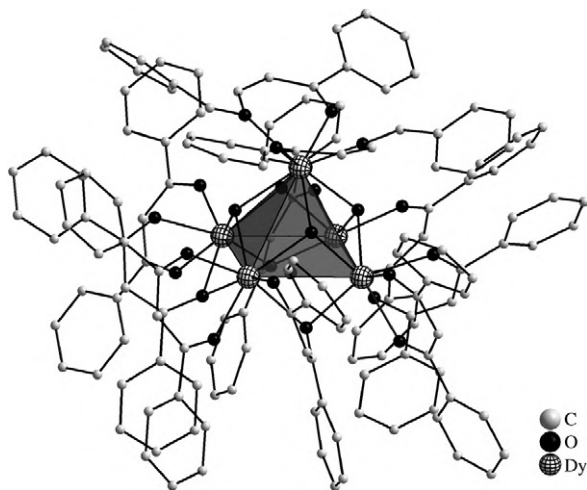


Figure 6.35 Crystal structure of $[\text{Dy}_5(\mu_4\text{-OH})(\mu_3\text{-OH})_4(\mu, \eta^2\text{-Ph}_2\text{acac})_4(\eta^2\text{-Ph}_2\text{acac})_6]$ [25]. (Reproduced from Z.P. Zheng, “Cluster compounds of the f-elements,” in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

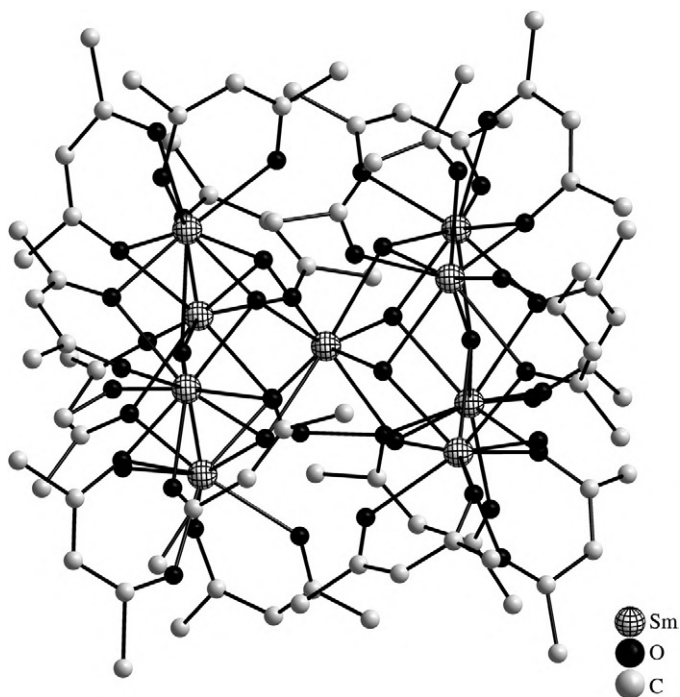


Figure 6.36 Crystal structure of $[\text{Ln}_9(\mu_4\text{-OH})_2(\mu_3\text{-OH})_8(\text{acac})_{16}]^+$, a nonanuclear cationic complex [25]. (Reproduced from Z.P. Zheng, “Cluster compounds of the f-elements,” in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

6.3.2.5 Hexanuclear Complexes

Capping of the basal plane of the square-pyramidal $[\text{Ln}_5(\mu_4\text{-OH})]$ unit leads to the octahedral, hexanuclear cluster core, with or without an interstitial $\mu_6\text{-oxo}$ group. The first lanthanide complex containing one such discrete octahedral core is $[\text{Ce}_6(\mu_3\text{-O})_6(\mu_3\text{-OH})_4(\text{acac})_{12}]$, isolated from the hydrolysis of $\text{Ce}(\text{OCHMe}_2)_2(\text{acac})_2$ [82]. Only four of the eight face-capping ligands are hydroxo groups of this “hollow” hexanuclear cluster core; the remaining are $\mu_3\text{-oxo}$ ligands. This combination is mandated by the $\text{Ce}(\text{IV})$ ions. In a recent report, a similar hollow octahedral core of $[\text{Gd}_6(\mu_3\text{-OH})_8]$ has been found in a heterometallic 3d–4f cluster assembly wherein the hexanuclear core is encapsulated by six (Cu_2) blades in a fan-like structure [104].

More frequently observed octahedral lanthanide hydroxide clusters display a perfect octahedron of the lanthanide atoms centered on an interstitial $\mu_6\text{-O}$ group. The crystal structure of a cationic cluster $[\text{Nd}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{H}_2\text{O})_{24}]^{8+}$ obtained by base-promoted direct hydrolysis of $\text{Nd}(\text{ClO}_4)_3$ is shown in Figure 6.37 [25, 98]. Analogous species have also been obtained with the use of iodides in place of perchlorates [96]. Complexes of the general formula $[\text{Ln}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{H}_2\text{O})_{12}(\text{NO}_3)_6](\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, possessing the same core but terminally coordinated with nitrate ligands, have been synthesized either by direct hydrolysis of lanthanide nitrates or via the thermal decomposition of hydrated $\text{Ln}(\text{NO}_3)_3$, followed by hydrolysis of the

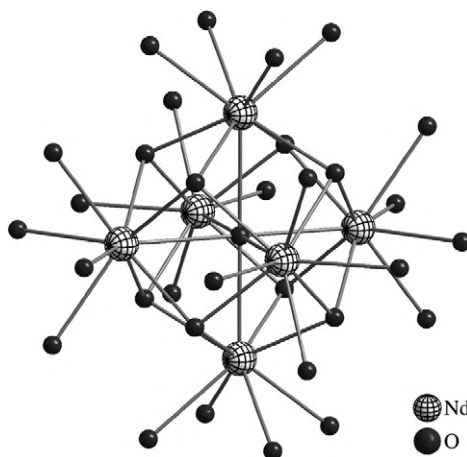


Figure 6.37 Crystal structure of $[\text{Nd}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{H}_2\text{O})_{24}]^{8+}$ [25]. (Reproduced from Z.P. Zheng, “Cluster compounds of the f-elements,” in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume **40**, 2010, with permission from Elsevier.)

decomposition products [95–98]. Interestingly, the hydrolysis of lanthanide ions in the presence of a trivacant Wells–Dawson polyoxo-anion $\alpha\text{-}[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ also produced a μ_6 -oxo centered hexanuclear cluster encapsulated by two polyoxo anions [89].

A combination of two square-pyramids of $[\text{Ln}_5(\mu_4\text{-OH})(\mu_3\text{-OH})_4]$ with one “hollow” octahedron of $[\text{Ln}_6(\mu_3\text{-OH})_8]$ by vertex-sharing leads to the assembly of esthetically pleasing tetradecanuclear complexes with a rod-like cluster core (Figure 6.16). Complexes characterized by such a core have been successfully prepared using aryloxide [34, 35], β -diketonate [87], and amino acid ligands [104].

The structural relationship between the pentanuclear, nonanuclear, and tetradecanuclear species can be easily discerned from Figure 6.38.

In addition to the regular octahedral cluster core structure, there exists a rare example of an open, chair-like hexanuclear lanthanide hydroxide motif (Figure 6.39) in the hydrothermally synthesized coordination polymers $[\text{Ln}_3(\mu_3\text{-OH})_2(\text{BDC})_{3.5}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{Y}, \text{Yb}, \text{Er}$; $\text{BDC} = 1,4\text{-benzenedicarboxylate}$) [25, 76]. The hexanuclear building block, consisting of six lanthanide ions and four $\mu_3\text{-OH}$ groups, can be conveniently described as four edge-sharing units of $[\text{Ln}_3(\mu_3\text{-OH})]$.

6.3.2.6 Octanuclear Complexes

The octanuclear lanthanide hydroxide cluster core was first identified in $\text{Er}_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\text{THD})_8$ ($\text{THD} = 2,2,6,6\text{-tetramethylheptane-3,5-dionate}$) [25, 87]. It is a triangulated dodecahedron with an interstitial oxo group; each of its triangular faces is capped by a $\mu_3\text{-OH}$ group. The same cluster core has also been found in $[\text{Eu}_8(\mu_6\text{-O})(\mu_3\text{-OH})_{12}(\mu_2\text{-OTf})_{16}(\text{OTf})_2]$ (Figure 6.40) [99] and $[\text{Eu}_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\text{DMF})_8(\text{Se}_3)(\text{Se}_4)_3(\text{Se}_5)_2]$ [105]. That the same cluster core is obtained with different ancillary ligands suggests the prevalence of this motif in the lanthanide hydroxide coordination chemistry.

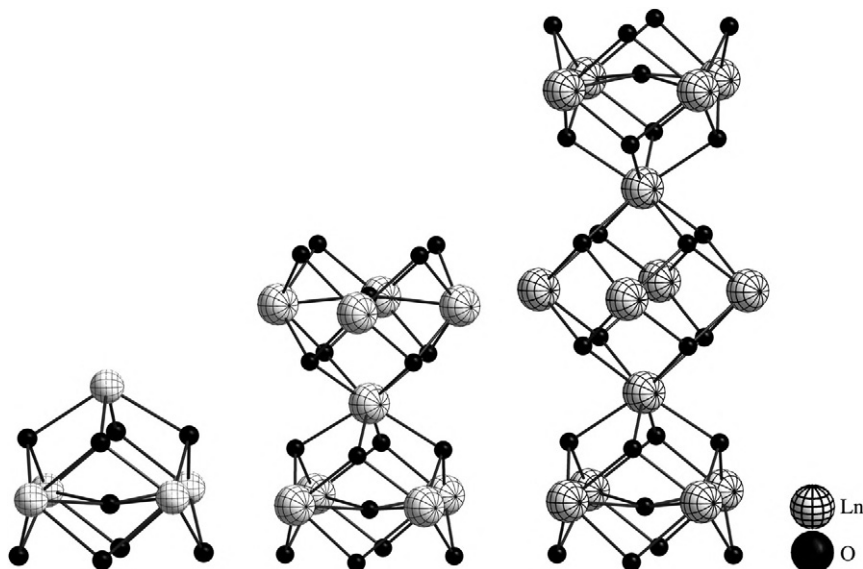


Figure 6.38 Core structures of pentanuclear, nonanuclear, and tetradecanuclear complexes, by which the modular relationship between different species is revealed.

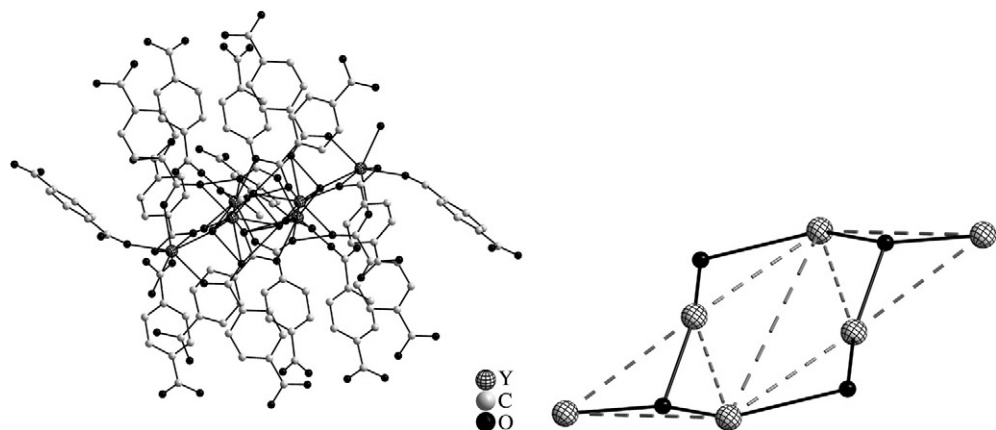


Figure 6.39 Crystal structure of $[Y_3(\mu_3\text{-OH})_2(\text{BDC})_{3.5}(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ with its chair-like core motif [25]. (Reproduced from Z.P. Zheng, “Cluster compounds of the f-elements,” in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

6.3.2.7 Complexes with Unusual Core Structures and Nuclearities

Besides the aforementioned commonly observed lanthanide hydroxide cluster cores, there are a number of unique lanthanide hydroxide motifs that are generally associated with the assembly of large 3d–4f heterometallic clusters. Although they are not as prevalent as those discussed

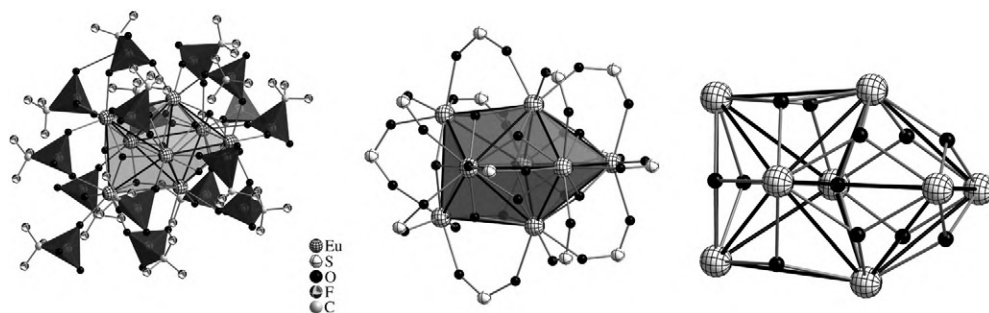


Figure 6.40 Crystal structure of $[\text{Eu}_8(\mu_4\text{-O})(\mu_3\text{-OH})_{12}(\mu_2\text{-OTf})_{14}(\text{OTf})_2]$ with its cluster core (left) and coordination sphere (middle) [25]. (Reproduced from Z.P. Zheng, “Cluster compounds of the f-elements,” in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

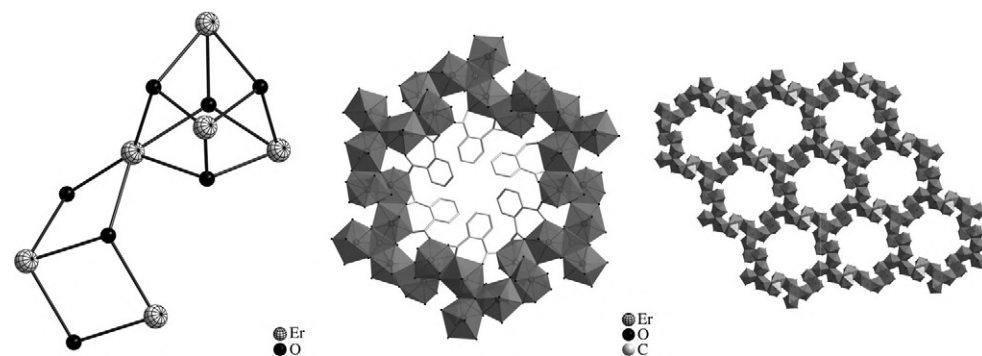


Figure 6.41 An assembly comprised of a cubic $[\text{Er}_4(\mu_3\text{-O})(\mu_3\text{-OH})_3]^{7+}$ and a diamond-shaped $[\text{Er}_2(\mu_3\text{-OH})_2]^{6+}$ unit (left); showing of one unit of the nanosized 36-Er wheel-like structure (middle); and the two-dimensional network of wheel-shaped cationic cluster $[\text{Er}_{36}(\mu_3\text{-OH})_{30}(\mu_3\text{-O})_6(\text{BDC})_6]^{56+}$ (right) [25]. (Reproduced from Z.P. Zheng, “Cluster compounds of the f-elements,” in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

above, their stunning structural beauty is worthy some discussion, and may inspire future efforts to search for novel lanthanide hydroxide cluster cores whose structures lie beyond our present considerations.

A notable example is the wheel-shaped cationic cluster $[\text{Er}_{36}(\mu_3\text{-OH})_{30}(\mu_3\text{-O})_6(\text{BDC})_6]^{56+}$ (Figure 6.41) present in the lanthanide–transition metal sandwich framework comprising (Cu_3) cluster pillars and layered networks of (Er_{36}) wheels [25, 77]. The Er^{3+} ions are linked by hydroxo and oxo bridges to give two types of smaller cluster cores: cubic $[\text{Er}_4(\mu_3\text{-O})(\mu_3\text{-OH})_3]^{7+}$ (Er_6) and dimeric $[\text{Er}_2(\mu_3\text{-OH})_2]^{4+}$ (Er_2) cores (Figure 6.41a). Different from the familiar cubane $[\text{Ln}_4(\mu_3\text{-OH})_4]^{8+}$ which contains four $\mu_3\text{-OH}$ groups, the present (Er_4) cluster

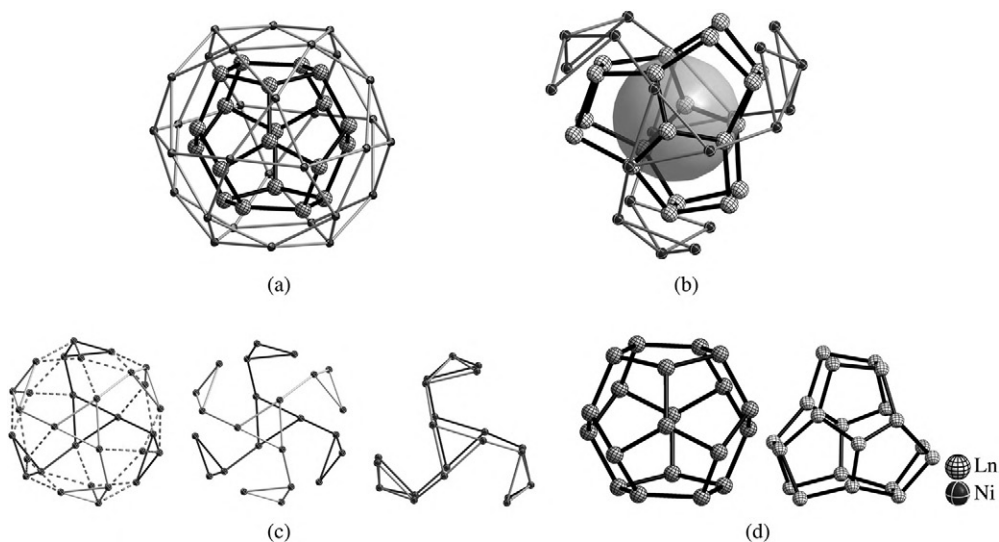


Figure 6.42 (a) The cluster core structure showing an outer Ni_{30} icosidodecahedron encapsulating an inner La_{20} dodecahedron; (b) the cluster core structure showing an outer Ni_{21} framework encapsulating an inner Pr_{20} framework; depiction of the formal transformations toward the making of the (c) outer and (d) inner frameworks of $\text{Pr}_{20}\text{Ni}_{21}$ from respective polyhedrons of cluster $\text{La}_{20}\text{Ni}_{30}$ [25]. (Reproduced from Z.P. Zheng, “Cluster compounds of the f-elements,” in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

core consists of three $\mu_3\text{-OH}$ groups and one $\mu_3\text{-O}$ atom. The (Er_4) and (Er_2) cores are organized alternately to form a nanosized (Er_{36}) wheel structure.

A series of discrete, high-nuclearity 3d–4f cluster complexes have appeared in recent literature [106–108]. A salient feature shared by these various clusters is the multishell cluster core structure. Shown in Figure 6.42 are two distinct examples of these hydro-bridged polynuclear structures. Figure 6.42a is a fascinating double-sphere structure with the outer sphere of 30 Ni(II) ions encapsulating the inner sphere of 20 La(III) ions [25, 106]. The 30 Ni(II) ions span an icosidodecahedron, one of the Archimedean solids formed by 12 pentagonal and 20 triangular faces, while the 20 La(III) ions occupy the vertices of a perfect dodecahedron, one of the Platonic solids featuring 12 pentagonal faces. Displayed in Figure 6.42b is another double-shell structure of $\text{Ni}_{21}\text{Ln}_{20}$ ($\text{Ln} = \text{Pr}, \text{Nd}$) with an outer shell of 21 Ni(II) ions encapsulating an inner shell of 20 Ln(III) ions [107]. Though distinctly different, this core structure can be viewed as being formally transformed from the foregoing $\text{Ln}_{20}\text{Ni}_{30}$ structure. By removing nine uniquely positioned Ni(II) ions from the outer Ni(II) shell of $\text{Ln}_{20}\text{Ni}_{30}$, followed by a rotation of 60° of the red-colored set of Ni(II) ions with respect to the green-colored set, the Ni_{21} framework is generated. The formal transformation necessary to obtain the inner Ln_{20} core from the dodecahedron in $\text{Ni}_{30}\text{La}_{20}$ is even more straightforward; a proper C_6 rotation of the red-colored fragment with respect to the light blue set is adequate.

Figure 6.43 shows a giant heterometallic complex formulated as $[\text{Eu}_{54}\text{Ni}_{54}(\text{IDA})_{48}(\text{OH})_{144}(\text{CO}_3)_6(\text{H}_2\text{O})_{25}](\text{NO}_3)_{18} \cdot 140\text{H}_2\text{O}$ ($\text{IDA} = \text{iminodiacetate}$). Its 108 metal ions are organized

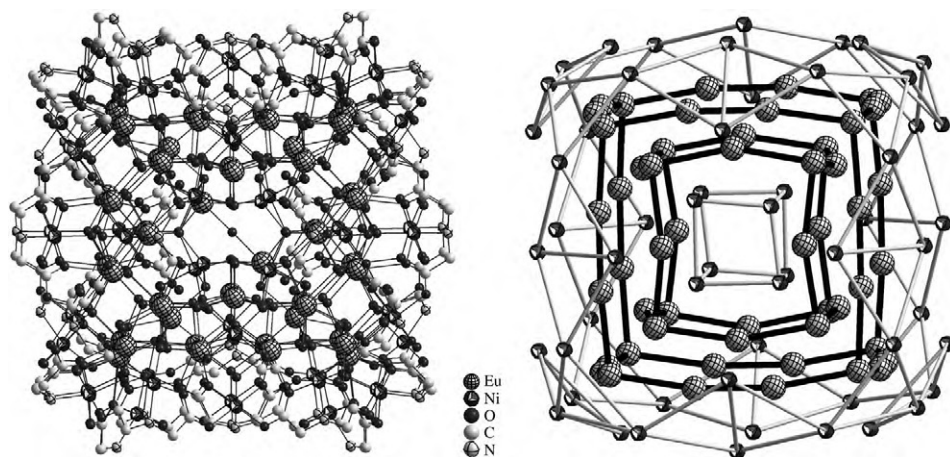


Figure 6.43 (a) A ball-and-stick view of the cationic cluster of $[\text{Eu}_{54}\text{Ni}_{54}(\text{IDA})_{48}(\text{OH})_{144}(\text{CO}_3)_6(\text{H}_2\text{O})_{25}]$; and (b) a four-shell presentation showing only its metal frameworks [25]. (Reproduced from Z.P. Zheng, “Cluster compounds of the f-elements,” in K.A. Gschneidner, Jr., J.C.G. Bünzli, and V.K. Pecharsky (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, volume 40, 2010, with permission from Elsevier.)

into a four-shell Russian doll-like structure [25, 108]. Moving outward, the innermost shell contains 8 Ni(II) ions, followed by a shell of 20 Eu(III) ions, a shell of 32 Eu(III) ions, and the outermost shell of 48 Ni(II) ions. The geometry of the shells approximates that of a cube. Connections between neighboring shells are provided primarily by triply bridging hydroxo groups, affording a highly compact, brucite-like core structure.

6.3.3 Properties and Possible Applications

As is clear from the above discussion, lanthanide hydroxide complexes display a great variety of structures with a unique arrangement of metal ions within a specific core. More importantly, due to the Lewis acidity of the metal ion, luminescent and magnetic properties, and the presence of a large number of basic hydroxo groups, diverse applications in developing novel catalysts, hybrid materials, molecular magnetic materials, and bioimaging contrast agents are envisioned.

6.3.3.1 Catalysis

Lanthanide hydroxide complexes have been found to catalyze the hydrolytic cleavage of DNA and RNA analogs, mimicking the function of natural nucleases [66–68]. The reaction proceeds via the coordination of the phosphate group by the Lewis acidic lanthanide ion, followed by nucleophilic attack by the metal-bound OH group. The metal ion is believed to (i) activate a substrate by removing part of the electron density from the negatively charged phosphate O atom; (ii) enhance the nucleophilicity of an OH group, and (iii) facilitate the departure of the leaving group following the nucleophilic attack. Added advantages of using lanthanide hydroxide complexes include the large size of the metal ion and the kinetic lability of the

complexes; the former renders possible the simultaneous accommodation of the substrate and nucleophile in the same coordination sphere, while the latter facilitates any necessary reorganization of the coordination sphere in order to achieve an optimal substrate/nucleophile arrangement for reaction.

The catalytic potential of lanthanide hydroxide complexes have also been shown in more chemistry-oriented schemes. For example, the air- and moisture-stable pentanuclear complex, $[\text{Y}_5(\mu_4\text{-OH})(\mu_3\text{-OH})_4(\mu, \eta^2\text{-Ph}_2\text{acac})_4(\eta^2\text{-Ph}_2\text{acac})_6]$, has been found to catalyze the oxidation of aldehydes to the corresponding carboxylic acids in the presence of air [109].

6.3.3.2 Cluster–Polymer Hybrids with Enhanced Properties

Three-dimensional cationic lanthanide hydroxide frameworks structures have been prepared by using amino acids or other types of bridging ligands [56, 74]. These materials possess nanosized pores that are occupied by water and counterions from the original synthesis. These materials may find zeolitic applications such as their uses for anion exchange or occlusion and activation of electron-rich substrates.

In addition, hybrid materials have been made by doping diketonate cluster complexes of lanthanide hydroxide into organic polymers. The resulting materials exhibit lowered coefficients of thermal expansion, increased moduli, reduced solvent sensitivity while preserving acceptable thermal and mechanical properties [110].

6.3.3.3 Novel Molecule Based Magnetic Materials

There has been a recent resurgence of research activities in developing lanthanide-based molecular magnetic materials stimulated by the large magnetic anisotropy of lanthanide ions, in particular toward the search for single-molecule magnets (SMM) [111]. For example, the trinuclear Dy(III) hydroxide complexes shown in Figure 6.15 has been shown to exhibit SMM-like slow relaxation behavior within its excited states, even though it possesses an almost diamagnetic ground spin state [36, 37, 103]. This peculiar magnetic showing has been ascribed to noncolinearity of the easy axes of magnetization of the Dy(III) ions that lie in the Dy_3 triangular plane, but are disposed at 120° with respect to each other. Clearly the trimetallic arrangement bridged by two $\mu_3\text{-OH}$ groups is critical in determining the observed magnetic properties. A more recent report describes an anion-dependent slow magnetic relaxation behavior in two tetranuclear Dy(III) hydroxide complexes. Thus, it appears that there is a genuine possibility of realizing novel molecule-based magnetic materials whose properties may be tuned by altering the core structure of the magnetic clusters. Furthermore, depending on the nature of the lanthanide ions, magnetic properties ranging from ferromagnetic, ferromagnetic, to antiferromagnetic couplings have been observed for a series of structurally closely related 3d–4f heterometallic complexes [107]. These promising results portend a bright future in the development of novel lanthanide hydroxide based molecular magnetic materials.

6.3.3.4 New Paradigms of Biomedical Imaging Contrast Agents

Aqua complexes of Gd(III) with stabilizing ligands such as DTPA and DOTA have found extensive uses in clinical magnetic resonance imaging procedures [112, 113]. These contrast-enhancing agents work on the principle of altering the relaxation time (T_1) of water molecules

in the vicinity of the complex via exchange of the body fluid water molecules with the aqua ligand. As there is only one aqua ligand in such complexes, the current use of these contrast agents is not based on their efficiency. Rather, it is out of the consideration of costs and stability/clearance profile. In principle, the efficiency as judged by the contrast agent's relaxivity (the ability to enhance MR image contrast) will be drastically increased if a complex with a large number of exchangeable aqua ligands is used. Indeed, with the use of $[\text{Gd}_{16}(\mu_6\text{-OH})_2(\mu_3\text{-OH})_{16}(\text{H}_2\text{O})_8(\text{L-serine})_{20}]^{3+}$, a tetradecanuclear cluster with serine as supporting ligand [104], a significantly increased relaxivity over the clinically utilized Gd(III) contrast reagent has been achieved [114]. The potential use of high-nuclearity lanthanide hydroxide complexes as new paradigms for radiographic imaging has also been envisioned [115]. The key roadblock to further development appears to be the stability (or lack thereof) of the currently available complexes.

6.4 Summary and Outlook

Notwithstanding the significant progress in the coordination chemistry of lanthanide alkoxides and hydroxides, there appears to exist tremendous opportunities for further development in both areas. A large number of complexes displaying diverse and often pleasing structures have been obtained, but reliable reproduction of many of these species remains a challenge, in particular for polynuclear hydroxide complexes. Moreover, the identity of the complexes generally cannot be predicted, and may be rationalized only after they are structurally characterized. Instead of being the victim of this synthetic uncertainty, one may actively search for hints provided by the available substances, with an eye on identifying rational routes to the reproducible synthesis of known compounds and, ideally, for the production of new species. This practice is "like playing poker; if you play long enough you begin to make decisions based on probability, and if fortunate you may recognize how the cards are marked" [116]. It is probably with this kind of enthusiasm and keenness that the coordination chemistry of lanthanide alkoxides and hydroxides has been rapidly advancing. On the other hand, interesting properties and potentially significant applications of many lanthanide alkoxide and hydroxide complexes have been shown, promising great potential to perfecting their preparation, purification, and characterization as well as optimizing their materials performance. It is entirely reasonable to predict that research activities in both of these areas of lanthanide coordination chemistry will continue to grow with high possibility of producing many new species with novel structures and realizing useful applications that may not even have been contemplated.

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Rare Earth Metals Trapped Inside Fullerenes – Endohedral Metallofullerenes (EMFs)

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7.1 Introduction

Fullerenes are spherical molecules consisting of pentagonal and hexagonal carbon rings, of which the I_h -C₆₀ and D_{5h} -C₇₀ are representatives with the highest abundances (Figure 7.1a and b) [1]. Encapsulation of pure metal atom(s) or metallic clusters inside the inner cavities of fullerenes has generated a new class of hybrid materials, commonly called endohedral metallofullerenes (EMFs) [2]. Because of the presence of metallic species and the electron transfer from the encapsulated metals to the fullerene cage, EMFs have more fantastic structures and novel properties than empty fullerenes, as well as providing more promising applications [2].

7.1.1 History of Discovery

In 1985, fullerenes were discovered by Smalley, Kroto, Curl, and coworkers [3], who were awarded the 1996 Nobel Prize in Chemistry for this important achievement. Mere days after the recognition of fullerenes, their ability to incorporate atoms inside their hollow cavities was also predicted [4]. In 1991, the Rice group reported the first macroscopic synthesis of La-containing EMFs, and the extraction of LaC₈₂ using toluene [5]. In the paper describing that study, they suggested that the symbol of @ is useful to indicate the endohedral nature of EMFs, although at that time they lacked unambiguous evidence that the La atom was actually

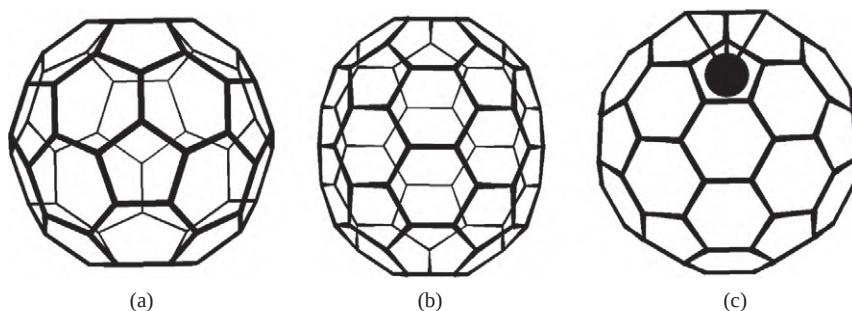


Figure 7.1 Optimized structures of (a) I_h -C₆₀, (b) D_{5h} -C₇₀, and (c) Y@C_{2v}-C₈₂.

inside. The IUPAC nomenclature is different: La@C₈₂ should be called [82] fullerene-*incar*-lanthanum and be written as *i*LaC₈₂. Because the conventional symbol of @ has been widely accepted, we prefer to use it here.

Soon after the arc-discharge method was invented for the microscopic production of empty fullerenes in 1990 [6], many EMF species were also generated by adding metal sources of different types to the graphite rods [2, 5, 7]. The endohedral nature of EMFs was implied by many experimental results [8]; the final confirmation was achieved on the molecular structure of Y@C₈₂ using the synchrotron XRD–MEM–Rietveld method (XRD = X-ray diffraction, MEM = maximum entropy method). Results show that the Y atom is indeed encapsulated in the C₈₂ cage. It is not located in the center of the cage, but instead binds tightly to the carbon cage [9]. Figure 7.1c portrays the theoretically optimized structure of Y@C₈₂, in which the bonds between the Y atom and the nearest carbons are also indicated.

7.1.2 What Can Be Encapsulated Inside Fullerenes?

The exohedral derivatives of fullerenes with organometallic compounds have received extensive attention and appropriate materials have been generated as catalysts, molecular devices, liquid crystals, and so on [10–13]. The discussion in this chapter will not address such materials but will only specifically examine endohedral metallofullerenes because they are viewed as more unique, fascinating, and promising due to the strong interactions between the encapsulated metallic species and the carbon cages [2].

7.1.2.1 Types of Encapsulated Elements

Both metallic and nonmetallic elements can be encapsulated inside fullerenes. Table 7.1 presents a Periodic Table in which the elements that have been trapped inside fullerene cages are shaded. Regarding nonmetallic molecules, H₂ [14], CO [15], and NH₃ [16] were trapped inside the open-cage derivatives of C₆₀ and C₇₀ using the so-called molecular surgery method [17]. Group 15(5A) elements (N and P) were trapped within C₆₀ and C₇₀ using an ion-implantation method [18]. Furthermore, Group 18(8A) noble gas atoms were trapped using a high-temperature/high-pressure method [19]. It is worth noting that a carbon atom of the fullerene cage can also be replaced by a nitrogen atom, forming hetero-fullerenes [20] and

Table 7.1 A Periodic Table showing elements trapped inside fullerene cages.

	1																18
	1A																8A
1	1	2										13	14	15	16	17	2
	H	2A										3A	4A	5A	6A	7A	He
2	3	4										5	6	7	8	9	10
	Li	Be										B	C	N	O	F	Ne
3	11	12	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
	Na	Mg	3B	4B	5B	6B	7B	8B				1B	2B	Al	Si	P	S
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
6	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85
	Cs	Ba	^a La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
7	87	88	89	104	105	106	107	108	109	110	111						
	Fr	Ra	^b Ar	Rf	Ha	Sg	Ns	Hs	Mt								
^a Lanthanide series				58	59	60	61	62	63	64	65	66	67	68	69	70	71
				Ce	Pr	Nd	Po	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
^b Actinide series				90	91	92	93	94	95	96	97	98	99	100	101	102	103
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

hetero-EMFs [21]. Metallic clusters containing C, N, and O, in the form of metal carbides, nitrides or oxides, can also be trapped inside fullerenes (see below). It seems that it is impossible to put other nonmetallic elements in Groups 14(4A), 15(5A), and 16(6A) inside fullerenes. A probable reason is their large radii, which render such elements incapable of being trapped together with 2–3 metals (in forms of metal clusters) by normal fullerenes. Halogen elements in Group 17(7A) are not capable of being trapped either, mainly because of their high electron affinities, which always result in the formation of substituted fullerene derivatives [22, 23] instead of endofullerenes.

For metallic elements, only metals in Groups 1(1A), 2(2A), 3(3B), and 4(4B) have been encapsulated inside fullerenes. Alkali metal containing EMFs were produced using the ion-implantation method [24]; for them, the yield is too low to supply sufficient samples for additional manipulations. Other EMFs, containing alkali earth metals (Ca, Sr, Ba) [25], rare earth metals (Sc, Y, and the lanthanide series except the radioactive promethium), some actinide series [26], and Ti [27], Zr [28], Hf [29], are produced by the direct current (DC) arc-discharge method (see Section 7.2.2 for details) [2]. It seems very difficult (perhaps impossible) to put other metal elements (from Group 5 to Group 16) into fullerenes using the arc-discharge method. The reason remains unclear, but this fact has led to the extensive use of transition metals (Fe, Co, Ni, and Cu) as catalysts in the arc-discharge process for producing fullerenes, EMFs, and carbon nanotubes [30].

Among all the endofullerenes produced to date, such species containing rare earth elements (Sc, Y, and the lanthanides) are particularly outstanding and intriguing, not only because of their

higher production yields than others, but also because of the unique structures and properties resulted from the strong interactions between the encaged metallic species and the fullerene cage. Accordingly, rare earth containing EMFs have been better investigated than others, and are more likely to be used in reality. This chapter presents the specific examination of the synthesis, isolation (separation), structures and properties, especially chemical reactivities, of rare earth containing EMFs, as well as their potential applications in various fields.

7.1.2.2 Number of Encapsulated Atoms

The interior cavities of fullerenes are so spacious that they can encapsulate more than one atom. In fact, from one to six atoms have reportedly been trapped inside [5, 7, 31]. According to the number of encapsulated metal atoms, the isolated EMFs are roughly categorized into three types.

1. **Fullerenes with only one metal atom inside – mono-metallofullerenes.** All rare earth metals can form mono-metallofullerenes. Although the carbon cages that can incorporate one metal atom range from C_{60} to bigger than C_{100} , as detected by mass spectrometry, the most extractable and stable species are exclusively $M@C_{82}$; normally, more than one cage isomer can be isolated. To date, only those mono-metallofullerenes with cages of C_{72} [32], C_{74} [33,34], and C_{82} [35] have been determined structurally.
2. **Fullerenes with two metal atoms inside – di-metallofullerenes.** $M_2@C_{2n}$ type EMFs are also found for most rare earth metals, but the isolated examples are less than the corresponding mono-metallofullerenes. The most stable and extractable species are always $M_2@C_{80}$ [7]; recently, $M_2@C_{2n}$ ($2n = 66, 72, 76, 78, 82, 84$) [36–39] were also isolated and structurally characterized. Di-metallofullerenes with two different metals were also produced inside one cage, such as $HoTm@C_{82}$ [40], but its structure has not been determined yet.

Encapsulation of more than two pure metals seems impossible. Actually, Sc_3C_{82} was previously demonstrated to be $Sc_3@C_{82}$ [41], but recent single-crystallographic results confirmed that it should be a cluster metallofullerene: $Sc_3C_2@C_{80}$ [42]. Moreover, Dy_3C_{2n} ($80 < 2n < 100$) was recently isolated, but no structural evidence has been presented [43]. Possibly, these tri-dysprosium EMFs are also cluster metallofullerenes, especially when taking account of the large carbon cages in which they are trapped. Accordingly, the symbol of @ should be used with care: two carbons can also be trapped inside the cage in the form of a metal carbide. A reasonable hypothesis is the following: three or more metal atoms tend to be co-encapsulated with nonmetallic elements, in the form of metallic clusters, when they are trapped inside fullerenes, according to the experimental facts indicating that (i) no $M_x@C_{2n}$ ($x > 2$) has been unambiguously reported to date; (ii) Coulomb repulsions among three or more trivalent cations are too strong; and (iii) stabilization effects between the metals and the nonmetallic elements when forming metallic clusters indeed exist.

A notable example is Sc_2C_{84} . It was initially assigned as $Sc_2@C_{84}$ using the synchrotron XRD–MEM–Rietveld method [44], but recent results confirmed that $Sc_2C_2@C_{82}$ is the correct structure [45,46]. Accordingly, some results of $Sc_2@C_{84}$ are not accurate: they are sometimes wrong. Therefore, we will only mention these results related to $Sc_2C_2@C_{82}$, although Sc_2C_{84} has indeed received extensive characterizations because of its high yield [47].

3. **Fullerenes with metal clusters inside – cluster metallofullerenes.** To date, only metal nitride and metal carbide clusters were found within fullerene cages, with one recent example of a metal oxide cluster, that is, $\text{Sc}_4\text{O}_2@\text{C}_{80}$ [31], but they constitute a large percentage of isolated EMFs.

The trimetallic nitride template (TNT) family – comprising TNT EMFs with the formula of $\text{M}_3\text{N}@\text{C}_{2n}$ – occupies a dominant portion of the cluster metallofullerenes [48]. Particular features are the high production yield, high stability, and the cage-selective character directed by the encapsulated metal clusters. For these smaller rare earth atoms such as Sc, Y, and lanthanides from Gd to Lu, the most abundant species in the TNT family is $\text{M}_3\text{N}@\text{C}_{80}$, whereas $\text{M}_3\text{N}@\text{C}_{78}$ and $\text{M}_3\text{N}@\text{C}_{68}$ are also abundantly produced for Sc [49, 50]. When larger M_3N clusters were trapped, larger cages were preferentially formed. For example, Nd, Pr, and Ce template a C_{88} cage, and the content of $\text{M}_3\text{N}@\text{C}_{96}$ is also increased [51, 52], whereas the biggest La_3N cluster prefers to template a C_{96} cage [53], instead of either a C_{80} or a C_{88} cage. This trend of increasing cage size is accompanied by a remarkable decrease in the production yield. Mixed metals were also trapped as TNT clusters, such as $\text{ScYErN}@\text{C}_{80}$, in which four different atoms are encapsulated within one carbon cage [54]. However, TNT EMFs containing Sm, Eu, and Yb have not been synthesized, and the strong tendency of these metals to retain the +2 valence is considered as a critical factor for this.

Regarding metal carbide EMFs, $\text{Sc}_2\text{C}_2@\text{C}_{84}$ was the first example reported in 2001 [55]. Subsequently, $\text{Sc}_2\text{C}_2@\text{C}_{68}$ [56], $\text{Sc}_2\text{C}_2@\text{C}_{82}$ [46, 57], $\text{Sc}_3\text{C}_2@\text{C}_{80}$ [46, 57], $\text{Y}_2\text{C}_2@\text{C}_{82}$ [58], and $\text{Gd}_2\text{C}_2@\text{C}_{92}$ [59] were also isolated and structurally determined. It is particularly interesting that the carbide cluster is always composed of two carbon atoms and two or more metal atoms. Accordingly, it is safe to conclude that either a single carbon atom or a lone metal atom is insufficient to stabilize the entire cluster.

As clarified later, such a classification is reasonable and useful because electron transfers exist from the encaged metallic species to the fullerene cages so that the structures and properties depend strongly on the encapsulated atom(s). Particularly, cluster metallofullerenes show different properties from those containing only metals (mono-metallofullerenes and di-metallofullerenes), which, in return, strongly affects the synthesis and extraction processes, structures, chemical reactivities, and their applications. Consequently, we must, to a certain degree, address cluster metallofullerenes separately in the following text.

7.2 Preparation and Purification of EMFs

7.2.1 Production Methods

Methods used to synthesize fullerenes are also adopted for metallofullerene production. Because metal sources are necessary for producing EMFs, only laser ablation [60] and DC arc-discharge [6] are effective methods.

7.2.1.1 Laser Ablation

The laser ablation apparatus consists of a quartz tube inside which a composite graphite disk is placed for laser irradiation. A furnace enwraps the quartz tube, thereby supplying a high

temperature to the device. As atmosphere gases, both argon and helium are useful; a temperature higher than the critical value of 800 °C is necessary for the formation of fullerenes and EMFs. Because of the high cost and the low output efficiency, this method has not been generalized for common use; it is only used to investigate the formation mechanisms of fullerenes and EMFs [61].

7.2.1.2 DC Arc Discharge

In fact, a DC arc discharge is the most effective and convenient method to date for EMF production. A typical setup of a DC arc discharge oven is depicted in Figure 7.2. A chamber containing a cathode and an anode is cooled by water. A graphite block is commonly used as the cathode, whereas the anode is a graphite rod doped with metal sources. Only helium is useful for metallofullerene formation, but its pressure and the floating conditions only slightly affect the yield of the most accessible $M@C_{82}$ species. To produce EMFs, additives containing metal elements must be added to the graphite rod. The most commonly used metal source is a metal oxide, but oxygen is found to suppress the formation of fullerene-related species. Direct use of a metal carbide reportedly promotes the yield of EMFs considerably [62,63].

Production of TNT cluster metallofullerenes is slightly different because the N-element is involved. The first formation of $Sc_3N@C_{2n}$ metallofullerenes resulted from an ‘accidental’ introduction of nitrogen into the arc discharge chamber [48]. Recently, it was found that NH_3 is a better ‘reactive gas’ than nitrogen [64]. A solid nitrogen source is also a good choice, but poor reproducibility of results impedes its generalized use.

Metal catalysts are useful to increase EMF yields. Alloys containing both the target rare earth metal and nickel, such as YNi_2 and $GdNi_2$, are commonly used for production of EMFs with pure metals [65, 66]. Regarding the catalysts used to promote the yield of TNT EMFs, CoO was first adopted but no obvious enhancement was observed [50]. The addition of YNi_2 alloy only improved the formation of carbon nanotubes. Recently, copper was found to be very effective for promotion of the overall yield of $Sc_3N@C_{2n}$ [67].

Raw soot contains a large portion of amorphous carbons and other unwanted materials. The percentage of fullerenes and EMFs is normally less than 10%. Because the symbiotic empty

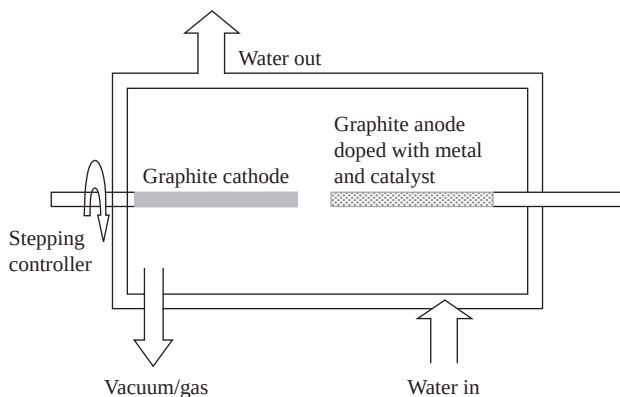


Figure 7.2 DC-arc discharge EMF generator.

fullerenes, especially C_{60} and C_{70} , are always dominant, the total yield of EMFs is generally lower than 1%.

7.2.2 Extraction of EMFs from Raw Soot

7.2.2.1 Sublimation

Sublimation is an efficient method to separate fullerene-related materials from other byproducts, such as carbon nanotubes and amorphous carbon [5]. This method can be scaled up easily and is solvent free, which is particularly suitable for industrial production. As discussed below, when sublimation is combined with other methods, some exciting results are obtained.

7.2.2.2 Solvent Extraction

It seems that chemists prefer solutions to solids. Solvent extraction is presently the most popular method for the isolation of EMFs from soot. Toluene, carbon disulfide, and xylene are popular solvents used to extract EMFs. The Soxhlet apparatus and ultrasonication technique [63] were applied to improve extraction efficiency. However, results show that nearly half of the EMFs remained in the extracted residue, which can be further processed using such solvents as pyridine and 1,2,4-trichlorobenzene (TCB).

Extracts of different organic solvents normally contain the same soluble species: empty fullerenes such as C_{60} , C_{70} , and C_{84} are dominant, whereas $M@C_{82}$ is always the most abundant EMF species and $M_2@C_{80}$ is normally the most abundant di-metallofullerene. Extraction of TNT cluster metallofullerenes is easier because of both the high production yield and the high solubility in common solvents. The general extraction process for TNT EMFs is the following: the soot is first washed by acetone to eliminate hydrocarbon byproducts; then the residue is subjected to solvent extraction with CS_2 or xylene [68, 69].

7.2.2.3 Extraction of Insoluble EMFs by Reduction/Oxidation Methods

As depicted in Figure 7.3, raw soot contains Gd-EMFs with cages ranging from C_{60} to larger than C_{100} . Many species are not extractable using common solvents, such as the fullerenes C_{2n} and EMFs $M@C_{2n}$ ($2n = 60, 70, 72, 74$): they are called ‘missing fullerenes,’ but they occupy a large portion of fullerene-related species. Theoretical calculations indicate that their small HOMO–LUMO (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital) band gaps account for their poor solubility and the low stability. As a result, many efforts have been undertaken to extract them into solution in recent years.

Aniline was found to be effective to extract the C_{60} -based EMFs, but some fullerene species other than $M@C_{60}$ can also be extracted because of complexation between aniline and the species [70]. With the assistance of sublimation, semi-pure samples of $Eu@C_{60}$ and $Dy@C_{60}$ in aniline were obtained after high-performance liquid chromatography (HPLC) separation, and the electronic valences of Eu and Dy were determined, respectively, to be +2 and +3.

As described earlier, TCB is effective for extraction of these EMFs with missing fullerene cages. In addition to the conventional EMFs such as $La@C_{82}$ and $La_2@C_{80}$, $La@C_{72}$ and $La@C_{74}$ were extracted in forms of their dichlorophenyl derivatives by refluxing the raw soot in TCB [32,33].

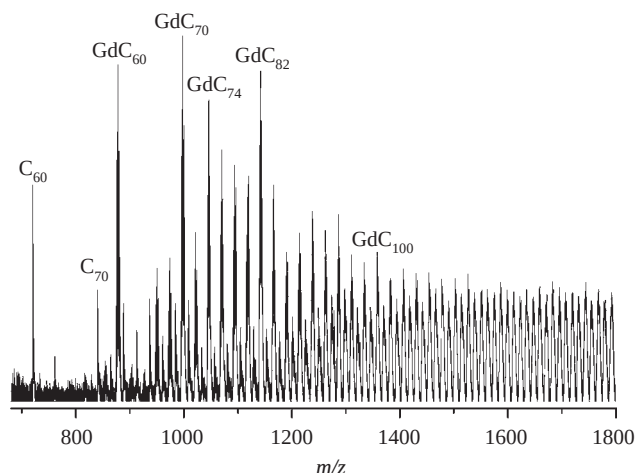


Figure 7.3 Mass spectrum of the raw soot containing Gd-EMFs.

An electrochemical reduction method was found to be more effective for extraction of these insoluble EMFs into solution [71]. After sublimation and washing with xylene, the insoluble residue was reduced electrochemically and a dark brown solution was obtained, indicating that almost all the insoluble materials entered the solution as anions, which are dominated by $\text{Gd}@C_{60}$ and $\text{Gd}@C_{74}$. This method is clearly more powerful than the solvent extraction; it is suitable for large-scale industrial production.

Chemical oxidation is also effective to extract insoluble species into solutions [72]. Similarly, the sublimate containing Gd-EMFs was used as a starting material. After washing with 1,2-dichlorobenzene (ODCB) and oxidation with different oxidants, almost all the insoluble materials entered into solution, and several branches containing different Gd-EMFs were obtained. Derivatization of one branch dominated by $\text{Gd}@C_{60}$ has produced water-soluble materials as high efficient magnetic resonance imaging (MRI) contrast agents [73]. This method is certainly useful for large-scale production of EMFs, although it supplies only mixtures of EMF cations.

7.2.3 Separation and Purification of EMFs

7.2.3.1 HPLC Separation

After solvent extraction, various species of fullerenes and EMFs enter into solution; they must be separated further to obtain isomer-free samples. Liquid chromatography is certainly the most effective means to separate fullerenes into pure form. However, because of their low production yield and the large number of EMF isomers, as well as the similarities between them, HPLC is always relied upon to obtain pure isomers of EMFs.

Toluene is commonly used as the eluent in HPLC separation. Specially designed HPLC columns are necessary. Sometimes recycling techniques are needed to obtain isomer-free samples. Figure 7.4 shows a representative HPLC profile of Gd-EMFs on a 5PYE column

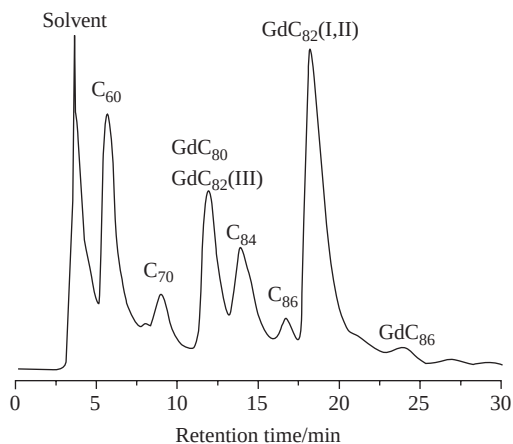


Figure 7.4 HPLC separation profile of Gd-EMFs with a 5PYE column.

[66]. As indicated, empty fullerenes contain such species as C_{60} , C_{70} , C_{84} , and C_{86} , whereas Gd-EMFs are dominated by GdC_{82} with lower abundances of GdC_{80} and GdC_{86} .

Currently, HPLC is the only general method that can yield isomer-free EMFs. Because it is expensive, extremely tedious, and time-consuming, alternative methods have been sought for effective separation of EMF isomers; some successes have been achieved recently.

7.2.3.2 Chemical Reduction

Selective reduction and separation of La-EMFs from empty fullerenes has been achieved [74]. After reduction, evaporation, and washing, experimental results confirm the complete separation of EMF species from empty fullerenes, as depicted in Figure 7.5. This method is more convenient than the HPLC technique and can be scaled up to large amounts. Consequently, it is a good choice for large-scale enrichment of EMFs.

Recently, a chemical reduction method was developed for the isolation of Gd-EMFs directly from raw soot [75]. Reduction of the raw soot with an Al–Ni alloy in toluene–THF gave rise to a solution of $Gd@C_{82}$ and $Gd_2@C_{80}$ anions, whereas empty fullerenes remained in the soot. The anions of $Gd@C_{82}$ and $Gd_2@C_{80}$ react with aqueous NaOH to form water-soluble Gd-metallofullerols, which are potential MRI contrast agents. It is particularly interesting that pure $Gd_2@C_{80}$ was isolated directly from the raw soot merely by tuning the ratio of toluene to THF.

7.2.3.3 Host–Guest Complexation with Azacrown Ethers

It is interesting that $La@C_{82}$ forms complexes with azacrown ethers that precipitate in toluene, but empty fullerenes do not and therefore remain in the solution [76]. These experimental facts spurred an attempt to use azacrown ethers to separate EMFs from empty fullerenes. When hexaazacyclooctadecane was added to a solution containing both empty fullerenes and La-EMFs, precipitates appeared immediately. Experimental data confirmed the separation of

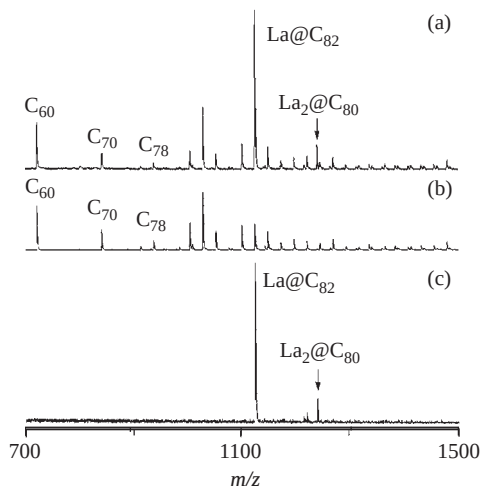


Figure 7.5 Separation of La-EMFs from the TCB extract by chemical reduction: mass spectra of (a) TCB extract, (b) the fraction not reduced, and (c) the reduced fraction [74]. (Reprinted with permission from T. Tsuchiya *et al.*, “Reduction of endohedral metallofullerenes: a convenient method for isolation,” *Chemistry of Materials*, **16**, 4343–4346, 2004. © 2004 American Chemical Society.)

La-EMFs from empty fullerenes: almost all empty fullerenes remained in the solution, whereas the solid contained only La-EMFs such as $La@C_{82}$ and $La_2@C_{80}$.

7.2.3.4 Chemical Methods for the Isolation/Separation of TNT EMFs

The TNT EMFs are less reactive in Diels–Alder reactions than other species. Accordingly, a cyclopentadiene-functionalized styrene–divinylbenzene resin was prepared for separation of TNT EMFs from others and shows high efficiency [77]. Later, an amino-functionalized silica gel was found to be more effective [78, 79]. By simply mixing the silica gel with the extract under continuous stirring, TNT EMFs remain in the solution whereas other contaminants (empty fullerenes and non-TNT EMFs) are bonded to the silica and are eliminated by filtration. Higher temperatures raise the binding rate but decrease the EMF recovery ratio. The amounts of samples were also scaled up easily from several milligrams to grams, so that it is also a good choice for industrial separation of TNT EMFs.

Chemical oxidation was also used to separate the two structural isomers of $Sc_3N@C_{80}$ [80]. Based on a 270 mV difference between the values of their first oxidation potentials, a suitable oxidant whose oxidation potential lies between these of the two EMF isomers was used to oxidize $Sc_3N@D_{5h}-C_{80}$ selectively. Removal of the cation using a silica column yielded a pure sample of $Sc_3N@I_h-C_{80}$ but the absorbed $Sc_3N@D_{5h}-C_{80}$ was difficult to recover.

7.3 General Structures and Properties of EMFs Encapsulating Rare Earth Metals

The EMF structures are more complicated than empty fullerenes because of the presence of metallic species and strong interactions between the encapsulated species and the fullerene

cage. Herein, we simply divide the structures of EMFs into geometrical and electronic structures to address them clearly, but it must always be borne in mind that they are strongly dependent on each other; in many cases they cannot be considered separately.

7.3.1 Geometrical Structures

Both the structures of fullerene cages and the positions and motions of the encaged metallic species are characteristic of EMFs.

7.3.1.1 Fullerene Cage Structures

Fullerene cages consist of 12 pentagonal rings and a variable number of hexagonal rings [81]. The isolated-pentagon rule (IPR) [82] states that all pentagons should be separated by hexagons because fused pentagons bear extremely high bond strains, such that the [5,5]-bonds are too reactive to remain intact. Because all the pure-carbon isomers of fullerenes isolated to date are IPR-satisfying, it is naturally expected that EMFs should also obey this rule.

Indeed, most isolated metallofullerenes have IPR-obeying cage structures. For example, the two isomers of $M@C_{82}$ ($M = \text{La, Ce, Pr, and so on}$), respectively, have IPR-satisfying cages with C_{2v} and C_s symmetries [35, 83, 84]. However, the cage symmetries of stable EMF isomers are normally different from those of the stable empty fullerenes. An impressive example is the extraordinary stability of the I_h -symmetric C_{80} cage when forming cluster metallofullerenes [48, 85] and di-metallofullerenes [86], whereas the most stable isomer of C_{80} cage has D_2 symmetry and the I_h - C_{80} is the least stable one among the seven IPR isomers [2,87].

More intriguing is the species with carbon cages violating the IPR, that is, non-IPR EMFs. Such a conformation was first predicted for $\text{Ca}@C_{72}$ by theoretical calculations in 1997 [88]; then $\text{Sc}_2@C_{66}$ and $\text{Sc}_3\text{N}@C_{68}$ were reported as the first examples of non-IPR fullerenes in 2000 [36,49]. Subsequently, non-IPR structures were also proposed for $\text{Sc}_2\text{C}_2@C_{68}$ [56], $\text{Sc}_3\text{N}@C_{70}$ [89], $\text{La}_2@C_{72}$ [90], $\text{La}@C_{72}$ [32], $\text{Tb}_3\text{N}@C_{84}$ [91], $(\text{Tm}_3\text{N}@C_{84}, \text{Gd}_3\text{N}@C_{84} [92])$, and $\text{Gd}_3\text{N}@C_{82}$ [93]. A point worth noting is that only fused pentagon pairs, instead of triply or multiply fused pentagons (which are common in non-IPR empty fullerene derivatives) are found in all of these non-IPR species. The number of fused pentagon pairs equals the number of encaged metals in most cases, except for $\text{M}_3\text{N}@C_{84}$ ($M = \text{Tb, Tm, and Gd}$) and $\text{Gd}_3\text{N}@C_{82}$, which have only one pair of fused pentagons. These indicate that the encapsulated metals are expected to account for the stabilization of fused-pentagon bonds (see Section 7.4.4 for more evidence).

7.3.1.2 Encaged Metals' Structures and Motions

The metal atom is not located in the center of the fullerene cage in mono-metallofullerenes. For $M@C_{2v}\text{-}C_{82}$ ($M = \text{Sc, Y, La, Ce, and so on}$), the metal atom tends to locate under a hexagonal ring along the C_2 axis [94, 95]. Anomalous structures have been proposed for $\text{Gd}@C_{82}$ [96] and $\text{Eu}@C_{82}$ [97] from the synchrotron XRD–MEM–Rietveld data indicating that the metal atom prefers to remain near a [6,6]-junction that is opposite the hexagonal ring. However, recent results confirmed that the Gd atom in $\text{Gd}@C_{82}$ also sits under a hexagonal ring [98, 99], as found in other $M@C_{82}$ species. Accordingly, it is expected that future experimental results

will elucidate the correct position of the Eu atom in $\text{Eu}@\text{C}_{82}$. It is worth noting that the metal atom in $\text{M}@\text{C}_{82}$ does not stay fixed under the hexagonal ring, but merely shows an energetic minimum there [100]. The off-center position of the metal ion creates a polar structure of the whole molecule, which is expected to account for the aggregation of these molecules in the solid state or on clean surfaces. It is responsible for the different chemical reactivity of the cage carbons.

For di-metallofullerenes, circular motion of the two La ions in $\text{La}_2@\text{C}_{80}$ is very interesting. Initially this was surprising [86]. However, ^{139}La NMR of $\text{La}_2@\text{C}_{80}$ actually displays only one signal, indicating that the two La ions are equivalent. Linewidth broadening of the ^{139}La NMR signal is also observed with increasing temperature, which reflects the circular motion of the two La ions because a new magnetic field inside the cage is produced by the movement. Such circular motions also exist in other di-metallofullerenes [101].

When metal carbide clusters are encapsulated, their structure depends on the type of metal. A rhombic structure of a Sc_2C_2 cluster is found in $\text{Sc}_2\text{C}_2@\text{C}_{84}$ [55]. In $\text{Y}_2\text{C}_2@\text{C}_{82}$, the C_2 unit is surrounded by the two Y ions, and the cluster rotates freely inside the $\text{C}_{3v}\text{-C}_{82}$ cage [58]. Recent single-crystal XRD measurements of a carbene derivative of $\text{Sc}_3\text{C}_2@\text{C}_{80}$ presents more direct observations of the carbide cluster. Although disorders of the Sc_3C_2 cluster exist, the C_2 unit always tends to be in the center of the cage, whereas the three Sc ions wrap round it and prevent the two carbons from connecting to the cage carbons [57]. Recent examples of $\text{Sc}_2\text{C}_2@\text{C}_{82}$ and $\text{Gd}_2\text{C}_2@\text{C}_{92}$ show similar orientations of the encapsulated carbide clusters. The chemical shifts of the C_2 unit were recently observed in the ^{13}C -enriched samples [46]. A signal at $\delta = 253.2$ was assigned for the C_2 unit in $\text{Sc}_2\text{C}_2@\text{C}_{82}$, and the corresponding value in $\text{Sc}_2\text{C}_2@\text{C}_{84}$ is $\delta = 249.2$, indicating that the two carbons are equivalent and that they rotate rapidly inside the cage. However, the ^{13}C NMR spectra of a carbene derivative of $\text{Sc}_3\text{C}_2@\text{C}_{80}$ presents two signals for the C_2 unit at $\delta = 257.2$ and 384.4 , respectively, which indicates that the free rotation of the carbide cluster is stopped by the open-cage structure of the derivative.

Structures of M_3N clusters in TNT metallofullerenes are also interesting; they depend strongly on the size of the encaged metals and also on the structures of the carbon cages. A planar structure of the TNT cluster is common in most of the isolated TNT EMFs [48, 50, 102–106] because it is the best way to minimize the repulsions among the three trivalent cations. A significant exception is $\text{Gd}_3\text{N}@\text{C}_{80}$, which has a distorted structure of the Gd_3N cluster with the N atom displaced $0.5 \text{ \AA}$ above the Gd_3 plane [85]. These are explainable by the large ionic radius of Gd: the C_{80} cage is too small to accommodate the planar structure of the Gd_3N . Consequently, it is expected that distorted structures of the M_3N cluster will be found in other EMFs with big metals and/or small cages [107]. In addition, the distances between the encaged metals and the adjacent cage carbons are shorter for TNT EMFs than those in mono-metallofullerenes and di-metallofullerenes, which is clearly attributable to the more crowded nature of the M_3N clusters.

7.3.2 Electronic Structures of EMFs: Intramolecular Charge Transfer

The most unique feature of EMFs, as distinguished from nonmetallic endofullerenes (such as $\text{N}@\text{C}_{60}$) and empty fullerenes, is the strong interaction between the encaged metallic species and the fullerene cage, as represented by the electron transfer from the inner metallic species to the outer fullerene cage: intramolecular charge transfer. Consequently, the EMF molecules are a type of superatom, or a type of salt, but remain undissociated in any solvent (see Figure 7.6).

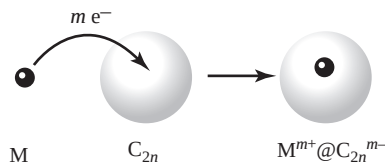


Figure 7.6 Intramolecular charge transfer within $M@C_{2n}$.

For mono-metallofullerenes with rare earth metals, three electrons are donated from the encaged metal to the fullerene cage, such as Y and most lanthanides (La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, and Lu) [2, 108, 109]. However, Sc, Sm [110], Eu [111], Tm [112], and Yb [113] are found to donate only two electrons and prefer to take the valence of +2. Consequently, the EMFs containing rare earth metals are classifiable into two categories according to the electronic state of the encaged metal(s): *trivalent EMFs* and *divalent EMFs*. For example, $La@C_{82}$ should be expressed as $La^{3+}@C_{82}^{3-}$, whereas $Yb@C_{82}$ has the formula of $Yb^{2+}@C_{82}^{2-}$. These two types of EMF differ markedly from each other in their structures and properties. (i) When three electrons are transferred to the carbon cage, the resultant $M^{3+}@C_{2n}^{3-}$ -type EMFs have an unpaired electron on the HOMO, and the paramagnetic character presents ESR signals, but hinders the direct NMR determination so that NMR measurements have to be performed on their anions [84, 114]. (ii) The yield of divalent metallofullerenes is much lower than that of the trivalent ones, resulting in the fact that divalent EMFs have been studied less [115]. The Sc-containing metallofullerenes are rather special because they have the highest production yields, although the Sc atoms are believed to take the +2 valency in most cases (see below). (iii) Isomerism of divalent EMFs is normally more diverse than that of trivalent ones. For example, two isomers are usually found for trivalent $M@C_{82}$, but $Yb@C_{82}$ has three isolated isomers [113].

Examples of isolated di-metallofullerenes are fewer than the corresponding mono-EMFs. The most accessible di-metallofullerenes are $M_2@C_{80}$ ($M = La, Ce, Pr$, and so on) in which six electrons are transferred from the two metal atoms (each denotes three) to the carbon cage [116]. Recent examples are $M_2@C_{2n}$ ($M = La, Ce$; $2n = 72, 78$) [90, 117, 118], in which the metals also take the +3 valency. To the best of our knowledge, no examples of di-metallofullerenes containing divalent metals have been recognized unambiguously.

It is significant that the electronic state of Sc is variable, and sometimes controversial. Both experimental and theoretical results recommend the divalent state for Sc in mono-metallofullerenes and di-metallofullerenes [119], but it was determined that the three Sc atoms in $Sc_3N@C_{80}$ take the +3 valency. Variable electronic states of Tm in different EMFs were also found. For example, Tm was found to be +2 in $Tm@C_{82}$, but +3 in $Tm_3N@C_{80}$ [120]. It is worth noting that a purely ionic picture is not valid to describe the electronic structure of the encaged metals because the charges are not 'observable' quantities [2].

The electronic structures for cluster metallofullerenes are more complicated because charge transfer within the cluster also exists. When the metal carbide is encapsulated, the metals bond tightly with the C_2 unit; the entire carbide cluster donates a certain number of electrons to the carbon cage. In $Sc_2C_2@C_{84}$, the Sc_2C_2 cluster exists as a divalent ion, which provides only two electrons to the C_{84} cage [55]. The electronic structure of $Y_2C_2@C_{82}$ is completely different: nearly six electrons are transferred from the carbide cluster to the C_{82} cage [58].

Table 7.2 Redox potentials of C_{60} , C_{70} and some EMFs (V versus ferrocene/ferrocenium).

Compound	$Ox E_2$	$Ox E_1$	$Red E_1$	$Red E_2$	Ref.
C_{60}	–	+1.21	–1.12	–1.50	[122]
C_{70}	–	+1.19	–1.09	–1.48	[122]
$Y@C_{2v}-C_{82}$	+1.07	+0.10	–0.37	–1.34	[123]
$La@C_{2v}-C_{82}$	+1.07	+0.07	–0.42	–1.37	[122]
$La@C_s-C_{82}$	+1.08	–0.07	–0.47	–1.41	[114]
$Ce@C_{2v}-C_{82}$	+1.08	+0.08	–0.41	–1.41	[124]
$Pr@C_{2v}-C_{82}$	+1.08	+0.07	–0.39	–1.35	[114]
$Pr@C_s-C_{82}$	+1.05	–0.07	–0.48	–1.39	[114]
$La_2@I_h-C_{80}$	+0.95	+0.56	–0.31	–1.71	[125]
$La_2@D_{5h}-C_{80}$	+0.78	+0.22	–0.36	–1.72	[125]
$Ce_2@I_h-C_{80}$	+0.95	+0.57	–0.39	–1.71	[125]
$Sc_3N@I_h-C_{80}$	+1.09	+0.62	–1.24	–1.62	[126]
$Sc_3N@D_{5h}-C_{80}$	–	+0.34	–1.33	–1.68	[105]
$Sc_3C_2@I_h-C_{80}$	–	–0.03	–0.50	–1.64	[42]

The nitride cluster in TNT EMFs can also be viewed as a whole, which always gives six electrons to the carbon cage [121]. This is interpreted by the high electron affinity of the I_h-C_{80} cage: six electrons are necessary to make it the most stable hexa-anion. Because N prefers to take the -3 valence, each metal in M_3N has a $+3$ valence. Therefore, it is easy to understand why Sm, Eu, and Yb have not been trapped as TNT EMFs because they can donate only two electrons from their 6s orbitals.

Electronic structures of EMFs are also reflected by their electrochemical properties, which provide further valuable information of the chemical behaviors of EMFs. As presented in Table 7.2, trivalent $M@C_{2v}-C_{82}$ EMFs have similar redox potentials, although different metals are encaged. When compared with C_{60} , $M@C_{82}$ EMFs both have more positive first reduction potentials ($^{red}E_1$) and more negative first oxidation potentials ($^{ox}E_1$), which means that they are both better electron acceptors and better donors than C_{60} .

For TNT metallofullerenes, the first reduction potentials of $Sc_3N@C_{80}$ are even more negative than C_{60} , which is expected to explain their high stability [126]. Size effects of the carbon cage on the electrochemical behaviors were also observed in TNT EMFs. For example, $Gd_3N@C_{88}$ shows two reversible reduction steps and two reversible oxidation steps, although the reduction processes of $Gd_3N@C_{80}$ are all irreversible [127].

7.4 Chemistry of EMFs

7.4.1 Chemical Reactions of EMFs: An Overview

Chemical modifications on EMFs are very useful for disclosing the structures and properties of EMFs, and more importantly, for generating useful materials based on EMFs. This is because different functional groups can be attached to the fullerene cages so that the solubility, stability, and physicochemical properties of pristine EMFs can be tuned precisely.

A general description of the reported results for EMFs is given below, according to the type of reactions instead of the class of EMFs, because such a classification is understood better. Some pronounced results, which are characteristic of EMFs will be addressed separately in greater detail.

7.4.1.1 Disilylation

In 1995, the first exohedral adducts of EMFs were obtained through the disilylation of La@C_{82} (Figure 7.7); the results disclosed that this new class of materials (EMFs) can also be modified using organic reagents, as in the case of empty fullerenes [122]. However, it was later found that mono-metallofullerenes and di-metallofullerenes are generally more reactive than empty fullerenes because they (for example, M@C_{82} and $\text{M}_2\text{@C}_{80}$) undergo both photochemical and thermal reactions with 1,1,2,2-tetramesityl-1,2-disilirane (**1**) [128, 129]. Resembling C_{60} , cluster metallofullerenes such as $\text{Sc}_2\text{C}_2\text{@C}_{82}$ [128] and $\text{Sc}_3\text{N@C}_{80}$ [126] do not react thermally with **1** but only photochemically because of their more negative initial reduction potentials (refer to Table 7.2).

Disilirane is a very useful probe to investigate the chemical reactivity of EMFs, but it normally generates many structural isomers of the derivatives when an EMF isomer with a lower cage symmetry is involved [130]. Recent structural characterizations of the disilylated adducts of $\text{Sc}_3\text{N@C}_{80}$ [131] and $\text{La}_2\text{@C}_{80}$ [132] disclosed a 1,4-addition pattern, and presented valuable information related to the motions of the encaged metals and the dynamic behavior of the disilirane moiety. Silicon has stronger electron-donating ability than carbon. Therefore, such disilylated derivatives of EMFs have more negative reduction potentials and are expected to be very useful.

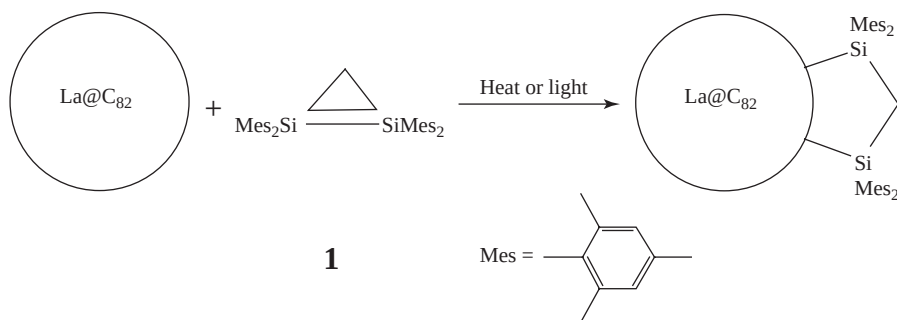


Figure 7.7 Disilylation of La@C_{82} with **1**.

7.4.1.2 1,3-Dipolar Addition of Azomethine Ylides

Azomethine ylides, exhibiting 1,3-dipole character, react smoothly with C_{60} in good yields. Their high selectivity has made them the most efficient means for introducing pyrrolidine rings onto the carbon cage along with widely various functional groups [133]. When EMFs were used as starting materials, they showed higher reactivity but lower selectivity toward

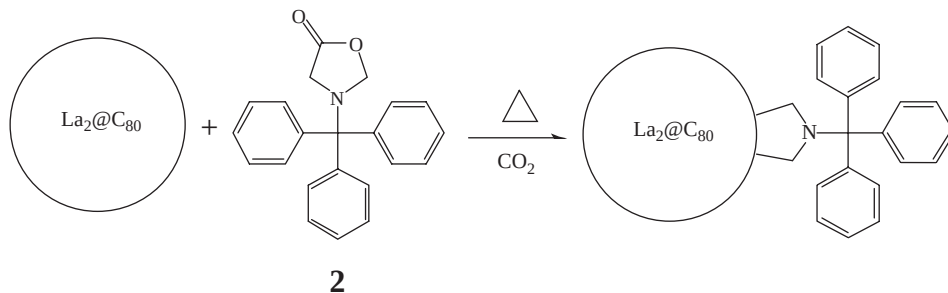


Figure 7.8 Reaction of $\text{La}_2\text{@C}_{80}$ with **2**.

azomethine ylides. Aside from several isomers of mono-adducts, bis-adducts were also found for La@C_{82} [134], and up to octa-adducts were observed for Gd@C_{82} [135].

Exclusion of carbon dioxide from *N*-triphenylmethyl-5-oxazolidinone (**2**) under heating generates the corresponding 1,3-dipolar reagent, which adds readily to $\text{La}_2\text{@I}_h\text{-C}_{80}$ yielding both [5,6]-adducts and [6,6]-adducts [136]. The [6,6]-adduct can be crystallized from the mixture, although exhaustive HPLC separations were ineffective. X-ray data present a [6,6]-close structure and the motion of the two La atoms was found to be stopped by the cycloaddition of the adduct (Figure 7.8).

Reactions between azomethine ylides and TNT EMFs have also been reported, and the effect of the size of the encapsulated clusters on the reactivity and selectivity of the cage carbons was observed. Addition of *N*-ethyl azomethine ylide to $\text{Y}_3\text{N@C}_{80}$ affords exclusively [6,6]-adducts of mono-isomers [137], but occurs regioselectively on a [5,6]-bond of $\text{Sc}_3\text{N@C}_{80}$ [138]. The resultant pyrrolidino- $\text{Sc}_3\text{N@C}_{80}$ undergoes electrochemical retro-cycloaddition in high yield [139].

Reaction of $\text{Sc}_3\text{N@C}_{80}$ with **2** afforded two regio-isomers: the kinetically favored [6,6]-adduct and the thermodynamically stable [5,6]-adduct, and the transformation of [6,6]-adduct into the [5,6]-adduct was observed [140]. The pyrrolidino reaction of $\text{Sc}_x\text{Gd}_{3-x}\text{N@C}_{80}$ ($x = 0 - 3$) provides more direct evidence of the size effect of engaged clusters on the exohedral chemistry of TNT EMFs: with increasing cluster size, the [6,6]-adduct becomes more stable [141]. Reaction of $\text{Sc}_3\text{N@C}_{78}$ with **2** shows a high selectivity, affording exclusively [6,6]-isomers of mono-adducts. The DFT calculations disclosed that the engaged cluster plays a critical role in determining the reactivity of the cage carbons [142].

7.4.1.3 Cycloaddition of Diene and Benzyne

The [4+2] cycloaddition of metallofullerenes, known as the Diels–Alder reaction, was first achieved on $\text{Sc}_3\text{N@C}_{80}$ with ^{13}C -labeled 6,7-dimethoxyisochroman-3-one, which forms an *o*-quinone under heating. The addition sites occurred at a [5,6]-bond, as confirmed by both NMR and single-crystallographic results [143]. The same reaction was also performed on $\text{Gd}_3\text{N@C}_{80}$ and a bis-adduct was isolated, but no structural information was reported [144].

Addition of cyclopentadiene (**3**) to La@C_{82} shows a surprisingly high selectivity: only one regioisomer was formed (Figure 7.9). However, the derivative undergoes a retro-reaction even under ambient conditions, which hinders the determination of its molecular structure [145].

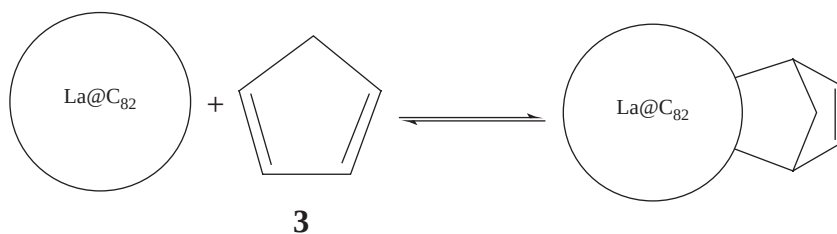


Figure 7.9 Addition of cyclopentadiene (**3**) to La@C_{82} .

Benzyne, generated by the diazotization of anthranilic acid with isoamyl nitrite, is added to Gd@C_{82} forming two isolable isomers of mono-adducts. Electrochemical measurements disclosed that the electronic structure of pristine Gd@C_{82} has changed dramatically. Because of the high reactivity of benzyne, multiple adducts are not avoidable, even at lower temperatures [146].

7.4.1.4 Carbene Addition

Extrusion of N_2 from 2-adamantane-2,3-[3*H*]-diazirine (**4**, AdN_2) at elevated temperatures or under photo-irradiation generates the corresponding carbene reactant (Ad), which shows both high reactivity and high regio-selectivity to EMFs, especially to M@C_{82} . It was unexpected that addition of Ad to $\text{La@C}_{2v}\text{-C}_{82}$ gave only one dominant isomer of the mono-adduct with an open-cage structure [147]. Similar results were also achieved on $\text{La@C}_s\text{-C}_{82}$ [148] and $\text{Gd@C}_{2v}\text{-C}_{82}$ [98]. Theoretical calculations of $\text{La@C}_{2v}\text{-C}_{82}$ disclosed that one carbon on the six-membered ring adjacent to the metal atom has both higher p-orbital axis vector (POAV) and charge density values than others, and is accordingly more reactive toward Ad , which acts as an electrophile in this reaction. Figure 7.10 shows that the nearly identical molecular structure of $\text{Gd@C}_{82}(\text{Ad})$ to that of $\text{La@C}_{82}(\text{Ad})$ disclosed unambiguously that the Gd atom also locates under the hexagonal ring, as found in La@C_{82} , instead of sitting on the opposite [6,6]-bond as deduced from the synchrotron XRD–MEM–Rietveld data [96].

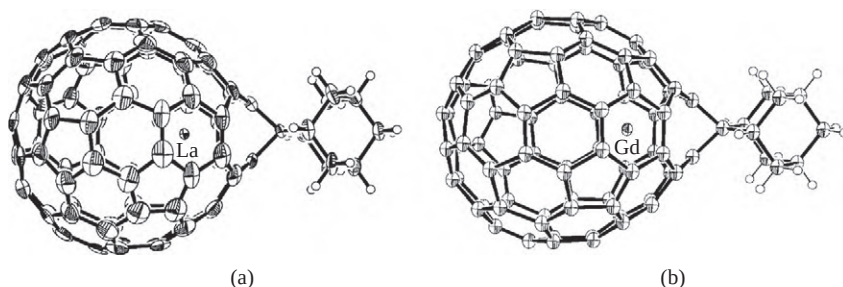


Figure 7.10 Molecular structures of (a) $\text{La@C}_{82}(\text{Ad})$ and (b) $\text{Gd@C}_{82}(\text{Ad})$.

7.4.1.5 Radical Addition

Trifluoromethylation of empty fullerenes has been investigated extensively, which has led to the finding of some new isomers of higher fullerenes [149, 150].

Similar methodologies were applied recently to the functionalization of EMFs. An $Y@C_{82}$ -enriched starting material was used in the radical reaction at an elevated temperature. Mass spectrometric results disclosed that an odd number of CF_3 groups is added to $Y@C_{82}$, and that the maximum number is five, whereas the maximum number for $C_{60}/C_{70}(CF_3)_n$ is up to 22. After chromatographic purification, two isomers of $Y@C_{82}(CF_3)_5$ were obtained and characterized using ^{19}F NMR. In combination with DFT calculations, it was proposed that $Y@C_{82}(CF_3)_5$ should also have the 1,4-addition patterns, as found for empty fullerenes [151]. Radical trifluoromethylation of $Sc_3N@C_{80}$ was also achieved by heating the mixture of the I_h -isomer and D_{5h} -isomer together with CF_3I at 520 °C. In contrast to the previous results showing that the I_h -isomer is more stable than the other, both show fundamentally identical reactivity in this reaction. Because of the diamagnetic property, CF_3 groups of an even number were attached; the maximum number is up to 12. Characterizations of the isolated bis-adducts disclosed that they also have the 1,4-addition pattern. Addition of two CF_3 groups to the I_h -isomer caused an obvious decrease of the HOMO–LUMO band gap, but such an addition has less effect on the electronic structure of the D_{5h} -isomer [152].

Recently, results showed that dichlorophenyl radicals, generated by refluxing TCB, react readily with such EMFs with missing fullerene cages, for example, $La@C_{2n}$ ($2n = 72, 74$) in raw soot [32, 33]. This reaction afforded several adducts of $La@C_{2n}$ ($2n = 72, 74$), which are more stable and soluble than the pristine ones. Such achievements have paved the way to achieving the structures and properties of missing cage fullerenes, and their possible applications.

Radical coupling reactions of paramagnetic species of EMFs are more interesting. The reaction of **2** with $La@C_{82}$ in toluene did not afford the pyrrolidino adducts, as found previously for diamagnetic EMFs such as $La_2@C_{80}$ and $Sc_3N@C_{78}$, but gave unexpected benzyl adducts (Figure 7.11) [153]. Surprisingly, similar adducts with singly bonded structures were also obtained by irradiating the toluene or ODCB solution of $La@C_{82}$ without **2**. These experimental results proved that paramagnetic species such as $M@C_{82}$ more easily undergo radical coupling reactions than 1,3-dipolar reactions. Single-crystallographic results on an isolated isomer confirmed that the cage carbons with higher spin densities have higher reactivity than others. However, when benzene is used as the solvent instead of toluene or ODCB, such radical reactions do not take place. For example, the reaction of $La@C_{82}$ with **2** in benzene afforded the normal pyrrolidino-cycloadducts.

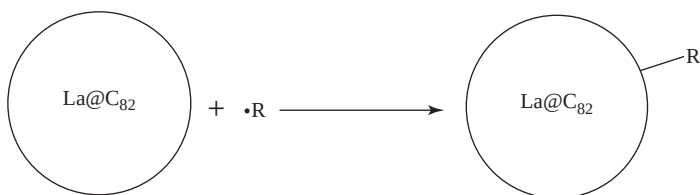


Figure 7.11 Radical coupling reaction of $La@C_{82}$.

The Mn(III)-catalyzed free radical addition to $M_3N@C_{80}$ ($M = Sc, Lu$) has also been reported [154]. Up to eight substituents can be attached to the cage when $M = Sc$, whereas the maximum number for $Lu_3N@C_{80}$ is ten. Structural investigations on an isolated adduct of $Sc_3N@C_{80}$ disclosed a [6,6]-open structure. Photochemically generated benzyl radicals add to $M_3N@C_{80}$ ($M = Sc, Lu$) to produce dibenzyl adducts with high yield and high selectivity [155]. Structural analyses confirmed a 1,4-addition pattern of the two benzyl groups.

7.4.1.6 Reaction with Carbanion

Addition of diethyl bromomalonate in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) to $La@C_{82}$ generated only one cycloadduct but four unexpected isomers with singly bonded structures [156, 157]. Single-crystal XRD results of the most abundant isomer show that the addend tends to attack the most positively charged carbon of the C_{82} cage (C23 in Figure 7.12), which is distant from the encapsulated La atom.

Malonate shows a lower reactivity than bromomalonate because of the lower acidity of the methylene protons, so that the reaction was performed at an elevated temperature. Aside from five isomers of mono-adducts (also four singly bonded isomers and one cycloadduct), one bis-adduct was also formed selectively [158]. Single-crystallographic analysis of the bis-adduct disclosed that the two malonate groups bond to the carbons with highest (C23) and third highest (C21) charge density values, respectively, also via single bonds.

Similar reactions were also performed on the EMF species with TNT clusters, but only cycloadducts were found. Cycloaddition of diethyl bromomalonate to $Y_3N@C_{80}$ gave rise to an unexpected [6,6]-open adduct whereas such an adduct of C_{60} has a closed-cage structure [159]. Attempts to perform the same reaction on $Sc_3N@C_{80}$ failed to give any identifiable adduct. This difference in reactivity originates from the encapsulated metallic species. Because $Sc_3N@D_{3h}-C_{78}$ has a lower symmetry than $M_3N@I_h-C_{80}$, it was expected that several isomers would be formed in the reaction with diethyl bromomalonate. Surprisingly, only one mono-adduct isomer and a dominant isomer of bis-adduct were generated [160]. The bis-adduct shows a nearly identical ^1H NMR spectrum to the corresponding one of the mono-adduct. Detailed analyses combined with theoretical calculations revealed that the second addition site was controlled by the encaged Sc_3N cluster. An interesting finding is that closed-propane between the appended malonate group(s) and the fullerene cage was formed, whereas cyclopropanation of other EMFs always results in the formation of open-cage structures.

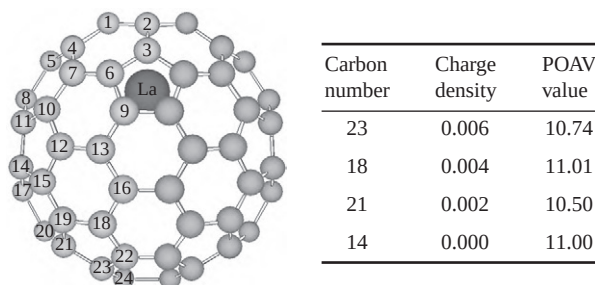


Figure 7.12 Optimized structure of $La@C_{2v}-C_{82}$ and charge density and POAV values of the positively charged carbons.

A zwitterion approach is used to functionalize Dy@C₈₂. It shows both high selectivity and efficiency [161]. Treatment of Dy@C_{2v}-C₈₂ with dimethyl acetylenedicarboxylate (DMAD) and triphenylphosphine gave rise to one mono-adduct with a yield of up to 90%. Structural analysis of the adduct confirmed an open-cage structure, and the addition sites are the same as those found previously for the carbene derivative of La@C₈₂(Ad), which accordingly leaves an open question about the reaction mechanism.

7.4.1.7 Host–Guest Chemistry

The first host–guest supramolecular system of EMFs was obtained by the incorporation of Dy@C₈₂ into calix[8]arene (C8A), which was compared with the better known [C₆₀-C8A] [162]. Perhaps attributable to the larger sizes and different conformational changes, it is more difficult for Dy@C₈₂ to form a complex with C8A than C₆₀, as evidenced by the longer reaction time and lower yield. However, once formed, [Dy@C₈₂-C8A] is much more stable than the C₆₀ analog.

Recently, more efficient systems for the host–guest incorporation of EMFs were developed with azacrown ethers, which were able to form supramolecular complexes with La@C₈₂, with the accompanying electron transfer between them [76, 163]. Because the complexation is characteristic of EMFs, it was applied to the isolation of EMFs from the raw extracts; thereby, exciting results were obtained (see also Section 7.2.3.3).

7.4.2 Positional Control of Encapsulated Metals by Exohedral Modifications

Since the first proposal of the endohedral structure of EMFs, there has been a desire to control the positions or motions of the encaged metals. Recent results show that the positions or movements of ‘untouchable’ metals in EMFs can be controlled certainly by exohedral modifications.

The most pronounced examples are the halt of the three-dimensional circular motions of the two metal atoms in M₂@C₈₀ (Figure 7.13a) [86] by exohedral modifications. X-ray crystallographic and ¹³C NMR characterizations on a disilylated adduct of Ce₂@C₈₀ clearly disclosed that the two Ce atoms are localized at two positions directing the hexagonal ring at the equator [164]. Regarding the disilylated derivatives of La₂@C₈₀, the two La atoms were found to hop two-dimensionally along the equator of the C₈₀ cage (Figure 7.13b shows all possible positions of the La atoms) [132]. Recent experimental results of the carbene derivatives of M₂@C₈₀ (M = La, Ce) disclosed that the two metal atoms remain steadily inside the cage, which are collinear with the spiro carbon of the adamantylidene (Figure 7.13c) [125]. These results show unambiguously that the movements of the encapsulated metals are controlled by exohedral modifications and are certainly useful for the future design of EMF-based molecule devices.

7.4.3 Chemical Properties of Cage Carbons Dictated by the Encapsulated Metals

The chemical reactivity of EMFs strongly depends on the nature of the encaged metallic species because charge transfer takes place between them. A clear example is the different reactivity of Sc₃N@C₈₀ and La₂@C₈₀ toward disilirane (**1**) [126]. In fact, La₂@C₈₀ is reactive both

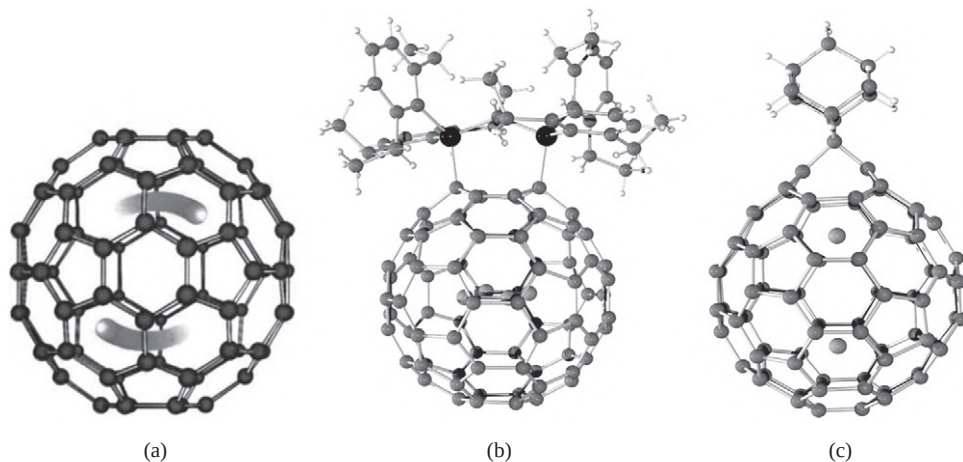


Figure 7.13 (a) Circular motions of the two La atoms in $\text{La}_2@C_{80}$; structures of (b) disylilated $\text{La}_2@C_{80}$ and (c) $\text{La}_2@C_{80}(\text{Ad})$.

thermally and photochemically, but only the photochemical reaction succeeded in $\text{Sc}_3\text{N}@C_{80}$ although the two EMFs have the same $I_h\text{-C}_{80}$ cage and the same electronic structure (C_{80}^{6-}).

The reactivity of the cage carbons is also induced by the encaged metals. $\text{La}@C_{2v}\text{-C}_{82}$ represents the most intensively investigated example. Because of its low cage symmetry, $\text{La}@C_{2v}\text{-C}_{82}$ had been expected to form many structural isomers of adducts. Indeed, silylation of $\text{La}@C_{2v}\text{-C}_{82}$ has produced several isomers of mono-adducts [122, 130]. Amazingly, results showed that the reaction between adamantylidene (**4**) and $\text{La}@C_{2v}\text{-C}_{82}$ produced only one dominant mono-adduct isomer [147]. Detailed calculations and structural analysis showed that one carbon on the hexagonal ring closest to the La atom has both highest POAV value and charge density; this particular carbon is accordingly the most reactive toward the electrophilic **4**. In contrast, addition of the carbanion to $\text{La}@C_{2v}\text{-C}_{82}$ occurs at the positively charged cage carbons, which are far from the encapsulated La atom (Figure 7.12) [156–158]. Based on these results, selective modification of different cage carbons becomes possible.

Cyclopropanation of $\text{Sc}_3\text{N}@C_{78}$ with diethyl bromomalonate also showed surprisingly high selectivity. An addition site for the mono-adduct occurs exclusively at a [6,6]-junction. It is more interesting to find that the addition site of the second addend was dictated by the first one. Figure 7.14 shows that three addition sites are most likely, but the second group was found to attack the *anti*-1 bond only, resulting in a symmetric bis-adduct [160].

7.4.4 Chemical Behaviors of EMFs Bearing Fused Pentagons

Fullerenes with abutted pentagons are not sufficiently stable to survive the extraction and isolation processes because of the high strains of the [5,5]-bonds. Consequently, only when the [5,5]-bond strain is released, for example by exohedral substitution, can stable derivatives of fullerenes with non-IPR structures be isolated. Reported examples are $C_{50}\text{Cl}_{10}$ [23], $C_{64}\text{H}_4$ [165], $C_{64}\text{Cl}_4$ [166], $C_{60}\text{Cl}_8$, and $C_{60}\text{Cl}_{12}$ [22]. It is particularly interesting that the [5,5]-bond carbons are exclusively substituted by Cl or H, indicating their extremely high reactivities.

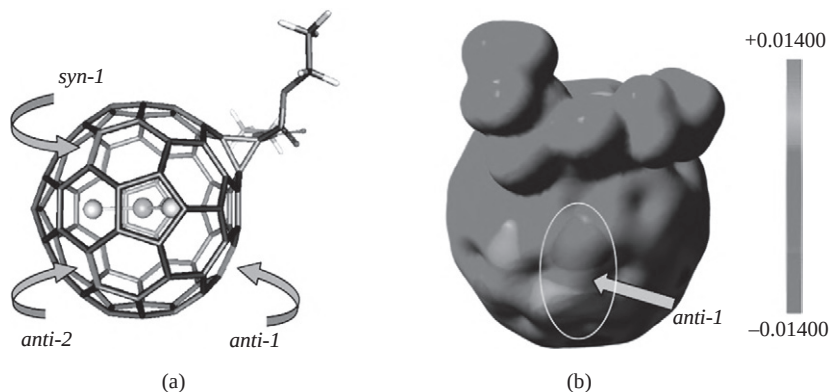


Figure 7.14 (a) Three most possible addition sites for the second addend in $\text{Sc}_3\text{N}@C_{78}\text{CH}(\text{COOC}_2\text{H}_5)_2$ and (b) projection of the HOMO onto the electron density surface of $\text{Sc}_3\text{N}@C_{78}\text{CH}(\text{COOC}_2\text{H}_5)_2$ [160]. (Reprinted with permission from T. Cai, *et al.*, “Selective formation of a symmetric $\text{Sc}_3\text{N}@C_{78}$ bisadduct: adduct docking controlled by an internal trimetallic nitride cluster,” *Journal of the American Chemical Society*, **130**, 2136–2137, 2008. © 2008 American Chemical Society.)

Another means to stabilize fused pentagons is to incorporate metallic species. This seems more efficient because more non-IPR EMF species with cages ranging from C_{66} to C_{84} are found (refer to Section 7.3.1.1 for detailed examples). Because the pentalene bonds are not substituted in non-IPR EMFs, it is particularly interesting to investigate their chemical properties and to elucidate how they are stabilized.

The first derivative of non-IPR EMFs is $\text{La}@C_{72}(\text{C}_6\text{H}_3\text{Cl}_2)_2$, which was obtained by refluxing the raw soot in TCB [32]. It is surprising that the dichlorophenyl group is not linked to either of the two [5,5]-junction carbons, but to an adjacent one. However, it is not possible to investigate the properties of pristine $\text{La}@C_{72}$ because it is not available.

Results that are more meaningful were obtained recently from the structural analyses of the carbene derivatives of $\text{La}_2@C_{72}$, which has two fused-pentagon pairs (Figure 7.15a). The Ad group (**4**) selectively attacks the carbons on the fused pentagons, which are adjacent to the [5,5]-junction carbons, instead of the [5,5]-carbons themselves, forming open-cage derivatives (Figure 7.15b) [167]. Consequently, it was confirmed experimentally that the two pentalene bonds interact strongly with the two La cations, respectively, and become less reactive. However, the two fused-pentagon regions are still more reactive than other parts of the molecule because additions are localized onto these two regions, as confirmed from X-ray data of other mono-adduct isomers and a bis-adduct (Figure 7.15c) [168].

7.5 Applications of EMFs and Their Derivatives

The unique structures and novel properties of EMFs suggest hugely important potential applications in many fields ranging from biology, medicine, and electronics to material science. However, because of the low availability, applications of EMFs and their derivatives have not been investigated widely during recent years. Nevertheless, preliminary results present us with the future prospects for the applications of EMFs.

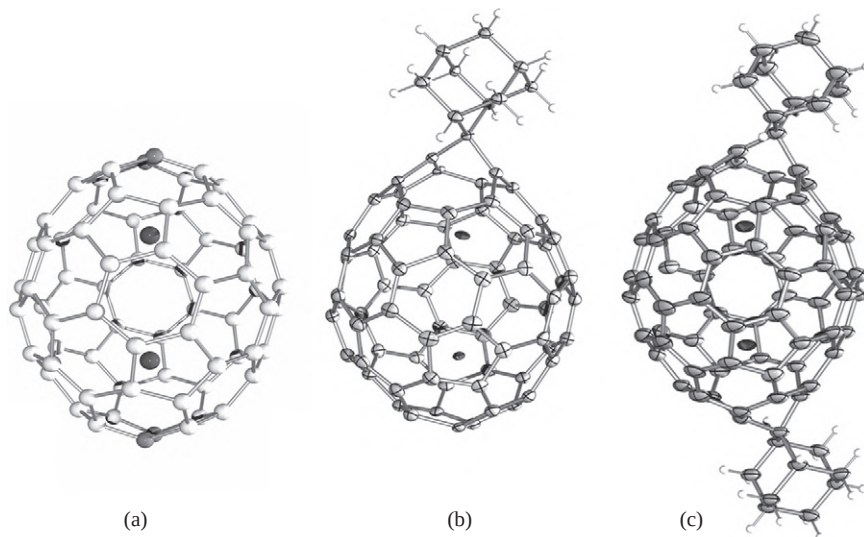


Figure 7.15 Molecular structures of (a) $\text{La}_2@\text{C}_{72}$, (b) $\text{La}_2@\text{C}_{72}(\text{Ad})$, and (c) $\text{La}_2@\text{C}_{72}(\text{Ad})_2$.

7.5.1 Applications in Biology and Medicine

7.5.1.1 Diagnostic/Therapeutic Radiopharmaceuticals

Use of metallofullerenes as radiopharmaceuticals is a promising application of EMFs because the encaged metal(s) is useful as a radiotracing element, whereas the fullerene cage serves as both a protector for the toxic metal ions, and a carrier with functional groups of various types.

Bio-distributions of EMFs were investigated by using holmium-containing metallofullerenes as radiotracers [169, 170]. A mixture of $\text{Ho}_x@\text{C}_{82}$ ($x = 1, 2$) was used as the starting material to synthesize water-soluble polyhydroxyl derivatives, $\text{Ho}_x@\text{C}_{82}(\text{OH})_y$, which were then neutron-irradiated to produce the corresponding radiotracer, that is, $^{166}\text{Ho}_x@\text{C}_{82}(\text{OH})_y$. Bio-distributions of this material in BALB/c mice are summarized in Figure 7.16. After 1 h injection, it had been presented to all the organs of the entire body, except tissues with limited blood flow such as the brain and adipose tissues, which indicated a blood-delivery character. However, it is difficult for the liver, bone, kidney, and spleen to metabolize the metallofullerols within 48 h, but it does not mean obvious toxicity, because slow and steady clearance of the metallofullerols was observed over 5 days in Fischer rats.

7.5.1.2 MRI Contrast Agents

Water-soluble derivatives of gadolinium–EMFs have proven to be promising magnetic resonance imaging (MRI) reagents; many successful results have been reported.

To make EMFs water soluble, hydrophilic groups must be attached to the fullerene surface. The best way is to introduce polyhydroxyl groups. The resultant derivatives are termed metallofullerols. In fact, $\text{Gd}@\text{C}_{82}(\text{OH})_{\sim 40}$, synthesized using a phase-transfer method, shows a longitudinal proton relaxivity ($r_1 = 81 \text{ mM}^{-1}\text{s}^{-1}$) that is more than 20 times higher than the commercial MRI contrast agent Magnevist (Gd-EDPA , $r_1 = 3.9 \text{ mM}^{-1}\text{s}^{-1}$) [171]. An *in vivo* MRI study of CDF1 mice at a lower dose of injection (1/20 of the Gd-EDPA) presents an

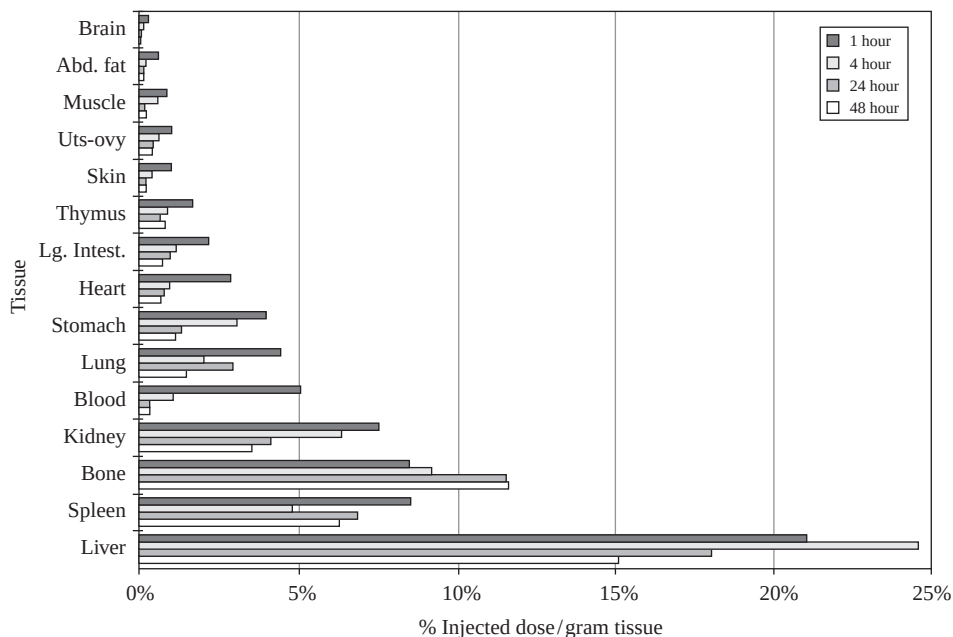


Figure 7.16 Bio-distribution of $^{166}\text{Ho}_x\text{@C}_{82}(\text{OH})_y$ in BALB/c mice at different timescales [169]. (Reprinted with permission from L.J. Wilson *et al.*, “*In vivo* studies of fullerene-based materials using endohedral metallofullerene radiotracers,” *Proceedings of the National Academy of Sciences of the United States of America*, **96**, 5182–5187, 1999. © 1999 National Academy of Sciences, U.S.A.).

obvious enhancement of the T_1 -weighted image, especially in such organs as the lung, spleen, liver, and kidney.

Systematic investigations of proton relaxivities of lanthanoid–metallofullerols encapsulating Er, Ce, La, Dy, and Gd were also performed [172]. As depicted clearly in Figure 7.17, Gd-related materials certainly present higher contrast than the corresponding reagents with other metals because of the large number of unpaired f-electrons of Gd^{3+} . It is significant that the $\text{M@C}_{82}(\text{OH})_n$ are always more effective than either free ions or M–DTPA. Even for ions with low magnetic moments such as La^{3+} and Ce^{3+} , their metallofullerols still show strong relaxivities, which must originate from the unpaired electron on the cage.

The relaxation mechanism is the so-called “second-sphere mechanism,” in which intermolecular aggregation of metallofullerols is crucial for high relaxivity [173]. Accordingly, Gd–metallofullerols with less hydroxyl groups or other water-soluble derivatives of Gd–EMFs have lower r_1 values because of their lesser aggregation [73, 174–176]. Such aggregates of water-soluble Gd–EMF derivatives can be disrupted by salt addition [177], which engenders smaller entities with higher penetration ability, but with lower relaxivity.

Water-soluble derivatives of Gd-containing TNT EMFs exhibit even higher relaxivities because three Gd^{3+} ions are encapsulated within one cage. For example, $\text{Gd}_3\text{N@C}_{80}[\text{N}(\text{OH})(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_3]_x$ ($x = 10\text{--}22$) has an r_1 value of $205 \text{ mM}^{-1}\text{s}^{-1}$, which is much higher than the data obtained for water-soluble Gd@C_{2n} derivatives [178]. *In vivo* studies on a BALB/c mouse used persistent image enhancement to investigate the aorta, revealing that such

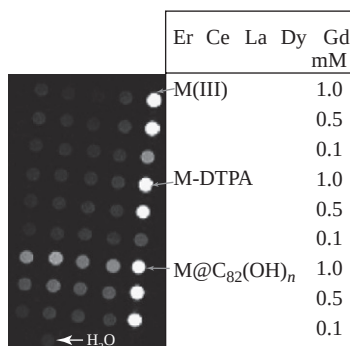


Figure 7.17 Phantom images of lanthanoid-metallofullerols [172]. (Reprinted with permission from H. Kato, *et al.*, “Lanthanoid endohedral metallofullerenols for MRI contrast agents,” *Journal of the American Chemical Society*, **125**, 4391–4397, 2003. © 2003 American Chemical Society).

materials are particularly suitable for vasculature diagnosis. The proton relaxation mechanism of the derivatives of $\text{Gd}_3\text{N@C}_{80}$ was proposed to be different from that of the water-soluble Gd@C_{2n} analogs.

Compared with the Gd–chelate complexes, water-soluble Gd–metallofullerene derivatives are more promising, mainly for the following reasons: (i) the relaxivities are much higher than Gd–EDTA and they would simultaneously provide comparable images with minimal exposure to the patient; (ii) the toxic Gd^{3+} is trapped by fullerene cages, rendering the materials safe for living bodies; and (iii) the carbon cage can carry numerous functional groups, including some antibodies together with hydroxylic groups [179].

7.5.1.3 X-ray Contrast Agents

Lutetium-containing TNT cluster metallofullerenes proved to be promising multifunctional contrast agents for both MRI and X-ray diagnosis [180]. When irradiated with X-rays, $\text{Lu}_3\text{N@C}_{80}$ demonstrates X-ray contrast after distribution onto a nonabsorbing Teflon block, but a blank Teflon block and one containing only C_{60} show no obvious X-ray contrast, which confirms that the contrast cannot be attributed to either the Teflon block or the carbon cage. However, $\text{Sc}_3\text{N@C}_{80}$ does not provide X-ray contrast because of the smaller cross section of the scandium atoms. Accordingly, it was expected that the TNT species with mixed-metal clusters (for example, $\text{GdLu}_2\text{N@C}_{2n}$) might prove useful as multimodality contrast agents.

7.5.2 Applications in Material Science

7.5.2.1 EMFs Inside Carbon Nanotubes – Nano ‘Peapods’

Incorporation of small molecules into the hollow cavities of carbon nanotubes (CNTs) generates a new class of hybrid materials, which show potential applications ranging from nano-size containers for chemical reactions or for drug delivery to data storage and possibly high-temperature superconductors [181]. Because of their unique structure, such materials are called nano ‘peapods’ [182].

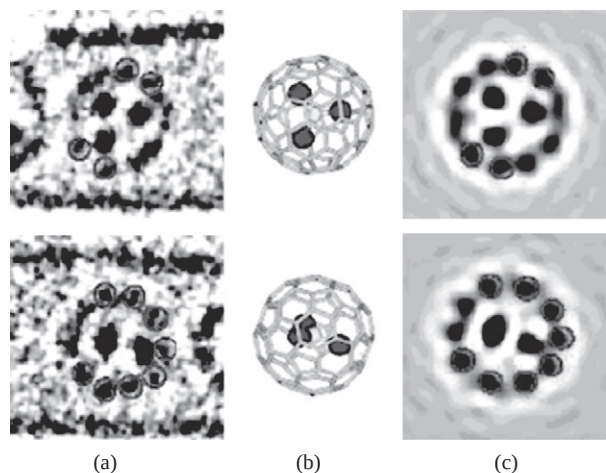


Figure 7.18 Direct observation of motions of the Er_3N cluster and $\text{Er}_3\text{N}@I_h\text{-C}_{80}$ in CNTs: (a) HRTEM images (upper, taken at 37 s; lower, taken at 2 s); (b) suggested orientations; (c) simulated images [185]. (Reprinted with permission from Y. Sato, *et al.*, “Structures of $D_{5d}\text{-C}_{80}$ and $I_h\text{-Er}_3\text{N}@C_{80}$ fullerenes and their rotation inside carbon nanotubes demonstrated by aberration-corrected electron microscopy,” *Nano Letters*, 7, 3704–3708, 2007. © 2007 American Chemical Society).

Fullerenes and EMFs are good candidates to be inserted inside CNTs; strong interactions between the inserted EMF molecules and the CNT walls were evidenced from many experimental results. For example, the Raman spectra of $\text{La}_2@\text{C}_{80}@\text{CNT}$ differ significantly from those of the empty nanotubes and some absorptions indicate a charge-transfer between them [183]. More supportive proof has been reported by Lee *et al.* After insertion of $\text{Gd}@C_{82}$, the bandgap of CNTs was narrowed down from about 0.5 to 0.1 eV at sites where the EMF molecules locate [184]. Such materials are particularly suitable for quantum computing, which is expected to be the technological mainstay for the next generation of computers.

With the confinement of CNTs, direct observations of the dynamic motions of EMFs and the encaged metallic species were also achieved using high-resolution transmission electronic microscopy (HRTEM). Figure 7.18 shows that the motions of the fullerene cage and the encaged Er_3N cluster are clearly resolved [185].

7.5.2.2 Nanorods of EMF Derivatives with Abnormal FET Properties

The carbene derivative $\text{La}@C_{82}(\text{Ad})$ can form nanorods during single-crystal growth, which shows an unusual FET (field effect transistor) property. Because thin films or whiskers of empty fullerenes and solids of EMFs are well known to show *n*-type semiconductivity, the nanorods are *p*-type [186], which will surely find applications in such fields as nanoelectronics.

7.5.2.3 Potential Applications in Electronics and Photovoltaics

Donor–acceptor systems based on empty fullerenes have been well investigated. Some useful materials have also been generated. Because of the charge transfer within EMFs, they are

expected to be more useful in donor–acceptor systems, but related results are rare. Recently, a donor–acceptor dyad was synthesized using the 1,3-dipolar reaction of $\text{Sc}_3\text{N}@C_{80}$ with sarcosine and ferrocene carboxaldehyde [187]. The NMR and electrochemical measurements indicated a [5,6]-addition pattern of the isolated adduct. Time-resolved transient absorption spectroscopy confirmed formation of the radical ion pair state. Such materials are believed to be more useful as solar-energy conversion materials than the C_{60} -analogs.

Moreover, metallofullerenes have shown interesting magnetic [188] and nonlinear optical properties [189] and are expected to support applications in related fields.

7.6 Perspectives: Challenge and Chance

The emergence of EMFs has not just provided a class of new hybrid materials with unusual structures, properties, and promising applications. It has also presented new concepts of molecular architecture and molecular jailing. During the first decade of research on EMFs, efforts were mainly devoted to the encapsulation of elements of different types inside fullerene cages and the relevant investigations on their endohedral structures and physical properties. In the recent decade, with progress achieved in the high-yield synthesis and high-efficiency isolation of EMFs, macroscopic samples of pure metallofullerene isomers have become available for chemical characterizations and applications.

Nevertheless, availability remains as the main obstacle. Presently available amounts of EMFs are much less than are required for future applications. Use of catalysts remains as a good choice to promote the production yield, and more powerful extraction processes are also critical. More convenient and effective separation processes will surely promote the availability of EMFs.

The formation mechanism of EMFs remains unclear. Informative results concerning the interactions between the encaged metals and the fullerene cage in isolated EMFs have been obtained, but many mysteries remain in the early stage of the arc–discharge process. Disclosure of these mysteries is helpful to increase the production yield and broaden the applications of EMFs.

Exploration of applicable materials based on EMF is the ultimate target. With progress recently achieved in chemical modifications on EMFs, useful derivatives of EMFs with outstanding properties can ideally be designed and synthesized. Furthermore, all EMF-based materials are expected to be friendly to both organisms and the environment, especially when they are used as biomedicines. However, to date, little is known about the toxicity and metabolism of EMFs and their derivatives in living bodies and on the earth. A great deal of investigation must be done in this regard.

In spite of difficulties that temporarily hinder research of EMFs, the unique structures and fantastic properties of EMFs continue to attract great attention and to promise future applications yielding fruitful results. Through multilateral endeavors, EMFs will become increasingly promising and find more uses.

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8

Organometallic Chemistry of the Lanthanide Metals

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8.1 Introduction

The valence electrons of lanthanide metals are located in the 4f orbitals, which are well shielded by filled 5s and 5p orbitals and hence experience only negligible interactions with ligand orbitals. Thus, anionic ligands are required to electrostatically balance the positive charge of the lanthanide ions that tend to form, rather than the ionic complexes. The large coordination numbers of these metal ions, normally 6–12, means it is not easy to saturate the coordination sphere around the ions. Therefore, organolanthanide chemistry was fairly limited up to the early 1980s, although the first organolanthanide complexes Cp_3Ln (Cp = cyclopentadienyl) were reported half a century ago [1]. The situation has changed since the availability of modern preparative and analytical techniques, in particular single-crystal X-ray diffraction, which have made it possible to handle these very air- and moisture-sensitive compounds, and thus to understand the structural features of these complexes. The development of organolanthanide chemistry has been spurred on over the past two decades specifically through the exploration of new ligand systems, and the discovery of the high potential of these complexes as reagents in organic synthesis and as very active catalysts in homogeneous catalyses [2]. There are many reviews available that cover the various topics in this area, including cyclopentadienyl lanthanide chemistry [3], non-cyclopentadienyl lanthanide chemistry [4], cationic lanthanide chemistry [5], the chemistry of lanthanide hydrides [6], reductive lanthanide chemistry [7], and so on. Thus, this chapter will focus on the main progress in organolanthanide chemistry in recent years, including the synthesis and reactivity of organolanthanide π -complexes, alkyls, hydrides, cationic alkyl complexes, *N*-heterocyclic carbene complexes, divalent complexes and tetravalent cerium complexes, in addition to their applications as homogeneous catalysts in organic transformation and polymerization.

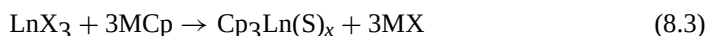
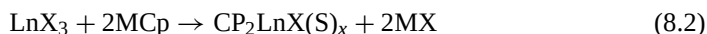
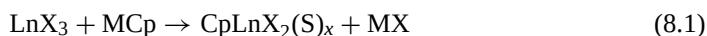
8.2 Synthesis and Reactivity of Organolanthanide Complexes Containing Ln–C Bonds

8.2.1 Synthesis and Reactivity of Organolanthanide π -Complexes

Following the synthesis of tris(cyclopentadienyl) lanthanide complexes, the first examples of organolanthanide derivatives, a vast number of organolanthanide π -complexes with cyclopentadienyl (Cp), indenyl (Ind), cyclooctatetraenyl (COT), and related substituted derivatives have been prepared and extensively reviewed [3]. Here we will briefly discuss cyclopentadienyl and allyl derivatives as representatives of organolanthanide π -complexes.

8.2.1.1 Synthesis

A metathesis reaction is a general method for the preparation of organolanthanide π -complexes, and three types of compounds can be synthesized, depending on the stoichiometry of the starting materials (Equations 8.1–8.3).



where

X is a halide, including Cl, Br, I

M is an alkali metal, including Li, Na, K

S is a solvent molecule.

To saturate the demand of the high coordination number of lanthanide metal ions, the cyclopentadienyl group adopts a η^5 -coordination mode, and occupies three sites in the coordination sphere of the metal center. A typical structure for LnCp_3 is shown in Figure 8.1.

For a bulky substituted cyclopentadienyl group, such as C_5Me_5 and $\text{C}_5\text{Me}_4\text{R}$ ($\text{R} = \text{Et}$, Pr , SiMe_3), tris(cyclopentadienyl) lanthanide complexes cannot be prepared via the above metathesis reaction because of the steric hindrance. The reaction of anhydrous LnCl_3 with three equivalents of alkali metal pentamethylcyclopentadienyl in THF (tetrahydrofuran) led to the THF ring-opened product (Equation 8.4) [8].

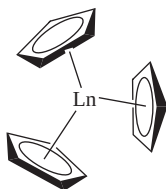
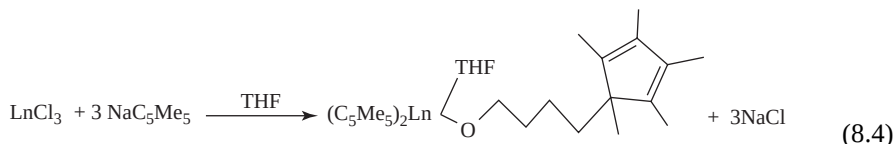
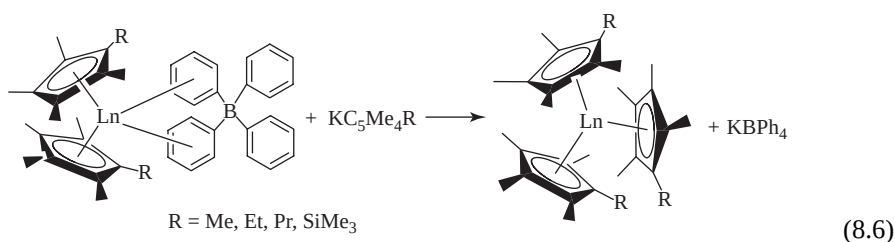
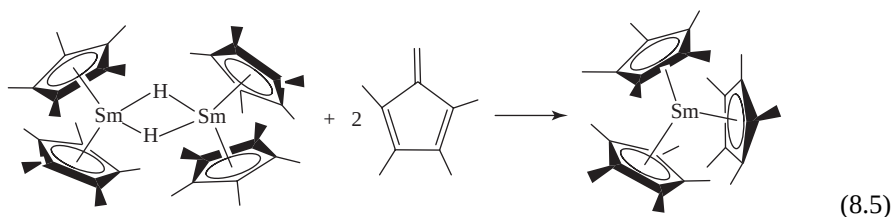


Figure 8.1 Structure of Cp_3Ln .

The first tris(pentamethylcyclopentadienyl)lanthanide complex was isolated accidentally from the reaction of a divalent samarium complex $(C_5Me_5)_2Sm$ with cyclooctatetraene [9]. Following this discovery, two more convenient methods were developed for the preparation of the sterically crowded complexes $(C_5Me_5)_3Ln$ [10].



Allyl lanthanide complexes are one of the important groups of organolanthanide π -complexes because of their wide applications in organic synthesis and catalysis. Metathesis reactions of anhydrous lanthanide chlorides with allyllithium in THF or dioxane give anionic allyl lanthanide complexes with various compositions, depending on the stoichiometry of the reagents, and on the reaction conditions. The first neutral triallyl lanthanide complexes $[La(\pi-C_3H_5)_3(\kappa^1\text{-dioxane})]_2(\mu\text{-dioxane})$ and $[Nd(\pi-C_3H_5)_3(\mu\text{-dioxane})]_\infty$ were prepared by using BEt_3 to abstract allyllithium from the anionic tetrakis(allyl) lanthanide complexes $[Li(\mu\text{-dioxane})_{1.5}][Ln(\pi-C_3H_5)_4]$ [11]. The structure determination revealed that each allyl group adopts a η^3 -coordination mode (Figure 8.2).

Recently, an improved one-pot method, that is, the metathesis reaction of anhydrous $LnCl_3$ with three equivalents of allylMgCl, instead of three equivalents of allyllithium in a mixture of THF–1,4-dioxane was developed for the synthesis of neutral triallyl lanthanide complexes.

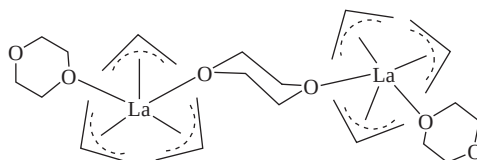
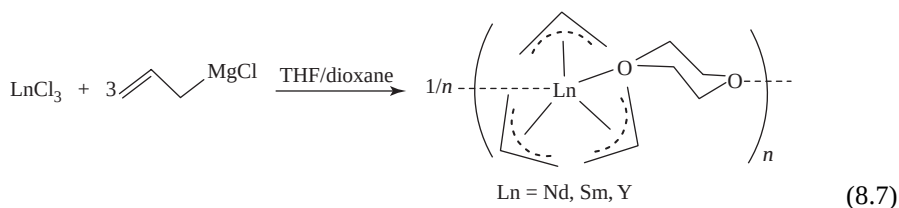


Figure 8.2 Structure of $[La(\pi-C_3H_5)_3(\kappa^1\text{-dioxane})]_2(\mu\text{-dioxane})$.

A series of neutral triallyl lanthanide compounds are prepared conveniently by use of this method (Equation 8.7) [12].



8.2.1.2 Reactivity

As a result of decades of study, η^5 -cyclopentadienyl groups are known to act as inert ancillary ligands in organometallic reaction chemistry. Recently, the normally inert $(\text{C}_5\text{Me}_5)^-$ group in the sterically crowded $(\text{C}_5\text{Me}_5)_3\text{Ln}$ was found to adopt three types of sterically induced reactivity [7, 13]. They can react with various small molecules, similar to that of an alkyl group (Figure 8.3).

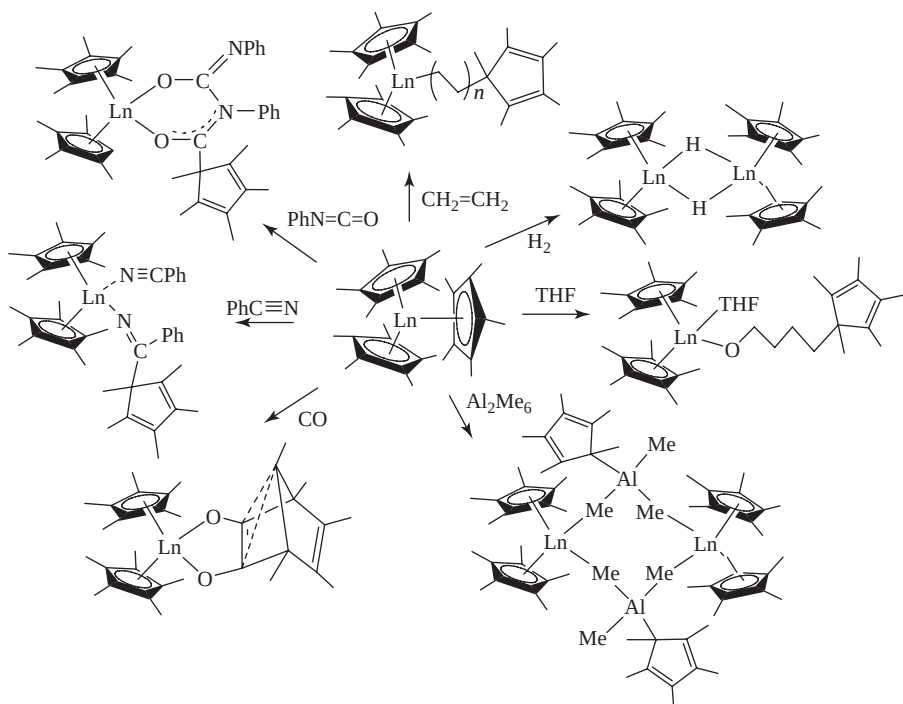
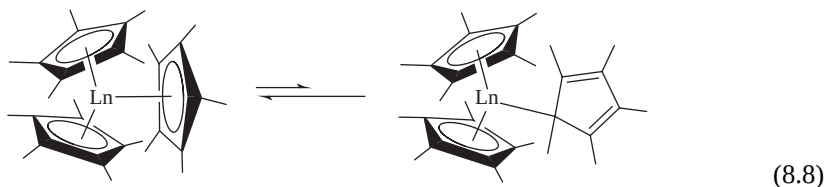


Figure 8.3 Reactivity of $(\text{C}_5\text{Me}_5)_3\text{Ln}$ with small molecules.

Therefore, it was proposed that in solution an equilibrium should exist between a $\eta^5\text{-C}_5\text{Me}_5$ and a $\eta^1\text{-C}_5\text{Me}_5$ group as the environment is sterically overcrowded (Equation 8.8).



The $(\text{C}_5\text{Me}_5)_3\text{Ln}$ complexes can also act as a one-electron reducing agent. Two representative examples are shown in Figure 8.4. A reasonable explanation is that $(\text{C}_5\text{Me}_5)_3\text{Ln}$ gives up one electron to form a $[(\text{C}_5\text{Me}_5)_2\text{Ln}]^+$ cation and a C_5Me_5 radical, followed by an electron transfer to the reactant and the dimerization of C_5Me_5 radicals.

The third type of reaction is ligand displacement of one of the $\eta^5\text{-C}_5\text{Me}_5$ groups by the typically monodentate ligand $\text{N}(\text{SiMe}_3)_2^-$ (Equation 8.9).

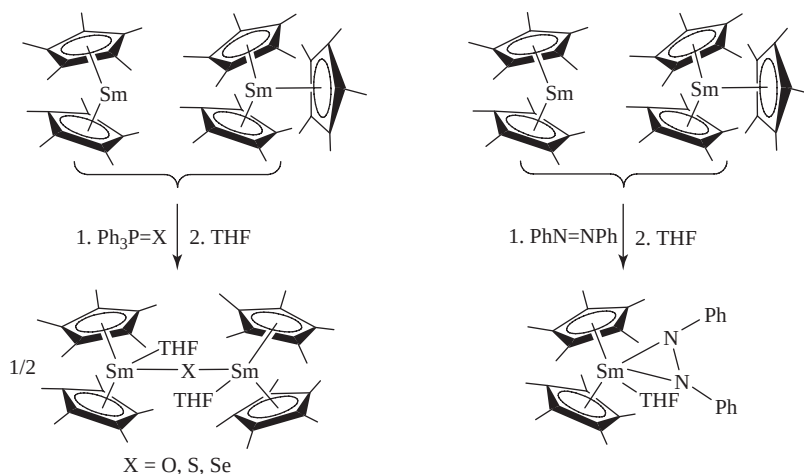
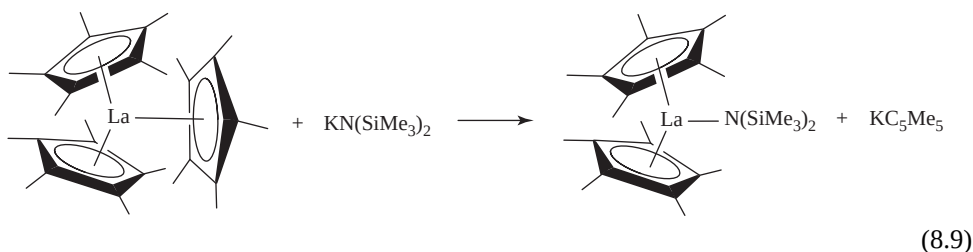


Figure 8.4 Comparison of reactivity between $(\text{C}_5\text{Me}_5)_2\text{Sm}$ and $(\text{C}_5\text{Me}_5)_3\text{Sm}$.



The cyclopentadienyl ring in the even less sterically bulky tris(cyclopentadienyl) lanthanide complexes, $(\text{C}_5\text{H}_5)_3\text{Ln}$ and $(\text{CH}_3\text{C}_5\text{H}_4)_3\text{Ln}$, has been found to be able to functionalize by a direct nucleophilic addition reaction under suitable reaction conditions. Reaction of $(\text{C}_5\text{H}_5)_3\text{Ln}$

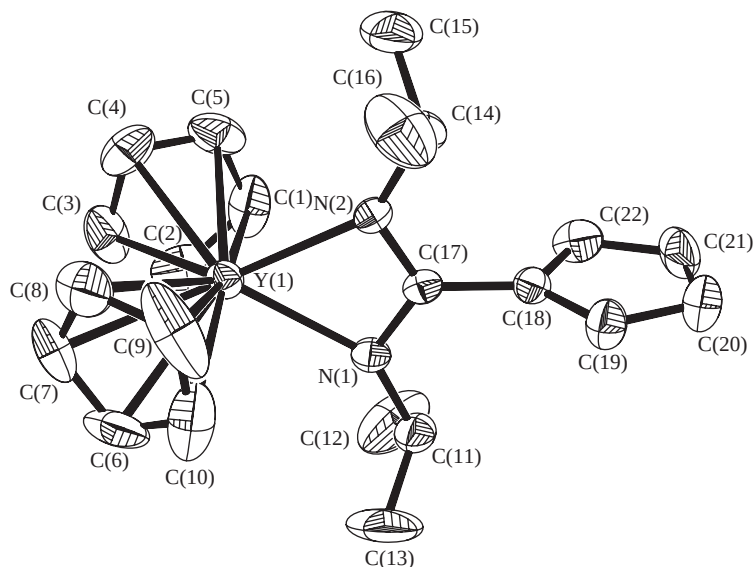


Figure 8.5 The molecule structure of $\text{Cp}_2\text{Ln}[\text{CyNC}(\text{Cp})\text{NCy}]$.

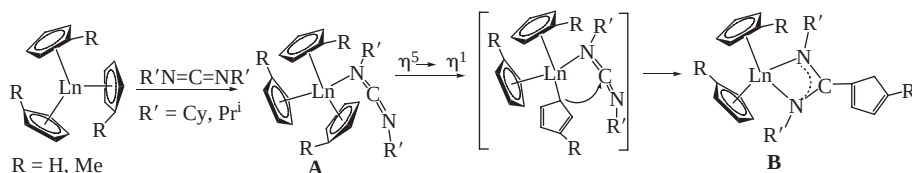


Figure 8.6 Reaction mechanism of $(\text{RC}_5\text{H}_4)_3\text{Ln}$ with carbodiimide.

or $(\text{CH}_3\text{C}_5\text{H}_4)_3\text{Ln}$ with a carbodiimide in toluene gives the substituted amidinate lanthanide complex by insertion of a carbodiimide into an Ln–cyclopentadienyl bond (Figure 8.5). The solvent plays a key role in the reaction. The reaction proceeds smoothly in toluene, whereas no reaction occurs in THF. The proposed reaction mechanism is as shown in Figure 8.6 [14].

Tris(cyclopentadienyl) lanthanide complexes can be used as precursors for the synthesis of lanthanide derivatives via a protonolysis reaction (Figure 8.7) [15, 16]. The biggest advantage of this method is that it excludes the formation of lanthanide “-ate” compounds [17].

8.2.2 Synthesis and Reactivity of Lanthanide Complexes Containing Ln–C σ -Bonds

8.2.2.1 Synthesis of Lanthanide Trialkyl and Triaryl Complexes

Lanthanide trialkyl and triaryl complexes are relatively unstable compared with lanthanide π -complexes because of their high coordination unsaturation. Thus trialkyl lanthanide complexes

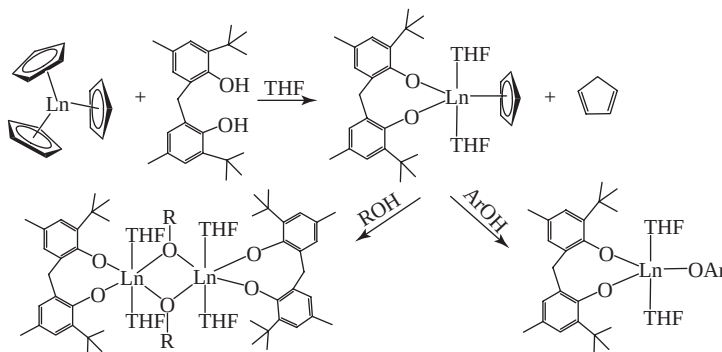
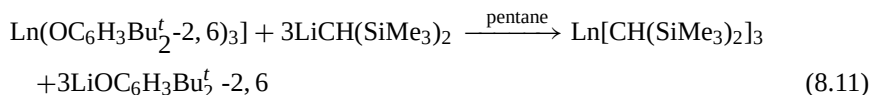


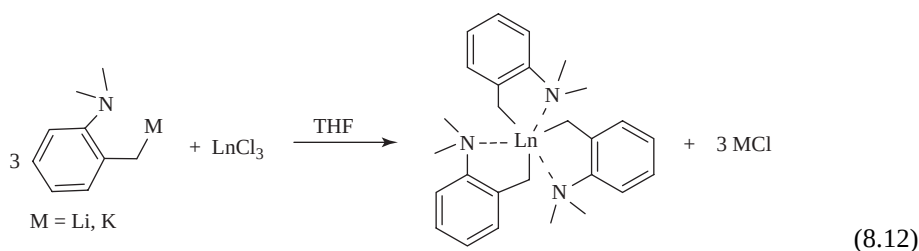
Figure 8.7 Synthesis of lanthanide derivatives using Cp₃Ln as starting materials.

with less bulky alkyl groups, such as methyl groups, could not be synthesized. The metathesis reaction of anhydrous LnCl₃ with MeLi leads to a series of stable anionic adducts with the MeLi, not the neutral trimethyl lanthanide complexes. Obviously, the small methyl group is not big enough to saturate the large coordination sphere around the lanthanide ion. Hence, only a few bulky alkyl groups are found to be suitable ligands for this type of complex. In addition, the ligands should be lacking in a β-H atom, otherwise the decomposition of trialkyl lanthanide complexes proceeds via β-H elimination. The bulky trimethylsilylmethyl group CH₂SiMe₃ and the bis(trimethylsilyl)methyl group CH(SiMe₃)₂ were chosen as the appropriate candidates. The trialkyl lanthanide complexes Ln(CH₂SiMe₃)₃(THF)_n, where Ln = middle to later metals, can readily be prepared from the reaction of lanthanide trichlorides with three equivalents of Li(CH₂SiMe₃) (Equation 8.10) [18, 19]. However, for the early lanthanide metals, the -ate complexes LiLn(CH₂SiMe₃)₄, instead of the neutral ones, are often isolated as the requirement for high coordination numbers of the metals. Even for the bulkier CH(SiMe₃)₂ ligand, the metathesis reaction of LnCl₃ with its lithium salt also gives the -ate complexes in some instances. In order to prepare the salt-free trialkyl lanthanide complexes with this ligand, an indirect approach is needed. Using the bulky lanthanide aryloxides Ln(OC₆H₃Bu^t₂-2,6)₃, instead of LnCl₃, as the starting materials, the neutral homoleptic lanthanide alkyls for all of the lanthanide metals Ln[CH(SiMe₃)₂]₃ can be synthesized (Equation 8.11) [20].

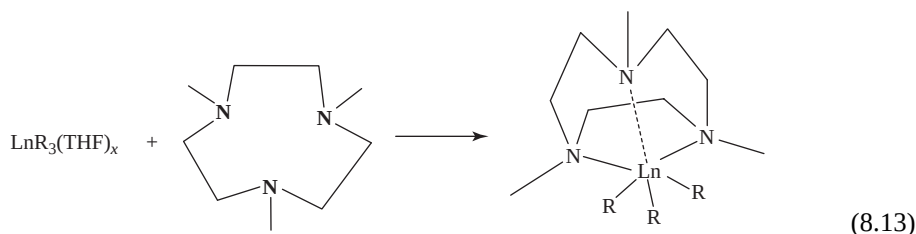


The preparation of a tribenzyl scandium complex has been known for a long time [21]. Recently, the neutral salt-free tribenzyl lanthanide complexes Ln(CH₂Ph)₃(THF)₃ (Ln = La, Lu, Sc) and La(CH₂Ph-4-Me)₃(THF)₃ have been successfully synthesized by the straightforward metathesis reaction of LnX₃ with three equivalents of KCH₂Ph-4-R (R = H, Me) [22, 23]. The neutral triaminosubstituted benzyl lanthanide complexes can be conveniently prepared by

a direct metathesis reaction (Equation 8.12), as the extra coordination of an amino group to the central metal meets the demand for the high coordination number of the metals [24].

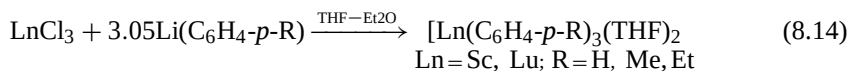


Lanthanide trialkyl complexes are extremely sensitive to air and moisture. Furthermore, most of the lanthanide trialkyl complexes are also thermally unstable. Introducing a strong multidentate donor ligand to this type of complex has recently been found to be a successful protocol to improving their stability and for synthesizing alkyl complexes with less bulky alkyl groups. A variety of heteroatom-containing donor ligands has been explored, including crown ethers, aza-crown ethers, thia-crown ethers, tris(pyrazolyl)methane, 1,1,1-tris[(*S*)-4-isopropylloxazolyl]ethane (*i*Pr-trisox), and so on (Figure 8.8). Various neutral lanthanide trialkyl complexes ligated by a multidentate ligand have been prepared and structurally characterized. One of the representations is shown in Equation 8.13 [25–32].



Using this strategy the first scandium trimethyl complex was successfully isolated by the reaction of ScCl_3 with three equivalents of MeLi in the presence of aza-crown ether (Figure 8.9) [33].

Lanthanide triphenyl complexes have been known for about 40 years. These neutral triphenyl complexes $[\text{Ln}(\text{C}_6\text{H}_5)_3(\text{THF})_n]$ are synthesized by a transmetalation reaction of the lanthanide metal with diphenyl mercury or triphenyl bismuth in THF [34]. Recently, it has been reported that metathesis reaction of anhydrous lanthanide trichloride with aryllithium is a more convenient and reproducible method than the transmetalation reaction used previously for the synthesis of triaryl lanthanide complexes. Several lanthanide triphenyl and substituted triphenyl complexes have been synthesized (Equation 8.14) [35].



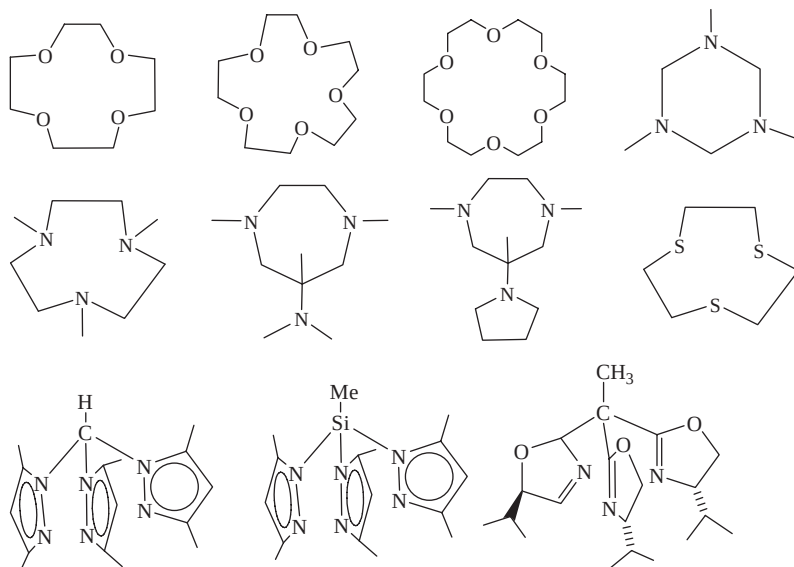


Figure 8.8 Representative multidentate donor ligands for stabilization lanthanide trialkyls.

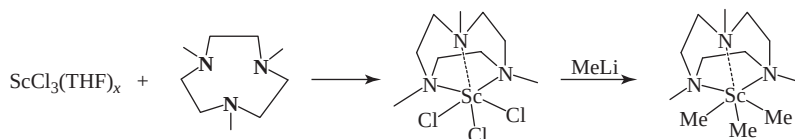
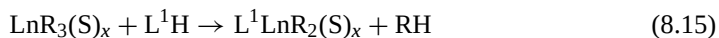


Figure 8.9 Synthesis of a neutral scandium trimethyl complex.

8.2.2.2 Synthesis of Lanthanide Dialkyl Complexes

The most convenient method for the synthesis of lanthanide dialkyl complexes is the alkane elimination reaction of lanthanide trialkyl complexes with a monoanionic preligand (L^1H) (Equation 8.15). The monoanionic preligands, which have tunable steric and electronic features, are favored for modifying the stability and reactivity of the complexes. Various bulky substituted cyclopentadienyl [4] and non-cyclopentadienyl derivatives have been used as the spectator ligands. The most common types of monoanionic non-cyclopentadienyl ancillary ligands are summarized in Figure 8.10 [36–48].



Another route to lanthanide dialkyls is a metathesis reaction. Lanthanide dihalides supported by a bulky monoanionic ancillary ligand, such as pentamethylcyclopentadienyl and related derivatives [4], β -diketiminato and guanidinato groups [49, 50], and so on, are generally used as the starting materials. A variety of lanthanide dialkyl compounds, including methyl compounds have been prepared and structurally characterized via successive metathesis reactions (Figure 8.11).

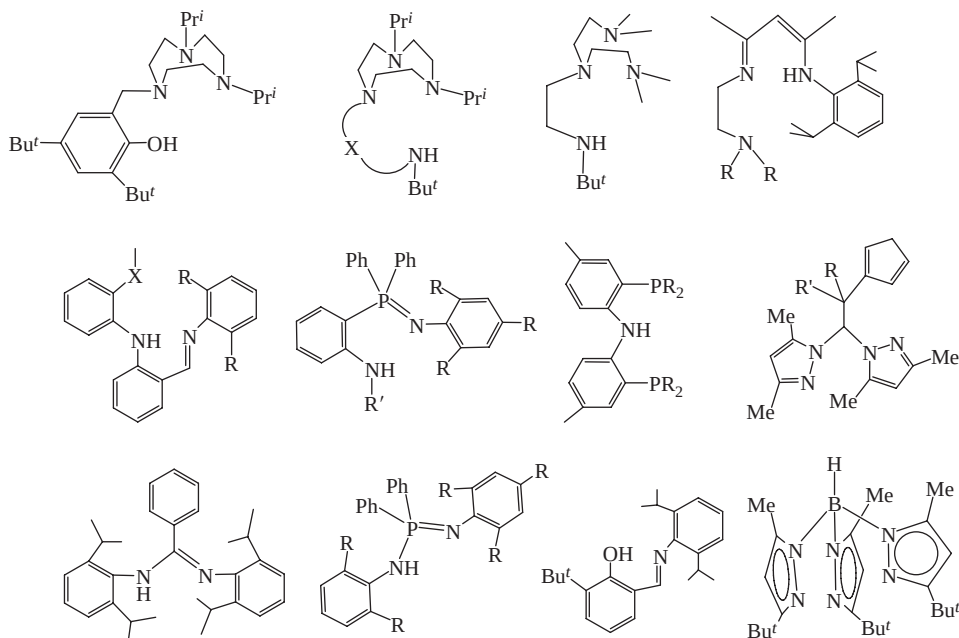


Figure 8.10 Representative monoanionic ligands for stabilization lanthanide dialkyls.

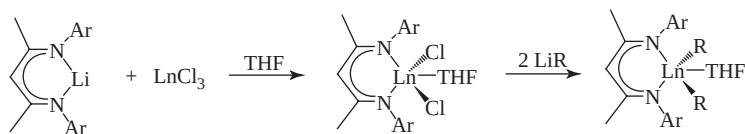


Figure 8.11 Synthesis of lanthanide β -diketiminato dialkyl via metathesis reaction.

8.2.2.3 Synthesis of Lanthanide Monoalkyl Complexes

Lanthanide monoalkyl complexes stabilized by two cyclopentadienyl groups or related π -ligands have already been extensively reviewed [4]. In recent years, the application of dianionic “geometry constrained” cyclopentadienyl groups and non-cyclopentadienyl groups (L^2H_2) in the synthesis of lanthanide monoalkyl compounds has received considerable attention. Various complexes with these ancillary ligands have been reported through an alkane elimination reaction (Equation 8.16) or successive transmetallation reactions (Figure 8.12). The ligands that have been explored and are used widely are presented in Figure 8.13 [51–58].

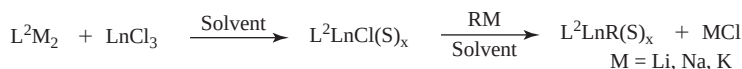
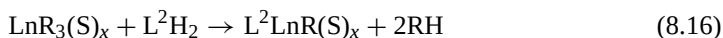


Figure 8.12 Synthesis of lanthanide monoalkyl complex via metathesis reaction.

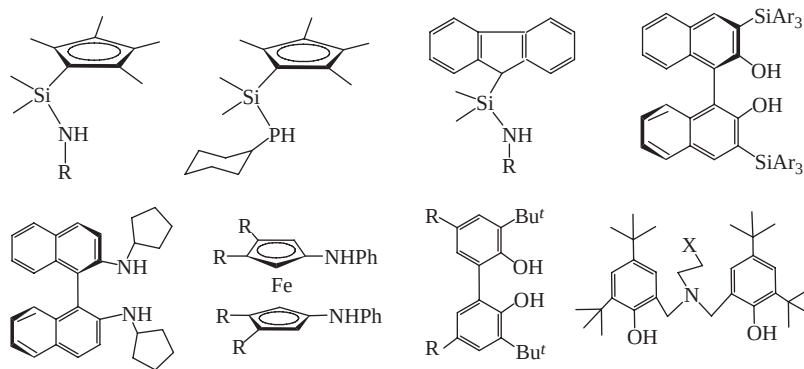


Figure 8.13 Representative dianionic ligands for stabilization lanthanide monoalkyls.

8.2.2.4 Reactivity

Lanthanide alkyl and aryl complexes can readily react with a range of substrates with “acidic” protons, such as alcohols, phenols, phenylacetylene, and amine, to be converted into the corresponding lanthanide derivatives. Lanthanide alkyl complexes react with H_2 to form the corresponding hydride complex, which is the popular route to lanthanide hydride. Various unsaturated small molecules can insert into an Ln –alkyl bond to form the derivatives containing Ln –heteroatom bonds. The reaction modes found are summarized in Figure 8.14 [59–62].

Some lanthanide alkyl complexes can induce intramolecular C–H bond activation via metalation of the ligand with elimination of CH_4 or $SiMe_4$ under suitable conditions [63–65]. A representative example of the sp^3 -hybridized C–H activation is presented in Figure 8.15 [65].

Unsolvated alkyl lanthanide metallocenes display intermolecular C–H activation reactivity. For example, $[(C_5Me_5)_2LnR]_x$ can metallate toluene, benzene, and $SiMe_4$ to give $(C_5Me_5)_2Ln(CH_2Ph)$, $(C_5Me_5)_2LnPh$, and $(C_5Me_5)_2Ln(CH_2SiMe_3)$, respectively [66]. The C–H activation of methane is also observed in the reaction of the *ansa*-scandocene complex $Me_2Si(C_5Me_4)_2ScCH_2CH(CH_2CH_3)_2$ with methane [67].

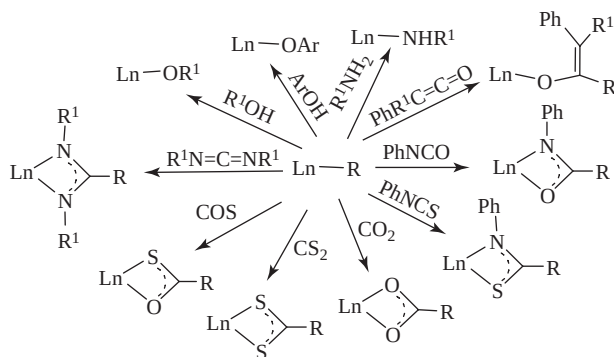


Figure 8.14 The reaction modes of organolanthanide alkyls.

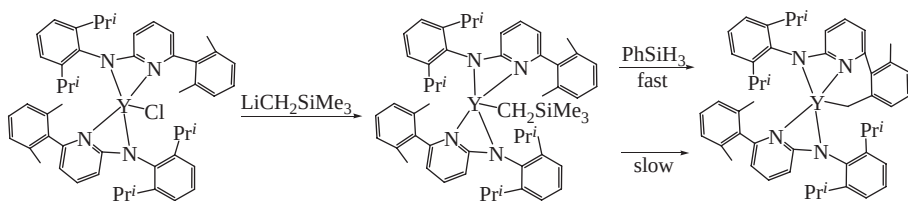


Figure 8.15 Example of intramolecular C–H bond activation of lanthanide alkyl.

8.2.3 Synthesis and Reactivity of Lanthanide *N*-Heterocyclic Carbene Complexes

N-Heterocyclic carbenes (NHCs) are two-electron σ -donor ligands through the NCN carbon atom and belong to soft ligands, which are less able to match the electropositive lanthanide metals. Although the first lanthanide NHC complex was synthesized via a displacement of a coordinated THF by an NHC in 1994 (Figure 8.16), only a few structurally characterized lanthanide complexes with NHC had been reported up to 2003 [68].

Investigation of the binding of NHC to electropositive lanthanide metals provides the opportunity for the development of lanthanide NHC chemistry. Following the first lanthanide amide complexes to be stabilized by an amino-functionalized NHC and prepared through a transamination reaction (Figure 8.17) [69], a series of functionalized NHC ligands have been designed (Figure 8.18) and various lanthanide amide, alkyl, and halide complexes supported by anionic-functionalized NHCs have been synthesized by protonolysis reaction of lanthanide complexes with the corresponding imidazolium salt (Equation 8.17, Figure 8.19) [69–75].

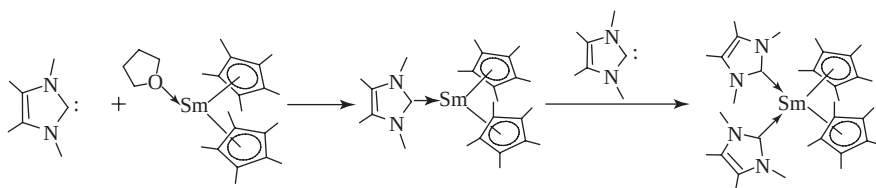


Figure 8.16 Synthesis of a samarium NHC complex from free NHC.

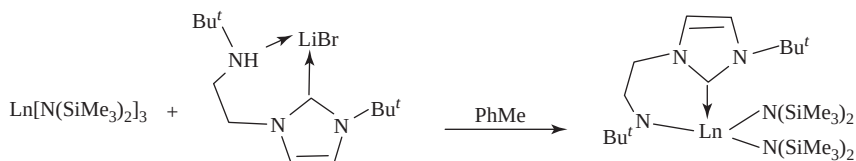


Figure 8.17 Synthesis of an amido functionalized NHC lanthanide complex.

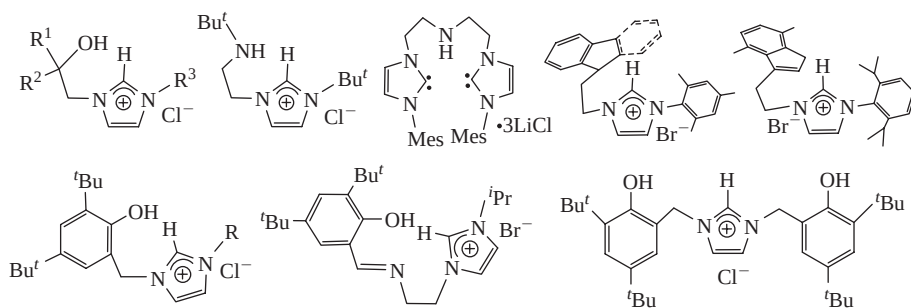


Figure 8.18 Representative functionalized NHC precursors.

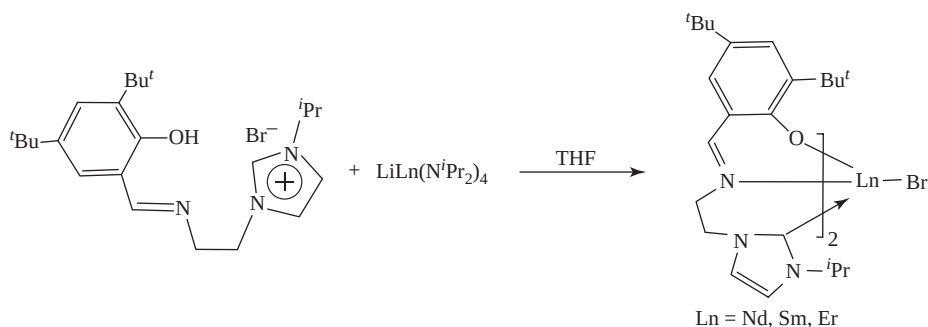
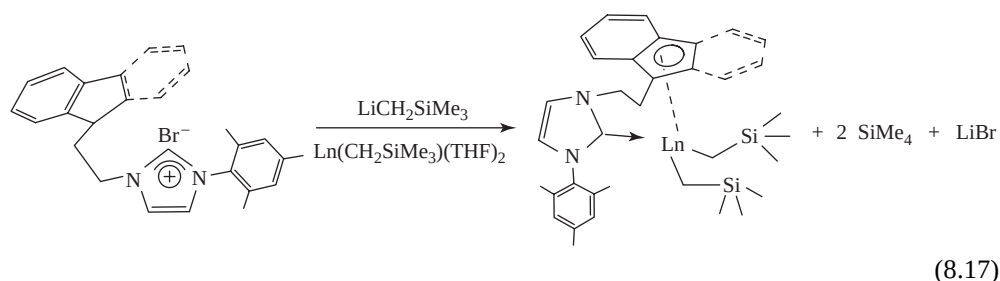
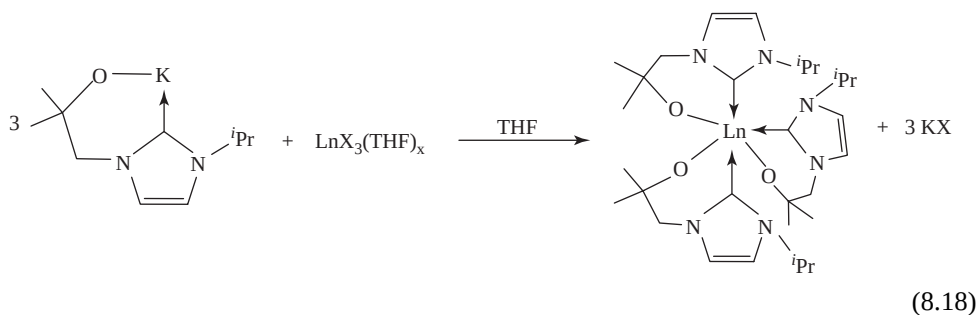


Figure 8.19 Synthesis of aryloxo functionalized NHC lanthanide bromides.

The metathesis reaction of anhydrous lanthanide halide with alkali metal alkoxo-functionalized NHC complex has recently proven to be another efficient and straightforward route to lanthanide NHC complexes (Equation 8.18) [69].



The amido-functionalized NHC yttrium bisamides have been found to react with potassium naphthalide leading to the lanthanide–potassium bimetallic complex formed via the regioselective C4 C–H activation/deprotonation (Figure 8.20). The lanthanide–potassium bimetallic complex can further react with a variety of electrophiles, for example, Me_3SiCl , to functionalize the backbone of the NHC ring. The regioselective C4 silylation can also be realized by treatment of an amido-functionalized NHC neodymium (cerium) amide complex with Me_3SiI in the solvent ether [69].

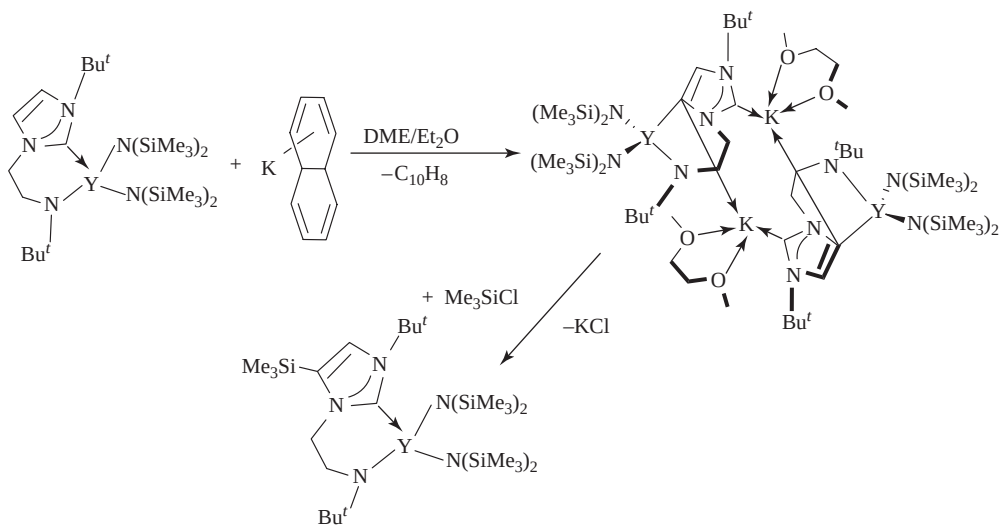
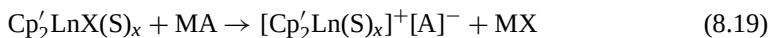


Figure 8.20 The regioselective C–H activation of amido-functionalized NHC yttrium amide.

8.2.4 Synthesis of Cationic Lanthanide Complexes

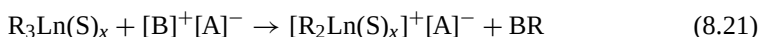
Cationic lanthanide complexes are relatively rare because of the large ionic radii and the highly electropositive nature of lanthanide metals, hence it is not easy to distribute the charge efficiently and stabilize the lanthanide cation through a suitable weakly coordinating anion [5, 76]. Several synthetic approaches have been developed and the main methods are summarized in the following sections.

8.2.4.1 Metathesis Reaction



The lanthanide halides are usually bi(cyclopentadienyl) and related lanthanide complexes; M is an alkali metal or silver, and A is an anionic transition metal carbonyl compound or tetraphenyl borate. The formation of the insoluble salt MX is a driving force for this reaction.

8.2.4.2 Alkyl Group Abstraction/Elimination Reaction



Organolanthanide complexes are those containing at least one alkyl group. LA represents a strong Lewis acid, such as triarylboranes BR_3 ($\text{R} = \text{Ph}$, C_6F_5), and trialkylaluminum AlR_3 . $[\text{B}]^+[\text{A}]^-$ is generally a borate, such as $[\text{Ph}_3\text{C}][\text{BPh}_4]$, $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{NR}_3\text{H}][\text{BPh}_4]$, and $[\text{NR}_3\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$.

8.2.4.3 Oxidation of Divalent Organolanthanide Complexes



The classical divalent organolanthanide complexes, mainly for Sm^{2+} and Yb^{2+} , have strong reducing potentials. They can reduce a series of transition metal carbonyls and AgBPh_4 to give the cationic lanthanide complexes.

The second approach is a popular route to cationic lanthanide alkyl complexes, which have proven to be the important intermediates for ethylene polymerization and the stereospecific polymerization of diene [5]. Various monocationic lanthanide monoalkyl complexes have been synthesized by the alkyl abstraction/elimination reaction of lanthanide dialkyl complexes. The reaction of a bisbenzyl scandium complex supported by β -diketiminate with $\text{B}(\text{C}_6\text{F}_5)_3$ affords the cationic complex with a “contact ion pair” structure, in which a weak bonding between the cation and the anion exists (Figure 8.21) [77]. The reaction of an amidinate

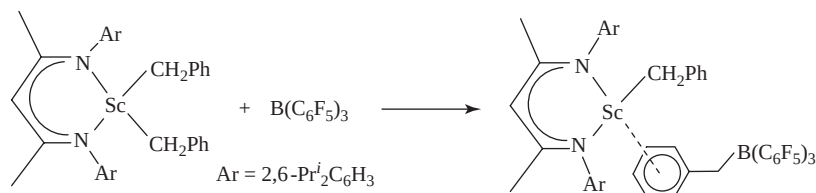
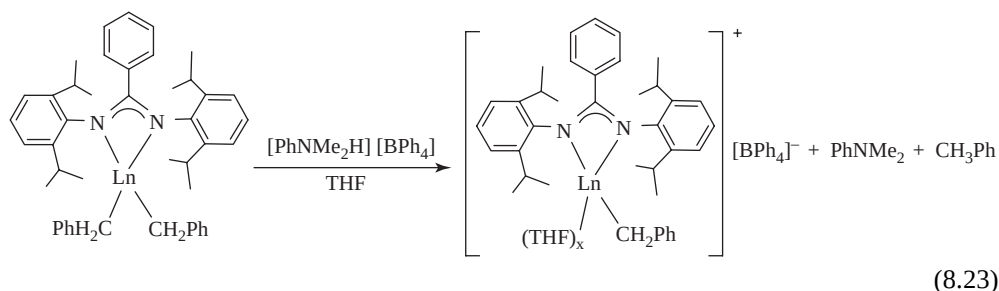


Figure 8.21 Synthesis of scandium cation with “contact ion pair” structure.

lanthanide bisbenzyl complex with $[\text{PhNMe}_2\text{H}][\text{BPh}_4]$ yields the cationic complex, it having a discrete ion pair structure (Equation 8.23) [22].



Using the trialkyl lanthanide complexes as starting materials, both monocationic and dicationic alkyl lanthanide complexes can be prepared. Reaction of $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ with one equivalent of $[\text{NEt}_3\text{H}][\text{BPh}_4]$ or $[\text{PhNMe}_2\text{H}][\text{BPh}_4]$ in THF gives the monocationic complex $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_x][\text{BPh}_4]$. The monocationic lanthanide alkyl complex can react further with one equivalent of $[\text{NEt}_3\text{H}][\text{BPh}_4]$ or $[\text{PhNMe}_2\text{H}][\text{BPh}_4]$ to generate the dicationic lanthanide alkyl complexes (Figure 8.22) [27]. The same reaction with triaryl lanthanide complexes $\text{Ln}(\text{C}_6\text{H}_4 - p\text{-R})_3(\text{THF})_2$ ($\text{R} = \text{H}, \text{Me}, \text{Et}$) gives mono- and dicationic lanthanide aryl complexes [35]. Furthermore, the mono- and di-cationic lanthanide methyl complexes can also be prepared by the reaction of the lanthanide tri(aluminate) $\text{Ln}[(\mu\text{-Me})_2\text{AlMe}_2]_3$ with one and two equivalents of $[\text{NEt}_3\text{H}][\text{BPh}_4]$ in THF, respectively; the structures of the cations are illustrated in Figures 8.23 and 8.24, respectively [78].

Cationic lanthanide complexes have been found to be efficient catalysts for various organic transformations and polymerizations. The details are given in Section 8.6.

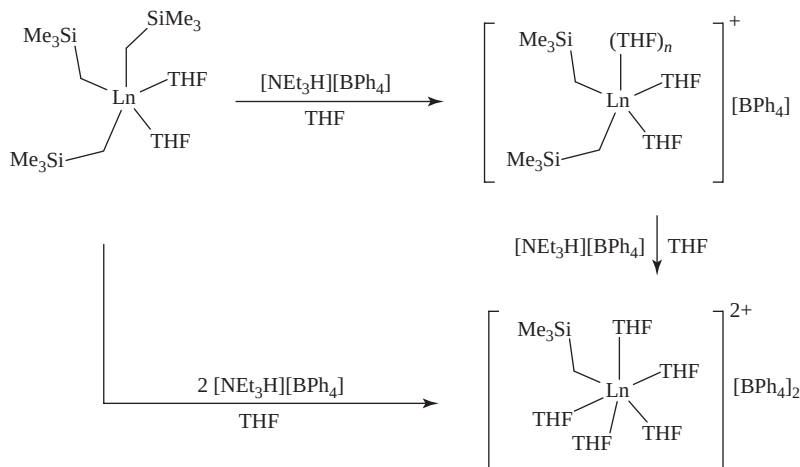


Figure 8.22 Synthesis of mono- and di-cationic lanthanide alkyl complexes.

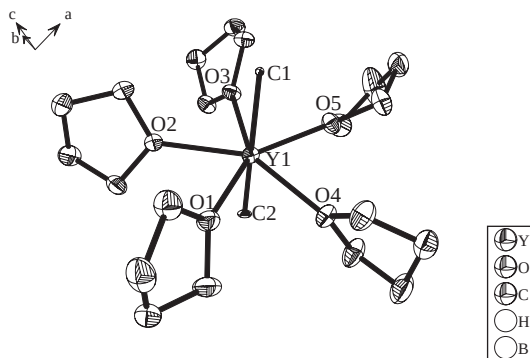


Figure 8.23 The structure of the cation $[\text{YMe}_2(\text{THF})_5]^+$ [78]. (Reproduced with permission from S. Arndt, *et al.*, “Cationic yttrium methyl complexes as functional models for polymerization catalysts of 1,3-dienes,” *Angewandte Chemie International Edition*, 2005, **44**, 7473–7477 (Figure 1). © Wiley-VCH Verlag GmbH & Co. KGaA.)

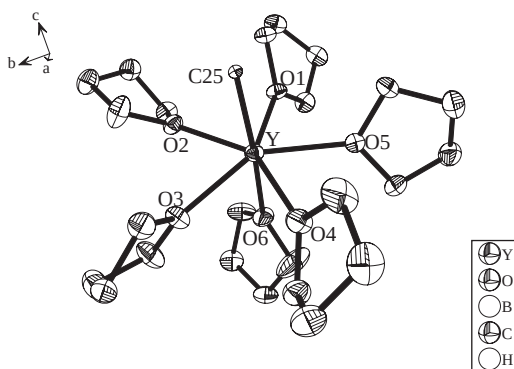


Figure 8.24 The structure of the dication $[\text{YMe}(\text{THF})_6]^{2+}$ [78]. (Reproduced with permission from S. Arndt, *et al.*, “Homogeneous Ethylene-Polymerization Catalysts Based on Alkyl Cations of the Rare-Earth Metals: Are Dicationic Mono(alkyl)Complexes the Active Species?,” *Angewandte Chemie International Edition*, 2003, **442**, 5075–5079 (Figure 2). © Wiley-VCH Verlag GmbH & Co. KGaA.)

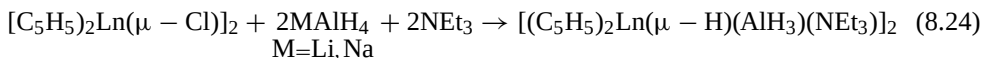
8.3 Synthesis and Reactivity of Lanthanide Hydride Complexes

8.3.1 Synthesis

Organolanthanide hydrides are intermediates for various homogeneous catalyses. There are basically four methods for generating organolanthanide hydride complexes: metathesis reactions, β -hydrogen elimination (controlled thermolysis of organolanthanide alkyl complexes), hydrogenolysis of organolanthanide alkyl or aryl complexes, and hydride transfer reactions.

8.3.1.1 Metathesis Reaction

A metathesis reaction is a convenient route to lanthanide tetrahydroaluminate and lanthanide tetrahydroborate complexes. Using tetrahydroaluminate complexes as the hydride source, a number of structurally characterized lanthanide tetrahydroaluminate complexes are prepared via metathesis reactions in the presence of an excess of a Lewis base (Equation 8.24) [79]. Metathesis reaction of organolanthanide chlorides with alkali metal tetrahydroborate generates the corresponding lanthanide tetrahydroborate. The same reaction with sodium hydride in THF is reported to afford a lanthanide hydride; however, no molecular structure for the hydride has been presented up till now.



8.3.1.2 β -Hydrogen Elimination

Lanthanide alkyls containing β -hydrogen atom(s) are unstable at and above room temperature. They decompose with increasing temperature to generate lanthanide hydride complexes. In general, anionic multimetallic lanthanide hydride clusters are isolated by this method. The first structurally characterized organolanthanide hydride complexes, the anionic trimetallic lanthanide hydride clusters, were prepared by β -hydrogen elimination of the *in situ* formed lanthanide *tert*-butyl complex as shown in Figure 8.25 [80].

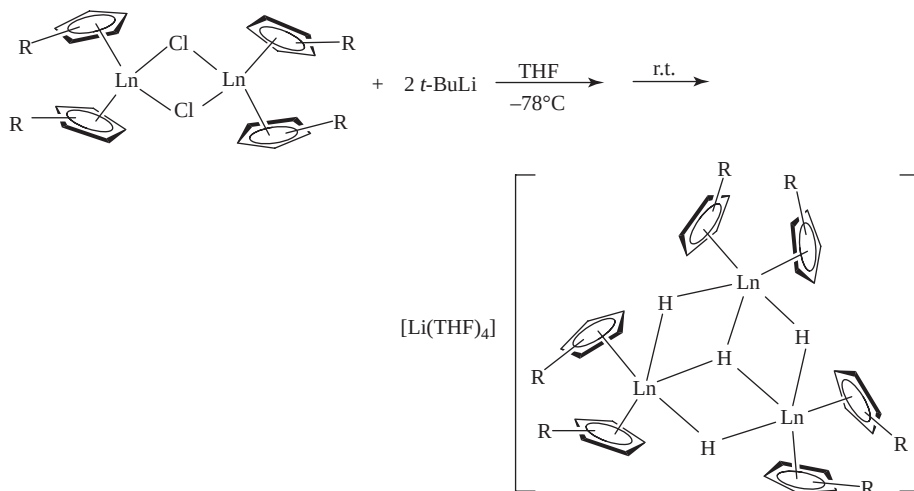


Figure 8.25 Synthesis of lanthanide hydride via β -hydrogen elimination.

8.3.1.3 Hydrogenolysis Reaction

Cleavage of Ln–C σ -bonds of lanthanide alkyls and aryls by a hydrogen molecule at ambient pressure and room temperature is a popular method for the synthesis of neutral lanthanide hydride complexes (Equation 8.25). The first structurally characterized neutral lanthanide hydrides were prepared by hydrogenolysis of bi(cyclopentadienyl) lanthanide alkyl

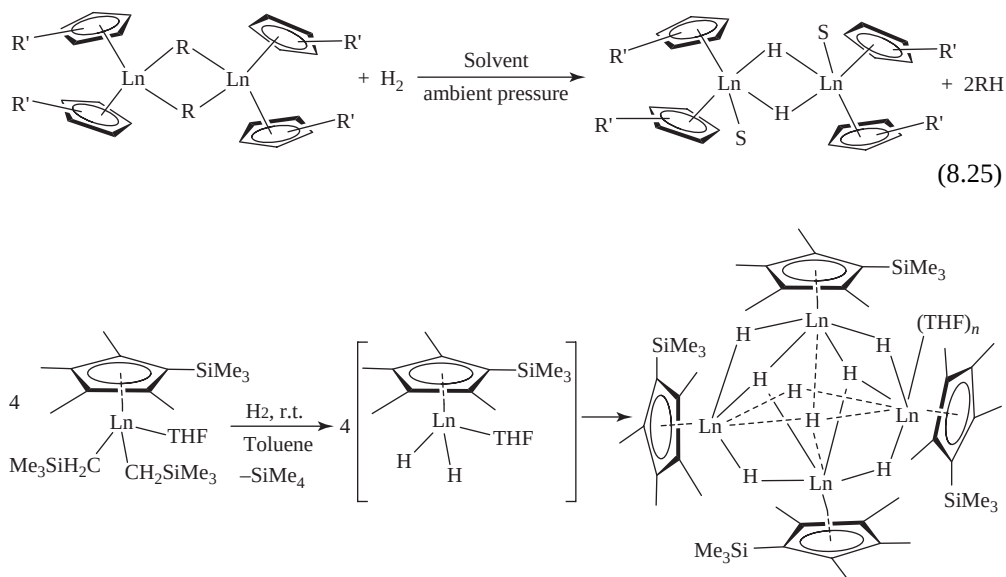


Figure 8.26 Synthesis of lanthanide dihydride clusters.

complexes [81]. Both the solvent and the steric bulkiness of the lanthanide complexes apparently have an effect on the reaction.

In contrast to numerous structurally characterized lanthanide monohydride complexes “ L_2LnH ” or “ $(L)(L')LnH$ ” (L and L' are monoanionic ancillary ligands), structurally characterized lanthanide dihydride complexes are elusive. Hydrogenolysis of substituted cyclopentadienyl lanthanide dialkyl complexes provides the lanthanide dihydride complexes “ $(C_5Me_4SiMe_3)LnH_2$ ” as intermediates, which convert into the novel tetranuclear lanthanide octahydride clusters as shown in Figure 8.26 [6]. These lanthanide polyhydride clusters react with borate affording the cationic lanthanide hydride complexes.

8.3.1.4 Hydride Transfer Reaction

Lanthanide alkyl and aryl complexes react with organoelement hydride compounds, such as hydrides of silicon, germanium, and tin, and so on, resulting in a hydride transfer to the lanthanide metal atom. Among the organoelement hydrides, organosilanes are the most popular source of the hydride.

Lanthanide monohydride complexes, such as bi(cyclopentadienyl)lanthanide hydrides, can be conveniently prepared by the reactions of lanthanide mono-alkyl or -aryl complexes with organosilanes under mild reaction conditions (Figure 8.27) [82].

$[{(C_5Me_5)SmCH(SiMe_3)_2[(C_5Me_5)K(THF)_2]}]_n$ with $PhSiH_3$ gives the unexpected trivalent lanthanide dihydride cluster $[{(C_5Me_5)Sm(\mu-H)_2}\{KH(THF)_2\}_3]_6$, which contains six “ $(C_5Me_5)Sm(\mu-H)_2$ ” units [83]. Direct reaction of lanthanide dialkyl complexes with silanes gives, in some instances, the mixed hydride-alkyl lanthanide clusters as shown in Figure 8.28 [84].

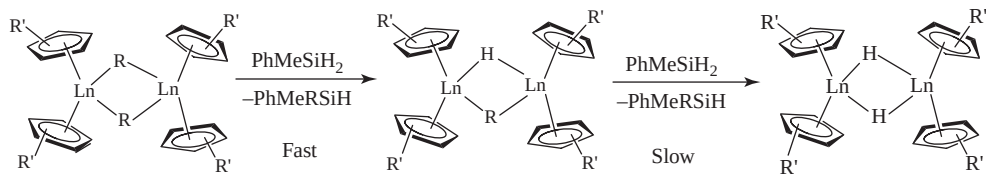


Figure 8.27 Synthesis of lanthanide hydride via hydride transfer reaction.

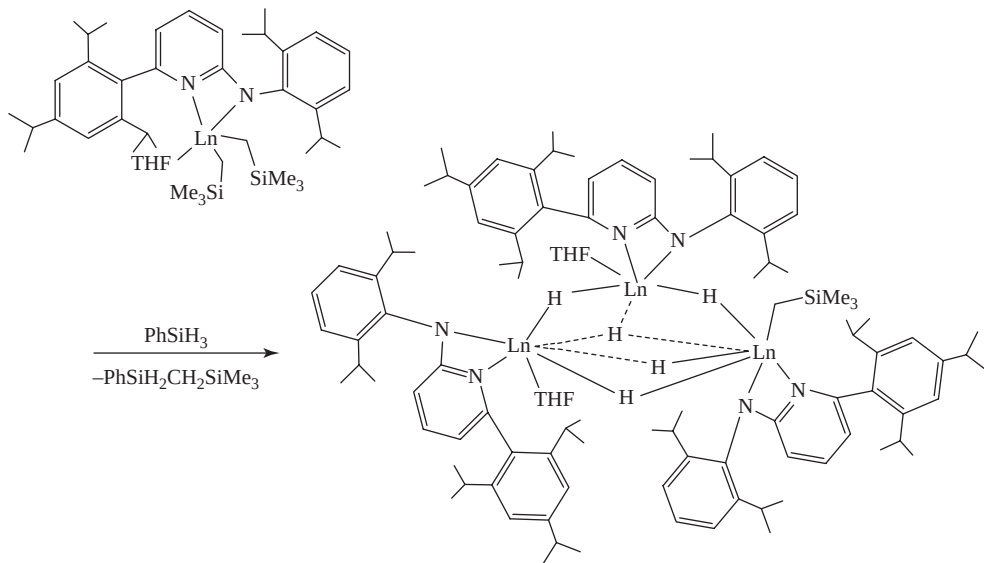
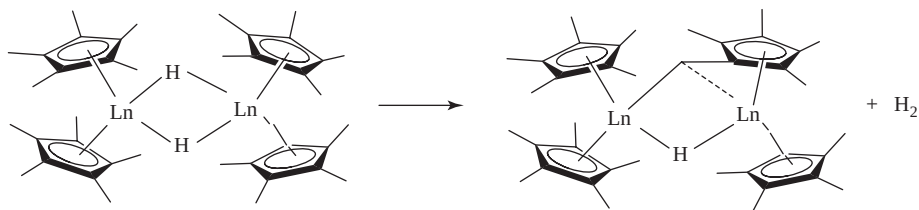


Figure 8.28 Formation of the mixed hydride-alkyl lanthanide complex.

8.3.2 Reactivity

Lanthanide hydride complexes are highly active species. They can activate unsaturated C–C, C–N, and even saturated C–H and C–O bonds.

Thermolysis of bi(pentamethylcyclopentadienyl) lanthanide hydride complexes in alkanes or benzene gives the internal metallation products $(\text{C}_5\text{Me}_5)_2\text{Ln}(\mu\text{-H})(\mu\text{-}\eta^1 : \eta^5\text{-CH}_2\text{C}_5\text{Me}_4)\text{Ln}(\text{C}_5\text{Me}_5)$ and releases H_2 via C–H activation of the methyl group of one pentamethylcyclopentadienyl group (Equation 8.26). When the reaction is conducted in toluene and other substituted arenes, the internal metalation products formed can undergo further C–H activation of solvent molecules to give bi(cyclopentadienyl) lanthanide aryl complexes [85,86].



(8.26)

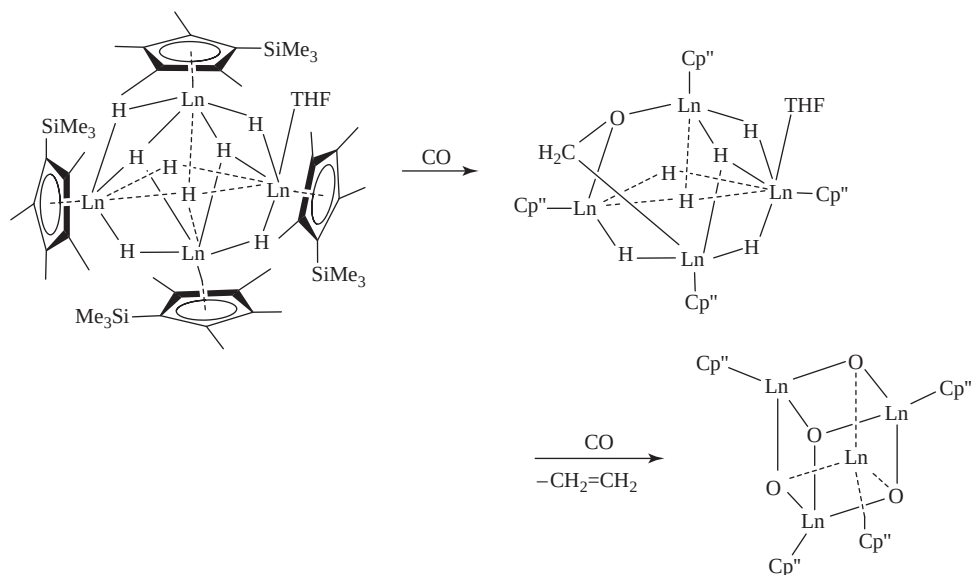


Figure 8.29 Reactivity of lanthanide dihydride with CO.

Lanthanide hydride complexes can cleave saturated C–O bonds. Unsolvated bi(cyclopentadienyl) lanthanide hydrides $[(C_5Me_5)_2Ln(\mu-H)]_2$ react instantaneously with diethyl ether to give the corresponding lanthanide alkoxides $(C_5Me_5)_2Ln(OEt)(Et_2O)$ and release an ethane. Complex $[(C_5Me_5)_2Ln(\mu-H)]_2$ dissolves in THF to give the solvated compounds first, and then decompose slowly to $(C_5Me_5)_2Ln(OBu)(THF)$ [85].

Lanthanide hydride complexes can also activate unsaturated C–O bonds. Trivalent cerium hydride Cp'_2CeH ($Cp' = 1,2,4-Bu'_3C_5H_2$) reacts with CO to form the *cis*-enediolate cerium complex $cis-(Cp'_2Ce)_2(\mu-OCH=CHO)$ in toluene, whereas it forms the oxomethylene cerium complex $Cp'_2Ce(OCH_2)CeCp'_2$ in pentane, and the latter can further react with H_2 to give Cp'_2CeOMe . Cp'_2CeOMe can also be prepared by the reaction of Cp_2CeH with a mixture of CO and H_2 [87]. Lanthanide polyhydride clusters react rapidly with CO at ambient pressure to give lanthanide tetraoxo clusters as the final products and release ethylene. The reaction is confirmed to undergo an enolate intermediate, as shown in Figure 8.29 [88]. In addition, lanthanide polyhydrides can also activate the C=O bond of γ -butyrolactone and CO_2 [6].

Reaction of tetranuclear lanthanide octahydrides with styrene provides lanthanide benzylic allyl heptahydride complexes through the insertion of a styrene molecule into one Ln–H bond. The lanthanide benzylic allyl complexes can be considered as the intermediates of styrene hydrogenation. Indeed, both the lanthanide octahydrides and the lanthanide benzylic allyl complexes can catalyze styrene hydrogenation efficiently in the presence of H_2 [89]. Lanthanide hydrides react with 1,3-cyclohexadiene to form lanthanide allylic complexes via 1,4-addition [90]. However, these lanthanide hydride clusters can not catalyze the polymerization of styrene and 1,4-cyclohexadiene.

Both bi(cyclopentadienyl) lanthanide hydrides and tetranuclear lanthanide octahydrides can react with nitriles, resulting in the reduction of the $C\equiv N$ triple bonds. However, the reducing

capabilities between these two types of lanthanide hydrides are different. The lanthanocene hydride complexes reduce the $C\equiv N$ triple bond of nitrile to a $C=N$ double bond via a single-insertion [91], whereas the lanthanide octahydrides can completely reduce the $C\equiv N$ triple bond to a $C-N$ single bond to form tetranuclear lanthanide imido complexes [89].

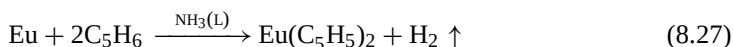
8.4 Synthesis and Reactivity of Divalent Lanthanide Complexes

8.4.1 Synthesis of Classical Divalent Lanthanide Complexes

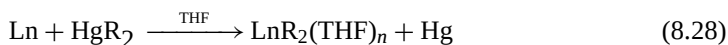
Divalent lanthanide chemistry has been dominated by the most readily accessible divalent lanthanide metals samarium(II), europium(II), and ytterbium(II) “(classical)” for decades, and a large number of divalent lanthanide compounds have been prepared [92]. There are three routes to generate divalent organolanthanide complexes: oxidative reaction of lanthanide metal, metathesis reaction of a divalent lanthanide halide, and reductive reaction of a trivalent lanthanide complex.

8.4.1.1 Oxidative Reaction of Lanthanide Metal

The first divalent organolanthanide complex is prepared by the redox reaction of europium with cyclopentadienyl in liquid ammonia (Equation 8.27) [93]. Ytterbocene can be prepared in an analogous manner.

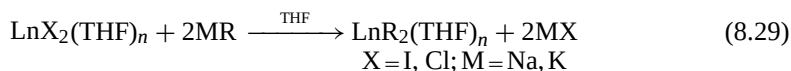


Transmetalation is a more convenient method to obtaining divalent organolanthanide complexes from lanthanide metals. Reaction of lanthanide metal powder with a mercury alkyl or aryl complex affords the corresponding divalent lanthanide complex (Equation 8.28) [94]. The preparation of divalent perfluorophenyl lanthanide complexes $\text{Ln}(\text{C}_6\text{F}_5)_2(\text{THF})_n$ ($\text{Ln} = \text{Eu}$, $n = 5$; $\text{Ln} = \text{Yb}$, $n = 4$) is a typical example. In most cases, the addition of a small amount of LnI_3 leads to acceleration of the reaction [95].



8.4.1.2 Metathesis Reaction of Divalent Lanthanide Halide

The exploration of $\text{LnI}_2(\text{THF})_x$, in particular, $\text{SmI}_2(\text{THF})_4$, which is prepared by the reaction of samarium metal with $\text{ICH}_2\text{CH}_2\text{I}$ in THF [96], or the reaction of iodine with an excess of samarium metal in THF, provides appropriate starting materials for divalent organometallic complexes (Equation 8.29).

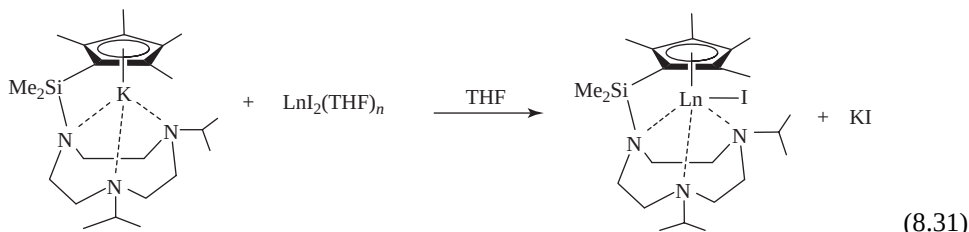


An alternative route to divalent lanthanide complexes is a metallation reaction: the acid–base reaction between a divalent organolanthanide complex with an acidic substrate

(Equation 8.30). Popular precursors are the readily accessible divalent bi(cyclopentadienyl) lanthanide complexes and $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ln}(\text{THF})_n$.

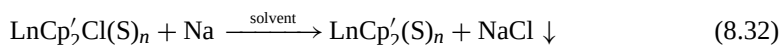


The divalent lanthanide monohalides, which are suitable precursors for mixed-ligand divalent lanthanide complexes, can also be synthesized via metathesis reaction. For example, the divalent samarium and ytterbium monohalides stabilized by a triazacyclononane-functionalized tetramethylcyclopentadienyl group have been prepared (Equation 8.31) [97].



8.4.1.3 Reductive Reaction of Trivalent Lanthanide Complexes

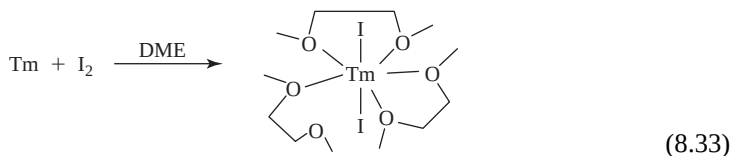
For most cases, a strong reductant, generally sodium metal, is required for reduction of trivalent organolanthanide complexes (Equation 8.32). However, a few examples have been reported where reactions of anhydrous LnCl_3 (especially for Eu and Yb) with organic alkali metal reagents, such as $\text{C}_5\text{Me}_5\text{Na}$ and sodium indenyl, generate the corresponding divalent organolanthanide complexes, and the organic alkali metal reagents are considered to be reductants [98].



In recent years, a series of divalent lanthanide heteroatom-functionalized indenyl complexes have been synthesized by the reaction of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ or $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}$ ($\text{Ln} = \text{Yb}, \text{Eu}$) with heteroatom-functionalized indene via so-called heteroatom coordination promoted homolysis of the $\text{Ln}\text{-N}$ bond as shown in Figure 8.30 [99, 100].

8.4.2 Synthesis of Non-classical Divalent Lanthanide Complexes

The first non-classical divalent lanthanide iodide $\text{TmI}_2(\text{DME})_3$ ($\text{DME} = \text{dimethoxyethane}$), which is prepared by the reaction of thulium metal with iodine under argon (Equation 8.33), was reported in 1997 [101]. Subsequently, $\text{DyI}_2(\text{DME})_3$ and $\text{NdI}_2(\text{THF})_5$ have been synthesized by an analogous manner. The success of the synthesis of non-classical divalent lanthanide iodides opens up a new area in divalent lanthanide chemistry [102, 103].



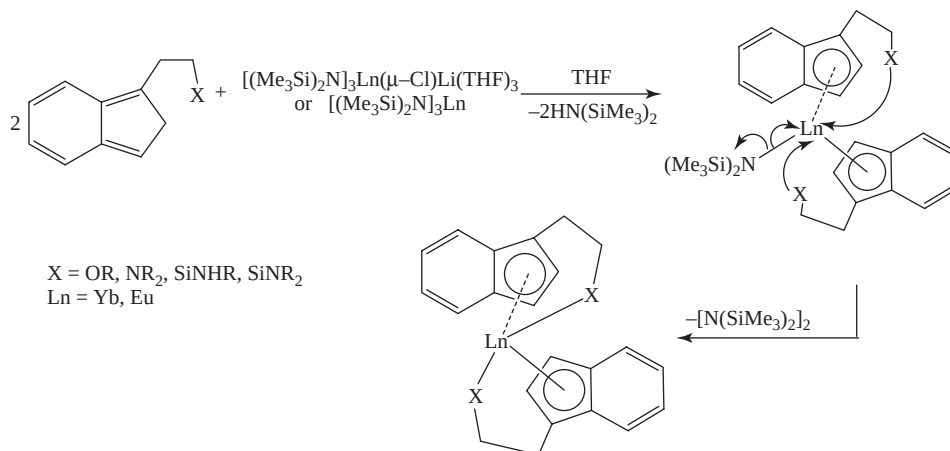
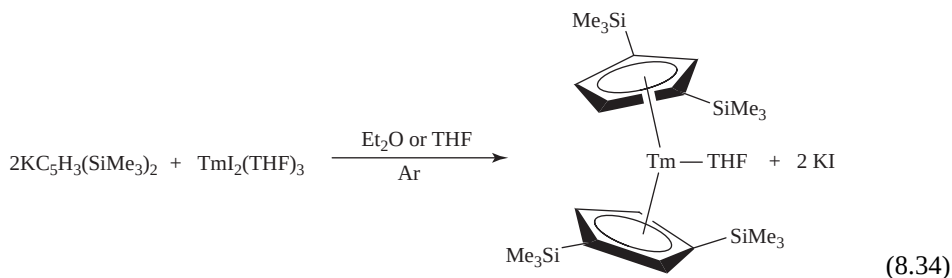


Figure 8.30 The proposed mechanism for the formation of the divalent lanthanide complexes.

$\text{TmI}_2(\text{DME})_3$, $\text{DyI}_2(\text{DME})_3$, and $\text{NdI}_2(\text{THF})_5$ have similar structures to those of the classical divalent lanthanide iodides. However, metathesis reaction with these iodides usually affords not a divalent complex but a trivalent lanthanide complex instead, because of their strong reductive ability [102]. To date, only one structurally characterized divalent organothulium complex has been synthesized by metathesis reaction (Equation 8.34) [104].



Reduction of a trivalent organolanthanide complex by potassium in the presence of a neutral multidentate ligand has been found to be a successful method for synthesis of non-classical divalent organolanthanide complexes [105]. Reaction of $(1,3\text{-Bu}_2^t\text{C}_5\text{H}_3)_3\text{La}$ with K in benzene in the presence of [18]crown-6 provided the first structurally characterized divalent lanthanum complex $[\text{K}(\text{[18]crown-6})(\eta^2\text{-C}_6\text{H}_6)_2][\{\text{La}(1,3\text{-Bu}_2^t\text{C}_5\text{H}_3)_2\}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_6)]$ (Figure 8.31) [106]. Similar reactions of $[1,3\text{-(Me}_3\text{Si)}_2\text{C}_5\text{H}_3]_3\text{La}$ and $[1,3\text{-(Me}_3\text{Si)}_2\text{C}_5\text{H}_3]_3\text{Ce}$ with K in the presence of crown ether or [2,2,2]crypt ([2,2,2]crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo [8,8,8]hexacosane) provided the corresponding anionic divalent complexes [107].

Reduction of trivalent bi(tri-*tert*-butylcyclopentadienyl)dysprosium complexes $(1,2,4\text{-Bu}_3^t\text{C}_5\text{H}_2)_2\text{DyX}$ ($X = \text{I}, \text{Br}, \text{BH}_4$) [108] and neodymium iodide $(1,2,4\text{-Bu}_3^t\text{C}_5\text{H}_2)_2\text{NdI}$ [109], respectively, with potassium-graphite in the presence of crown ether [18]crown-6 generated the anionic divalent organo-dysprosium and -neodymium complexes. Structural determination

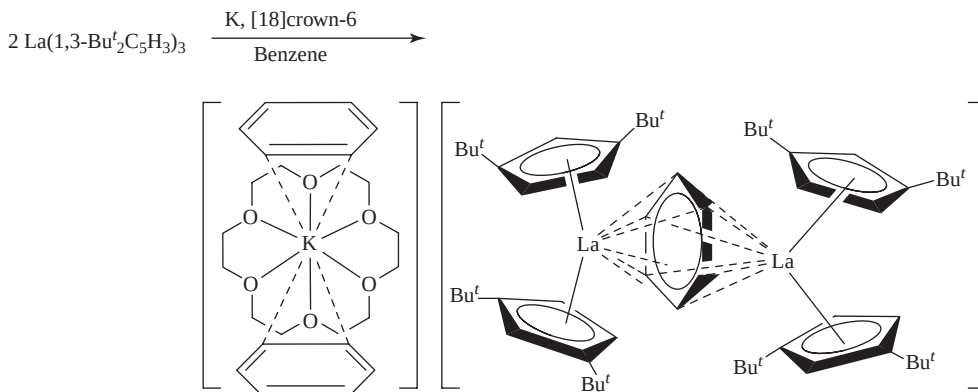


Figure 8.31 Synthesis of a divalent organolanthanum complex.

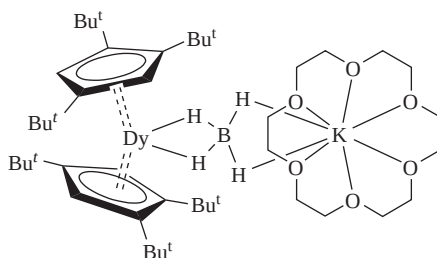


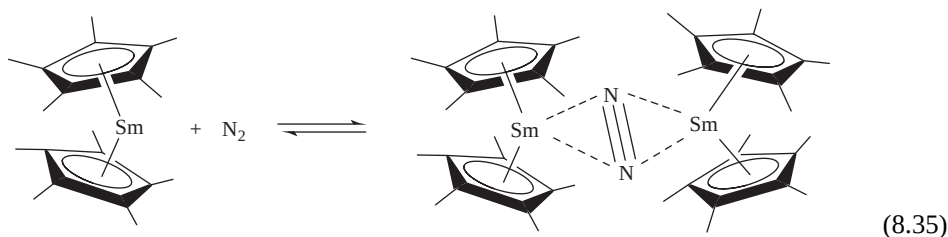
Figure 8.32 The structure of $(1,2,4\text{-Bu}_3\text{C}_5\text{H}_2)\text{Dy}(\mu\text{-BH}_4)\text{K}([18]\text{crown-6})$ [108]. (Adapted from F. Jaroschik, *et al.*, “Isolation of stable organodysprosium(11) complexes by chemical reduction of dysprosium (β) precursors,” *Organometallics*, **26**, 1123–1125 (Figure 2), 2007).

revealed that the lanthanide and potassium metals in these complexes are connected by the X group, and the molecular structure of dysprosium complex is shown in Figure 8.32 as an example.

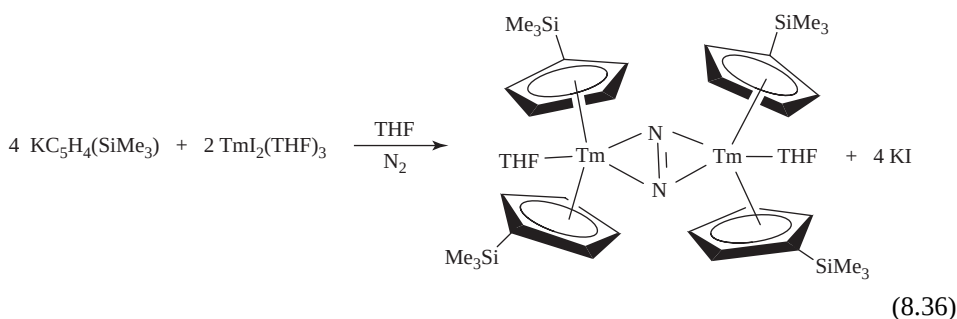
8.4.3 Reductive Reactivity

The reduction potentials of Ln(III)/Ln(II) range from -0.35 V (Eu) to -2.6 V (Nd). Therefore all of the divalent organolanthanide complexes, except for Eu(II) , have a strong reducing ability, and can be used as one-electron reducing agents.

$\text{Bi(pentamethylcyclopentadienyl)samarocene}$ (C_5Me_5) $_2\text{Sm}$ reacted with dinitrogen to generate the first dinitrogen complex of a lanthanide metal, and this is also the first example of the coplanar coordination of two metals to dinitrogen (Equation 8.35). This reaction is reversible, and the dinitrogen is not strongly activated in this complex because the $\text{N}\equiv\text{N}$ triple bond is not significantly elongated in comparison with that for free dinitrogen [110]. A divalent tetranuclear samarium cluster stabilized by dipyrroliide ligands can completely reduce dinitrogen via a four-electron reduction reaction [111].



The non-classical divalent lanthanide complexes have stronger reducing power than divalent samarium complexes because of their higher reduction potentials. Dinitrogen is not an inert atmosphere for these non-classical divalent lanthanide complexes. Therefore, attempts to prepare non-classical divalent organolanthanide complexes by metathesis reactions in dinitrogen atmosphere have been unsuccessful, and the dinitrogen-activated products were isolated. A typical example is shown in Equation 8.36 [112].



Because the 5d orbitals of lanthanide metals are shielded by 4f orbitals, the lanthanide metals cannot effectively back-bond like the transition metals, and the alkynes and the CO are expected to have no significant chemistry with organolanthanide complexes. However, the divalent samarium complex $(C_5Me_5)_2Sm(THF)_2$ can reduce diphenyl ethyne, and subsequently activate CO to generate a tetracyclic compound, as shown in Figure 8.33 [113].

A number of unsaturated substances, such as ketone, azobenzene, imine, α -diimine, carbodiimide, nitrile, CO_2 , and so on can be reduced by divalent samarium complexes. For example, reaction of bi(methylcyclopentadienyl) samarium complex with carbodiimide generates, via reducing-coupling reaction, the first structurally characterized bimetallic oxalamidino complex (Figure 8.34) [114].

It is worth noting that the sterically crowded tris(pentamethylcyclopentadienyl) lanthanide complexes $(C_5Me_5)_3Ln$ have similar reductive reactivity to the divalent samarium complex. This phenomenon has been termed sterically induced reduction (Section 8.2.1.2).

8.5 Organometallic Ce(IV) Complexes

Cerium is the only lanthanide metal with a readily accessible tetravalent oxidation state. Synthesis and molecular structure determination of organometallic Ce(IV) complexes are of interest and a challenge, because the Ce(IV) ion is strongly oxidizing and the anionic ligands typically

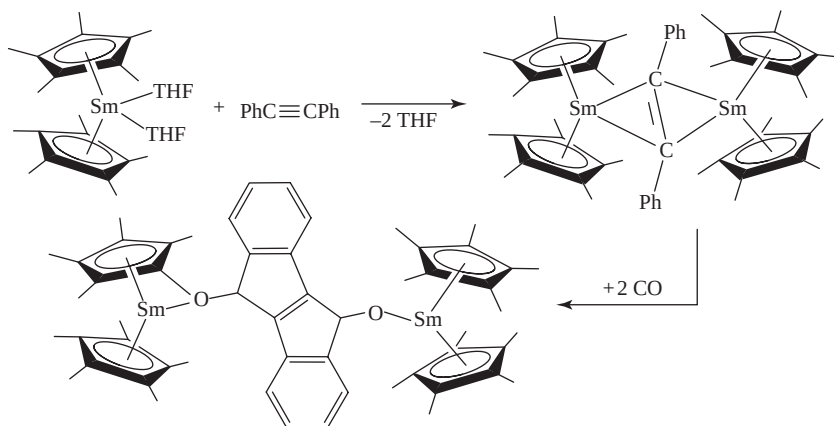


Figure 8.33 Reactivity of divalent samarium complex with diphenyl ethyne and CO.

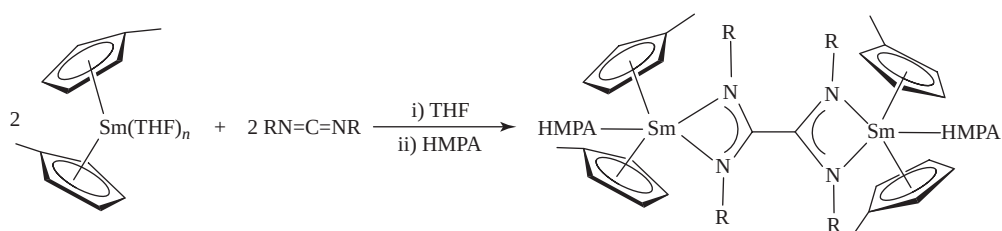


Figure 8.34 The synthesis of a bimetallic oxalamindino complex.

found in organolanthanide chemistry (such as C_5H_5^- , $\text{C}_8\text{H}_8^{2-}$, and R^-) are strongly reducing. To date, only a few structurally characterized organometallic cerium(IV) complexes have been reported.

The synthesis and preliminary X-ray structure of the first organometallic Ce(IV) complex $\text{Ce}(\text{C}_8\text{H}_8)_2$ was reported in 1976 [115] and reproduced in 1985 [116] by the reaction of cerium(IV) isopropoxide with triethylaluminum in the presence of cyclooctatetraene, as shown in Figure 8.35. The accurate sandwich molecule structure of cerocene has been confirmed by an X-ray structural study on the methyl substituted cerocene $[\text{Ce}(\text{MeCOT})_2]$ [117]. Subsequently, two more substituted cerocene analogs have been synthesized via a more efficient method, for example, controlled oxidation of cerium(III) precursors and one of these complexes has been structurally characterized [118].

$\text{Cp}_3\text{Ce}(\text{O}^i\text{Pr})$ is the first reported organometallic Ce(IV) complex to be stabilized by a cyclopentadienyl ligand [115]. The complex can be prepared in desired yields by the reaction of $\text{Ce}(\text{O}^i\text{Pr})_4$ with R_3SnCp [119, 120]. Using $\text{Ce}(\text{O}Bu^t)(\text{NO}_3)_2(\text{THF})_2$ as a reagent, the metathesis reaction with NaCp affords $\text{Cp}_2\text{Ce}(\text{O}Bu^t)_2$ and a mixture of $\text{Cp}_2\text{Ce}(\text{O}Bu^t)_2$ and $\text{Cp}_3\text{Ce}(\text{O}Bu^t)$ depending on the amount of NaCp used. The molecular structure determination

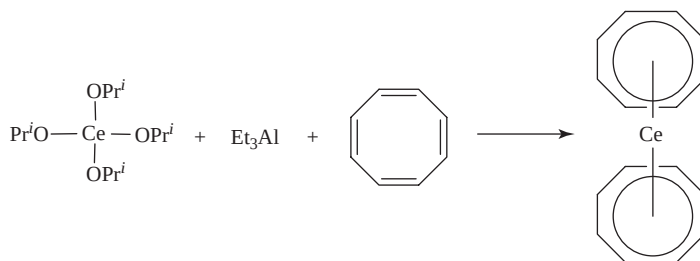


Figure 8.35 The synthesis of $\text{Ce}(\text{C}_8\text{H}_8)_2$.

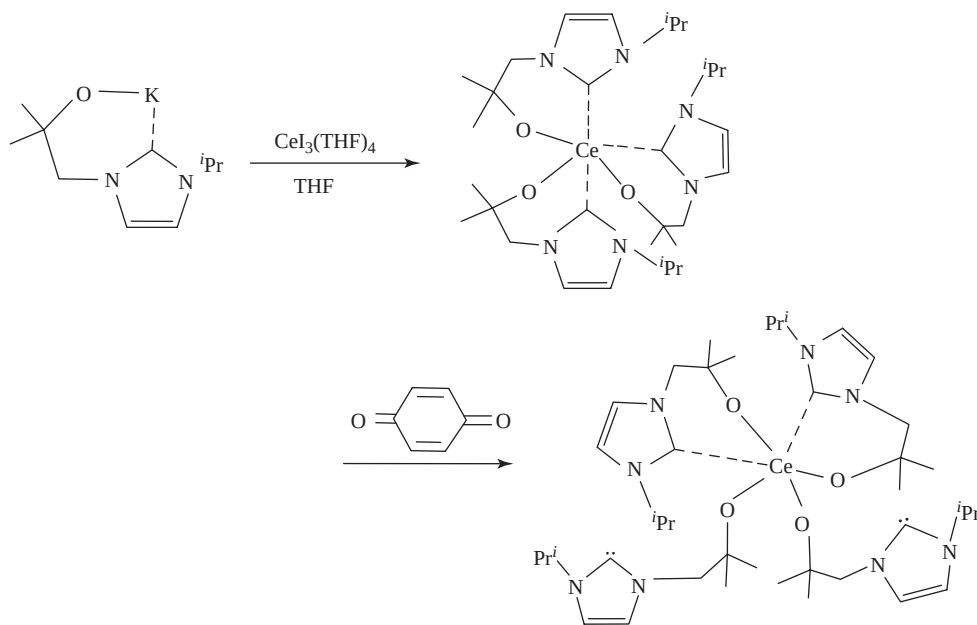


Figure 8.36 The synthesis of a Ce(IV) complex stabilized by functionalized NHC ligands.

for $\text{Cp}_3\text{Ce}(\text{O}^t\text{Bu})$ revealed that the three Cp ring centroids and the alkoxide oxygen atom roughly define a tetrahedron around the cerium metal [121].

The Ce(IV) complexes stabilized by substituted pentalene are synthesized and structurally characterized by similar controlled oxidation reactions of organocerium(III) precursors, where the pentalene moiety is appreciably nonplanar [122].

The first Ce(IV) complex stabilized by an alkoxo functionalized *N*-heterocyclic carbene anion has recently been reported. The complex is made by oxidation of the corresponding trivalent cerium complex using benzoquinone (Figure 8.36). The cerium cation is coordinated by two bidentate ligands and two monodentate ligands, in which the NHC groups are unbound [123].

8.6 Application in Homogeneous Catalysis

8.6.1 Organic Transformation

8.6.1.1 Hydroamination/Cyclization

Intramolecular hydroamination/cyclization, the addition of an N–H bond across an intramolecular carbon–carbon unsaturated bond, offers an efficient, atom economical route to nitrogen-containing heterocyclic molecules (Equation 8.37). Numerous organolanthanide complexes were found to be efficient catalysts for this transformation [124, 125]. The real active intermediates are organolanthanide amides, which are formed by the rapid protonolysis reactions of precatalysts with amine substrates. The proposed catalytic cycle of hydroamination/cyclization of aminoalkenes is presented in Figure 8.37 [124].

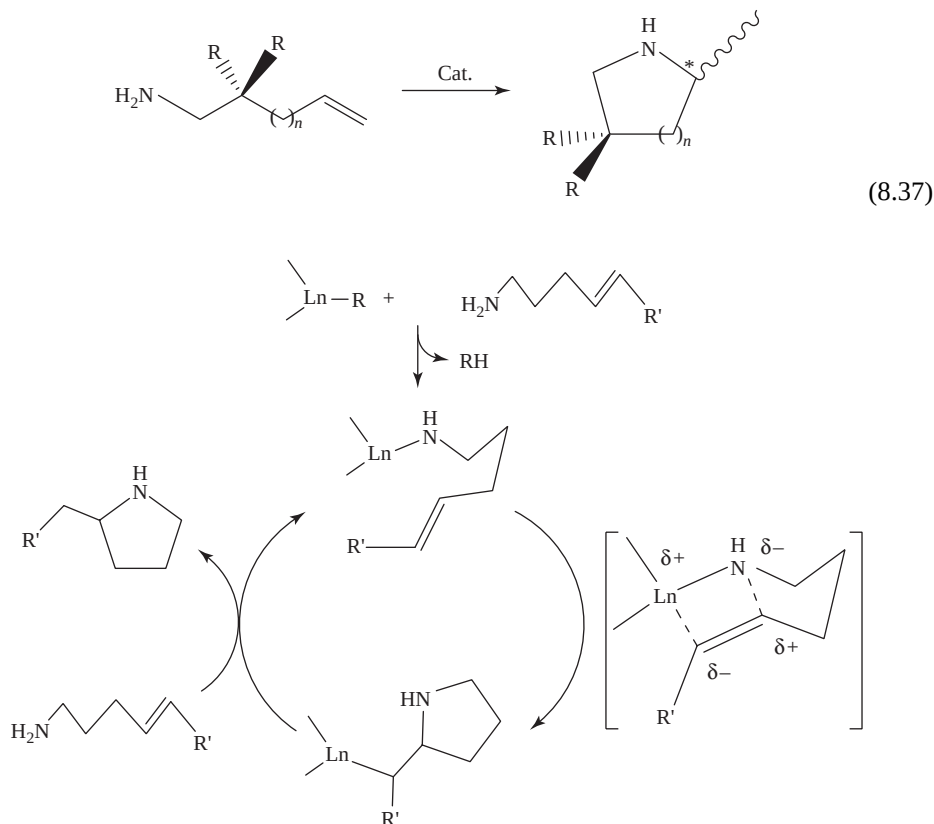


Figure 8.37 The proposed catalytic cycle of hydroamination/cyclization of aminoalkene.

The carbon–carbon unsaturated substrates have now expanded from aminoalkenes to aminoalkynes, aminoallenes, and aminodienes, and the hydroamination/cyclization reactions of these substrates have produced functionalized nitrogen-containing heterocycles. It is worth noting that the aminoallene hydroamination/cyclization reactions are highly diastereoselective, and can provide concise routes to the synthesis of some natural products (Figure 8.38) [126].

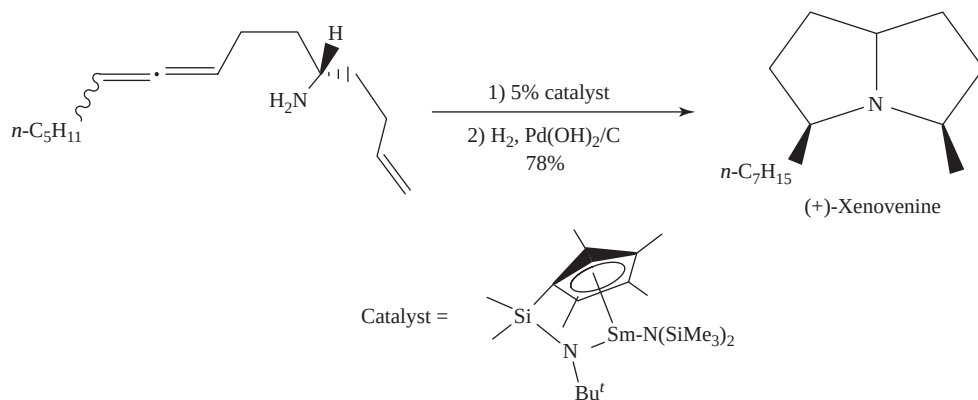


Figure 8.38 The synthesis of (+)-xenovenine.

Using chiral organolanthanide complexes as the catalysts, enantioselective hydroamination/cyclization reactions can be achieved [127, 128], which provide a convenient route for the synthesis of chiral amines from simple, readily available prochiral substrates in a single step. The ionic radii of lanthanide metals have a profound effect on the reaction. Lanthanides having the largest ionic radii exhibit the greatest turnover frequencies and enantioselectivities [129].

Other catalytic hydroelementation/cyclization reactions, the E–H (E = P, O) addition to C–C multiple bonds, are also efficiently mediated by organolanthanide complexes [130, 131]. Many are highly diastereoselective. Hydrophosphination/cyclization and hydroalkoxylation/cyclization appear to follow a catalytic pathway similar to hydroamination/cyclization. The active intermediates are Ln–phosphido or Ln–alkoxo species, which are generated from protonolysis of the precatalysts with the corresponding substrates.

8.6.1.2 Alkyne Dimerization

Organolanthanide complexes can catalyze the dimerization reaction of terminal alkynes, which is an atom economical and straightforward method for the synthesis of conjugated enynes [132]. However, in most cases a mixture of regio- and stereoisomers is obtained, as shown in Figure 8.39. “Geometry constrained” cyclopentadienyl lanthanide alkyl complexes were the first organolanthanide catalysts for highly regio- and stereoselective head-to-head (*Z*)-dimerization of terminal alkynes, which yielded solely the (*Z*)-enynes for aromatic alkynes. In addition, this catalyst system is recoverable and reusable [133]. Subsequently, cationic lanthanide alkyls were reported to also catalyze the linear head-to-head dimerization of a range

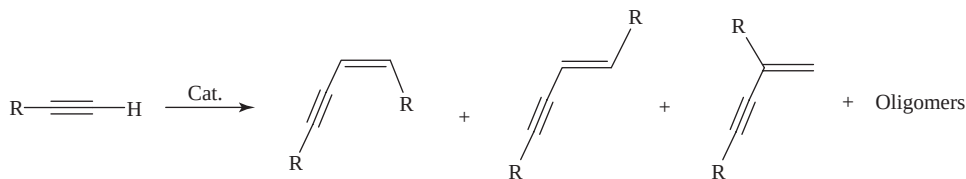
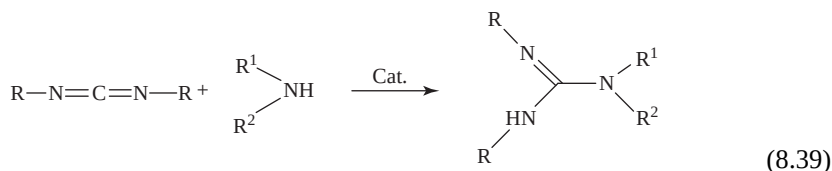
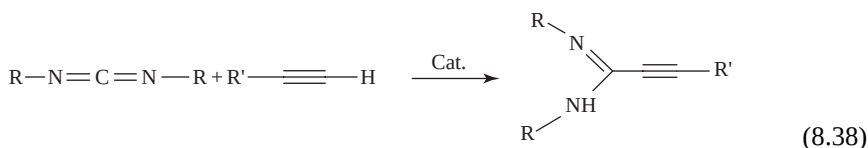


Figure 8.39 The dimerization of terminal alkyne.

of (hetero)aromatic alkynes to (*Z*)-enynes with 100% selectivity and high rates [134, 135]. In contrast, neutral lanthanocene alkyl complexes catalyze the dimerization of terminal alkynes to provide predominately the linear enynes dimer with a *trans*-configuration around the enyne double bond [132]. The real catalyst for this dimerization is a dinuclear organolanthanide bis(μ -alkynyl) species, which is structurally characterized in a cyclopentadienyl-amide lanthanide alkyl system [133].

8.6.1.3 Addition of Carbodiimide to Alkyne and Amine

Catalytic addition of carbodiimides to terminal alkyne C–H bonds and amine N–H bonds provides a straightforward and efficient method for the synthesis of propiolamidines and substituted guanidines, respectively (Equations 8.38 and 8.39), which are widely used as ancillary ligands for stabilization of various metal complexes.



Half-sandwich lanthanide alkyl complexes and, subsequently organolanthanide amides were found to be highly efficient catalysts for the cross-coupling reactions of carbodiimides with alkynes and amines, respectively [136, 137]. Although the half-sandwich lanthanide alkyl complexes can also catalyze the dimerization of alkynes, no homodimerization product is observed in the reaction of alkynes with carbodiimides. These reactions offer a wide scope for the substrates of terminal alkynes and amines, respectively [138].

The proposed mechanism for the addition of terminal alkynes and amines to carbodiimides is shown in Figure 8.40. The organolanthanide alkynyl or amide formed *in situ* is the active intermediate, and the key step is the hydrolysis of a lanthanide amidinate or guanidinate species.

8.6.2 Polymerization

8.6.2.1 Polymerization of Olefins and Dienes

Many neutral trivalent organolanthanide alkyl and hydride complexes can serve as single component homogeneous catalysts for the polymerization of ethylene, which can be used as a model for the mechanistic study of the Ziegler–Natta polymerization of ethylene [139, 140]. The polymerization undergoes a coordination–insertion mechanism (Figure 8.41). Generally, a lanthanide hydride complex is much more active than the corresponding alkyl complex. However, most of these organolanthanide catalysts show low to moderate activity, except for the dimeric bi(pentamethylcyclopentadienyl) lanthanide hydrides, which show very high activity

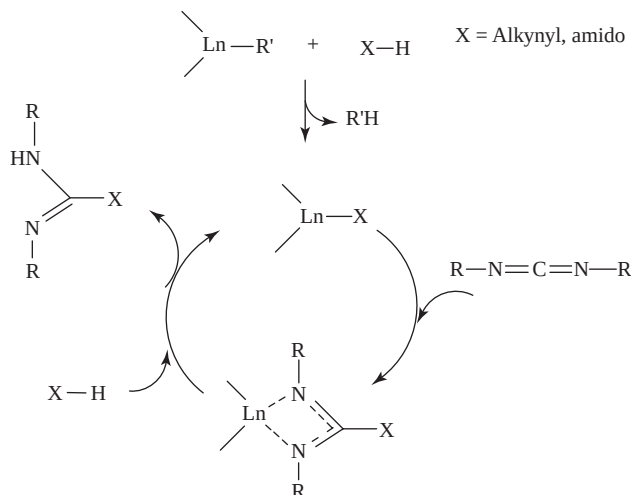


Figure 8.40 The proposed mechanism for the addition of alkyne and amine to carbodiimide.

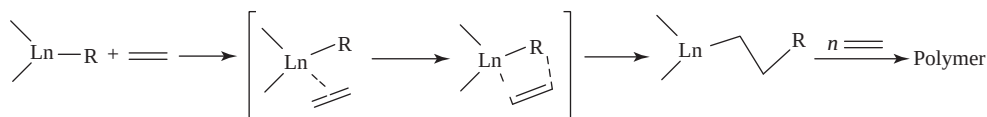


Figure 8.41 The polymerization mechanism of ethylene catalyzed by organolanthanide alkyl.

with the polymerization, to yield high molecular weight polyethylene [141]. The catalytic activity depends on the radius of the lanthanide metal and the structure of the ancillary ligand. The polymerization activity increases with the ionic radius. The *ansa*-lanthanocene complexes and “geometry constrained” half-sandwich lanthanide complexes show higher catalytic activity than the corresponding unlinked bi(cyclopentadienyl) lanthanide compounds because the former complexes provide a more open ligand sphere for the metal center. A complex with a large metal is more active relative to one with a small metal [142].

Divalent samarium complexes can also catalyze ethylene polymerization, initially through one-electron transfer from the Sm(II) species to an ethylene molecule to form a Sm(III)–carbon bond, which is the active intermediate that induces ethylene polymerization. The less reducing divalent organometallic ytterbium and europium complexes are generally inert [143].

In recent years, a large number of mono- and dicationic lanthanide alkyl complexes have been found to be efficient catalysts for ethylene polymerization, and in some cases, the dicationic lanthanide derivatives show higher activity and selectivity than their monocationic counterparts. Ionic radii of lanthanide metals also affect the catalytic behavior, and polymerization activity often increases with ionic radius [5, 76].

Organolanthanide complexes can catalyze not only the homopolymerization of ethylene, but also the copolymerization of ethylene with some nonpolar and polar monomers [139, 140]. A series of neutral, anionic, and cationic organolanthanide complexes catalyze the copolymerization of ethylene with styrene, α -olefins, methylenecyclopropane, norbornene,

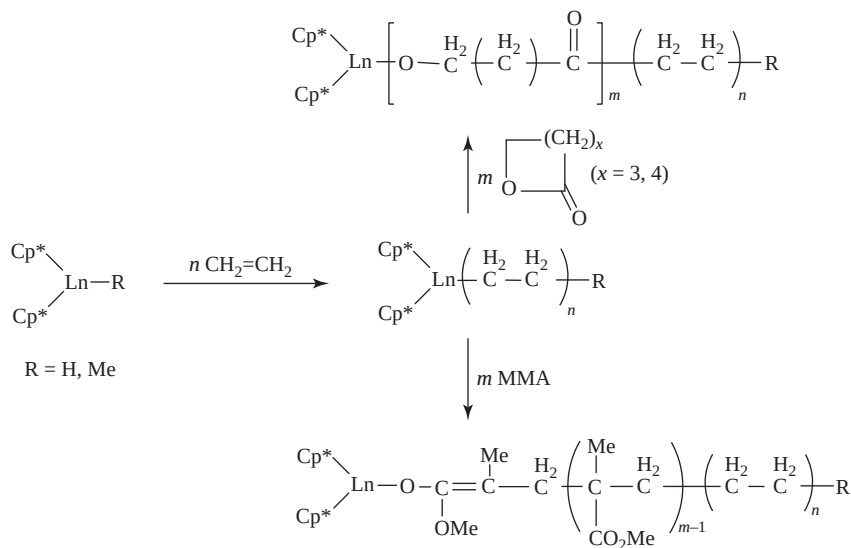


Figure 8.42 The copolymerization of ethylene with MMA or lactone.

and dicyclopentadiene. Furthermore, cationic half-sandwich lanthanide alkyl complexes can catalyze the selective copolymerization of styrene with ethylene to give a polymer with syndiotactic styrene–styrene sequences connected by repeating ethylene units [144]. Bi(pentamethylcyclopentadienyl) lanthanide hydride and methyl complexes, in addition to divalent samarocene, catalyze the copolymerization of ethylene or α -olefins with methyl methacrylate (MMA) or acrylates or cyclic esters by sequential monomer addition, as shown in Figure 8.42 [145, 146]. The reverse monomer addition, that is, a polar monomer followed by a nonpolar monomer, does not give the copolymers.

The styrene polymerization catalyzed by an organolanthanide complex is much more difficult than ethylene polymerization because of steric hindrance [147]. Some lanthanocene methyl complexes, half-sandwich lanthanide alkyls, anionic guanidinate lanthanide methyl complexes, and anionic divalent mixed-ligand samarium complexes can initiate styrene polymerization in moderate to high activity at high temperature, affording atactic polystyrenes. Recently, it has been reported that the bridged cyclopentadienyl-fluorenyl ($\text{Cp-CMe}_2\text{-Flu}$) allyl complexes and cationic half-sandwich lanthanide alkyl complexes catalyze the highly syndiospecific polymerization of styrene (Figure 8.43) [144, 148], whereas the single component bridged bi(indenyl) allyl lanthanide complexes catalyze the highly isospecific polymerization of styrene [149].

Generally, single component neutral organolanthanide complexes are inactive for the polymerization of conjugated dienes. However, in the presence of a co-catalyst, such as aluminum alkyls, MMAO (modified methylaluminoxane), and organic borate, these organolanthanide complexes can serve as excellent catalysts for regio- and/or stereoselective polymerization of conjugated dienes as presented in Figure 8.44 [150]. The real active species in these catalytic systems should be a cationic alkyl species.

In the presence of an activator, organolanthanide complexes stabilized by cyclopentadienyl, aluminate, carboxylate, bis(phosphinophenyl)amido, and aryldiimine NCN-pincer ligands and

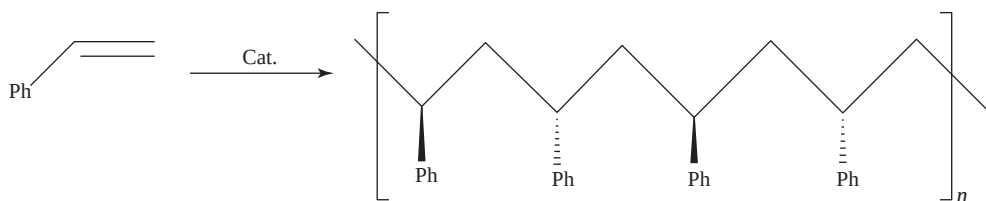


Figure 8.43 Syndiospecific polymerization of styrene.

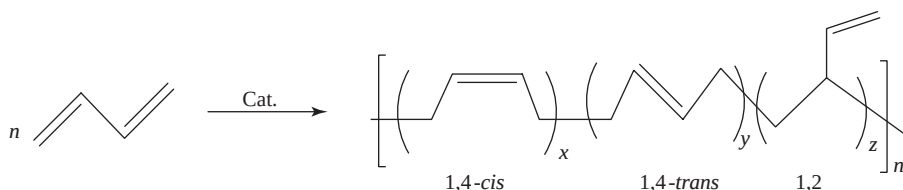


Figure 8.44 Stereoselective polymerization of butadiene.

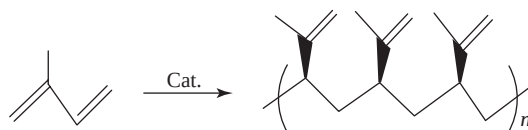


Figure 8.45 Isospecific 3,4-selective polymerization of isoprene.

cationic lanthanide methyl complexes, can catalyze controllable, or even living polymerization of butadiene with a *cis*-1,4 selectivity within 97–99% or as high as 99.9% at low temperatures [78, 151, 152]. However, the lanthanide dialkyl complexes bearing a thiophene-NPN ligand in combination with alkyl aluminum or borate, as well as some organolanthanide complexes in combination with dialkylmagnesium, can catalyze the highly *trans*-selective polymerization of butadiene [46].

The above organolanthanide catalyst systems can also catalyze the highly selective polymerization of isoprene. Most of these catalyst systems give high *cis*-1,4 selective polyisoprene. Whereas, $\text{Ln}(\text{allyl})_2\text{Cl}(\text{MgCl}_2)_2/\text{AlR}_3$, $(\text{C}_5\text{Me}_5)\text{Ln}(\text{BH}_4)_2(\text{THF})/\text{Mg}(n\text{-Bu})_2$, and $(\text{C}_5\text{Me}_5)\text{Ln}(\text{AlMe}_4)_2/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Al}(i\text{-Bu})_3$ catalyze the *trans*-selective polymerization of isoprene [153]. Recently, highly 3,4-selective polymerization of isoprene to produce isospecific polyisoprene has also been achieved (Figure 8.45) by half-sandwich lanthanide alkyls or amidinate lanthanide alkyls combined with organic borates [45, 52]. The most attractive feature of the latter system is that the regio- and stereoselectivity for isoprene polymerization can be switched conveniently. Addition of AlMe_3 to the amidinate lanthanide alkyl–borate system changes the regio- and stereoselectivity of the polymerization dramatically from 3,4-isospecific to 1,4-*cis* selective [154].

8.6.2.2 Polymerization of (Meth)Acrylates

$\text{Bi}(\text{pentamethylcyclopentadienyl})$ lanthanide hydride and methyl complexes $[(\text{C}_5\text{Me}_5)_2\text{Ln}(\mu\text{-R})]_2$ ($\text{R} = \text{H}, \text{CH}_3$) were the first to be reported as excellent initiators for the highly

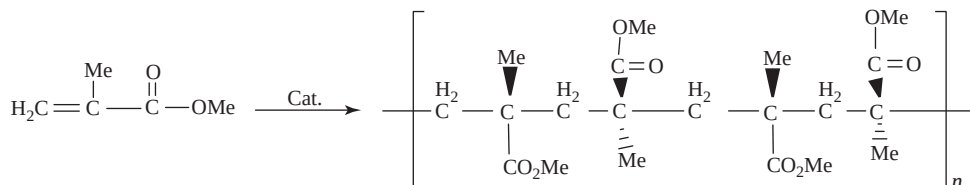


Figure 8.46 Syndiospecific polymerization of MMA.

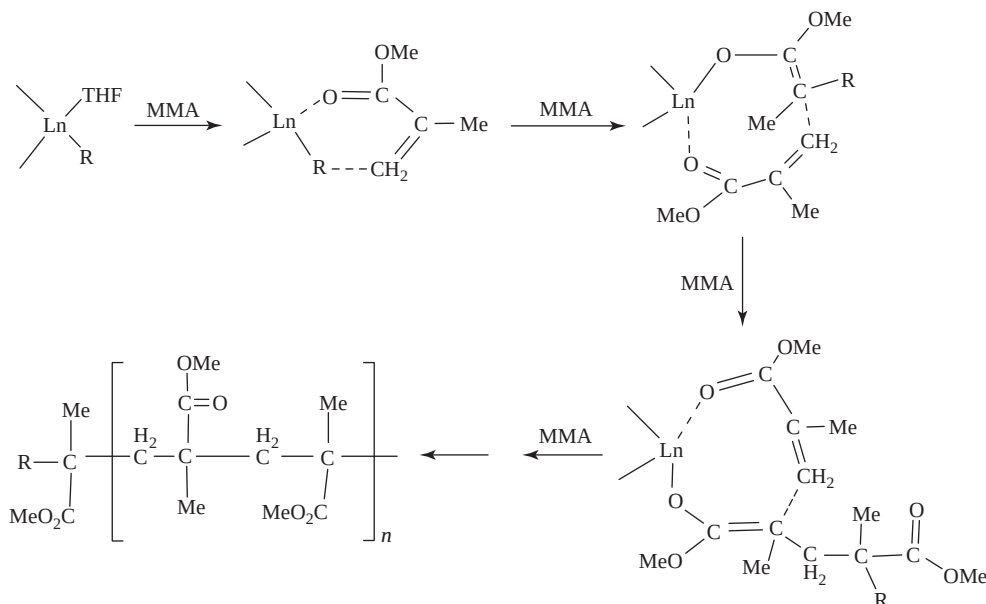


Figure 8.47 The proposed anionic polymerization mechanism of MMA.

syndiospecific polymerization of MMA to give PMMAs [poly(methyl methacrylate)] with high molecular weights and extremely narrow molecular distributions (Figure 8.46). The syndiotacticity of the polymer depends apparently on the polymerization temperature and increases with a decrease in temperature [155, 156]. The stereoselectivity in MMA polymerization initiated by organolanthanide complexes is susceptible to the coordination environment around the lanthanide metal. Most lanthanocene hydride, alkyl, and amide complexes initiate MMA polymerization to produce syndiotactic or syndio-rich PMMAs. However, the bulky lanthanocene complexes bearing the (+)-neomenthyl chiral auxiliary [157] and samarium alkyl complexes stabilized by the pyrrolalidinato ligand initiate the highly isospecific MMA polymerization [158]. The lanthanide allyl complexes initiate MMA polymerization to give atactic polymers [159].

A coordination anionic mechanism is proposed for this polymerization (Figure 8.47). At first, the R group attacks the CH₂ group of MMA to generate a transient Ln–O–C

(OMe)=C(CH₃)CH₂R species, and then the incoming MMA molecule participates in a 1,4-addition to afford the eight-membered ring enolate intermediate. In the propagation step, another MMA molecule attacks the growing end, and the coordinated ester group is liberated. The polymerization proceeds by repeating these reactions. The eight-membered ring intermediate has been isolated and structurally characterized with [(C₅Me₅)₂Sm(μ-H)]₂ as the initiator [155].

Divalent organolanthanide complexes can also initiate MMA polymerization. A divalent lanthanide complex, as a single-electron transfer reagent, can readily react with the monomer to generate a radical anion species, which subsequently couples into a bimetallic trivalent lanthanide enolate intermediate, which is the active center. Therefore, divalent organolanthanide complexes serve as bisinitiators for MMA polymerization [160].

[(C₅Me₅)₂Ln(μ-Me)]₂ can also initiate the living polymerization of a series of acrylates. Because of the living characteristic, these organolanthanide complexes can be used to synthesize ABA triblock copolymers of acrylates with MMA to provide thermoplastic elastomers [161]. Furthermore, bi(methylcyclopentadienyl) lanthanide amides can initiate effectively the coordination polymerization of (dimethylamino) ethyl methacrylate to give polymers with high molecular weights and narrow molecule distributions [162].

8.6.2.3 Polymerization of Lactones and Lactide

Ring-opening polymerization of lactones and lactide is a straightforward method for the synthesis of aliphatic polyesters with high molecular weight (Figures 8.48 and 8.49), which have received wide application in the medical field as biodegradable surgical sutures or as a delivery medium for controlled release of drugs due to their biodegradable, biocompatible, and permeable properties. Y(OCH₂CH₂NMe₂)₃ was the first to be reported to polymerize lactide in a rapid and controlled fashion [163]. Subsequently, a large number of organolanthanide complexes, including alkyl, hydride, amide, alkoxide, aryloxide, and so on were found to be efficient initiators for the ring-opening polymerization of lactones (ε-caprolactone, δ-valerolactone, and β-butyrolactone) and lactide to afford linear polyesters with high molecular weights and narrow molecular weight distributions [164–166]. The structure of the ancillary ligand has a profound

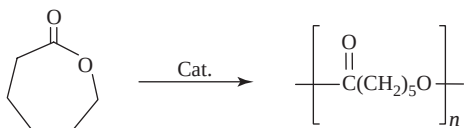


Figure 8.48 Polymerization of ε-caprolactone.

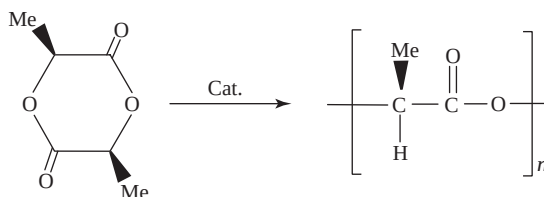


Figure 8.49 Polymerization of lactide.

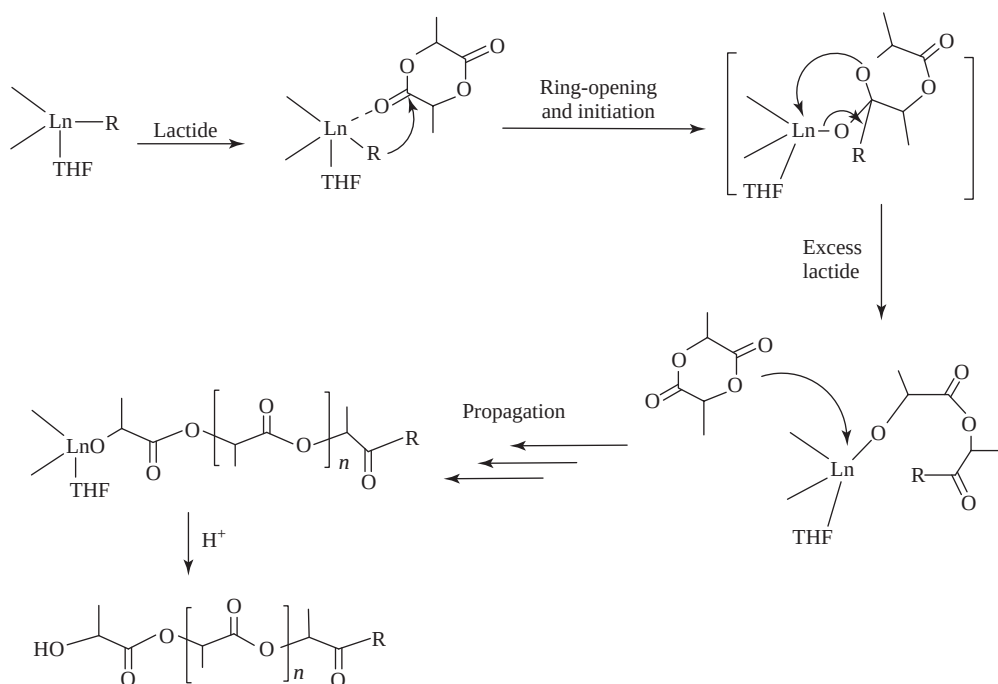


Figure 8.50 The polymerization mechanism of lactide initiated by lanthanide alkyl.

effect on the catalytic behavior of the organolanthanide complex. The steric bulky ancillary ligands are favorable for the synthesis of a controlled polymerization initiator.

The polymerization undergoes a coordination-insertion mechanism. The initiation step involves nucleophilic attack of the active group, such as a hydride, alkyl, amide or alkoxide group, on the carbonyl carbon atom of a lactide or lactone to form a new lanthanide alkoxide species via acyl–oxygen cleavage. The continued monomer coordination and insertion into the active metal–alkoxo bond formed completes the propagation step as shown in Figure 8.50.

8.7 Summary and Outlook

In past decades, the exploration of successful ligand systems including cyclopentadienyl and non-cyclopentadienyl groups has enabled the development of the chemistry of organolanthanide alkyls and their cationic partners, hydride, and divalent lanthanide complexes, and so on. The development of cationic lanthanide complexes has clearly added a new dimension to this organolanthanide chemistry. The success in the preparation of non-classical divalent lanthanide metal complexes indicates that a new era of reductive chemistry is beginning, and the lanthanide complexes in low oxidation state have much to offer the field of organolanthanide chemistry. Sterically induced reduction chemistry of the sterically crowded complexes $\text{Ln}(\text{C}_5\text{Me}_5)_3$ offers the possibility of carrying out reductive chemistry with all of the trivalent metals. Homogeneous catalysts based on lanthanides, as competitors of other already applied

d-block transition metals, behave excellently and have wide applications both in the multiform polymerization field, such as ethylene polymerization, stereospecific polymerization of dienes and methyl acrylate, and in organic synthesis.

However, there is still a lot to do. The chemistry of lanthanide carbonyl and olefin complexes, and the complexes containing a lanthanide to transition metal bond and/or a lanthanide to lanthanide bond is still underdeveloped. To fully utilize these new aspects of reductive chemistry clever approaches will be needed. The development of highly active “activatorless” olefin polymerization catalysts and chiral versions of these families of complexes, and the catalysts for C1 chemistry are still the challenges. So, organolanthanide chemistry will continue to be an attractive field for organometallic chemists and there are many opportunities for the future.

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9

Lanthanide Based Magnetic Molecular Materials

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9.1 Introduction

Rare earths have been widely used in traditional magnet technology for many years. For example, SmCo_5 and $\text{Nd}_2\text{Fe}_{14}\text{B}$ have found large markets as good permanent magnets to produce strong static magnetic fields in recent decades. Magnetic molecular materials are different species at least for three reasons. (i) The structures of the materials are more complex and more diverse than the type of structures in conventional inorganic/ionic materials. The number of such molecular materials could be very large, in theory probably even unlimited, for example, many types of molecular magnetic ordering systems including transition metal ions, radicals, lanthanide ions, and so on. (ii) They can be constructed from the bottom up using coordination chemistry methods. Thus identical structures and iso-orientated magnetic objects can be assembled in the form of molecular crystals. This provides an ideal model for the theoretical study of the origins of magnetism. For example, it is easier to understand the magnetic coupling mechanism from a dinuclear molecule than from a bulk material. (iii) Molecular systems often permit the incorporation of other useful functionalities to produce multifunctional materials. This could be a hybrid of different functional parts with no interaction using an inert linker, or it may be a more definite coupling of different physical properties, such as luminescent, ferroelectric, catalysis, gas sorption, and so on, for example, a conventional second-order ferroic material, or the less conventional light-induced magnetic ordering in spin crossover Prussian blue phases. These types of materials can not only offer model systems to test our theories on many of the body of problems facing scientists, but also offer methods for making new materials and for find highly specific and novel applications, such as, expanding human being's understanding of different macroscopic quantum phase behaviors.

Magnetic molecular materials are often composed of paramagnetic centers and inorganic or organic ligands to bridge the different spin carriers. Depending on the different paramagnetic centers, which can be transition metals ions, organic radicals, and lanthanide ions, the materials could be transition metal complexes, pure organic compounds, lanthanide containing species or hybrids of them.

As an important source of magnetism, the magnetic properties of rare earth ions are well known and are dominated by the internal nature of the *f* orbitals. Different from the 3*d* orbitals of transition metal ions in a ligand field and the *p* orbital of radicals, *f* orbitals of lanthanide ions have strong unquenched orbital angular momentum and effective spin–orbit coupling. The trivalent ions are characterized by *fⁿ* configurations, which give rise to ^{2*S*+1}*L* multiplets, further split by spin–orbit coupling to give *J* states:

$$E(^{2S+1}L_J) = (\lambda/2)[J(J+1) - L(L+1) - S(S+1)] \quad (9.1)$$

where

J is defined by the angular momentum summation rules $|L - S| \leq J \leq |J + S|$

$$\lambda = \pm \xi / 2S$$

ξ is the spin–orbit coupling constant which ranges from 600 to 3000 cm^{−1} throughout the lanthanide series, the highest values corresponding to the heaviest lanthanide ions.

The + sign applies for *n* < 7 and the − sign for *n* > 7. The sign of the spin–orbit coupling constant λ implies that in the ground state *J* = *L* − *S* for *n* < 7 and *J* = *L* + *S* for *n* > 7. For *f⁷* ions such as Gd (III), *L* = 0 and *S* = 7/2, the orbital momentum is completely quenched in the ground state.

The *g*-factor of the Zeeman Hamiltonian of a given *J* multiplet is given by:

$$g_r = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \quad (9.2)$$

The ground-state terms, *g*-values, calculated and experimental χT values at room temperature for the different lanthanide ions are listed in Table 9.1.

From the Table 9.1, the Ln(III) ions can have a large spin–angular momentum part and a large unquenched orbital–angular momentum part associated with the internal nature of the valence *f* orbitals. Compared with the *d* electrons of transition metal ions, the orbital component of the magnetic moment is much more important for the rare earth ions because the crystal-field effects are smaller and the spin–orbit coupling larger for *f* electrons. The magnetic properties of rare earth ions are strongly influenced by this, in particular the magneto-crystalline anisotropy is generally large. As far as the magnetic properties are concerned, the large anisotropic moments arise from the large spin–orbital coupling, making lanthanide ions attractive building blocks in the synthesis of magnetic molecular materials. As early as 1976, Landolt and coworkers [1] used Ln(III) ions for the preparation of a series of Prussian blue analogs that exhibited magnetic ordering with large hysteresis loops. Since then, numerous compounds containing lanthanide ions associated with paramagnetic centers, such as transition metal ions or organic radicals, have been described. They show an abundance of geometric structures and rich magnetic phenomena, such as ferromagnetic magnetic coupling, single molecular magnets, single chain magnets, magnetic ordering, especially single ion magnets, which has not been found in transition metal complexes and organic radical systems [2, 3]. In the following

Table 9.1 Ground state, g -values, calculated and experimental room temperature χT values for Ln(III) ions.

Ln(III)	Configuration	Ground state	g_J	$\chi T_{\text{cal}}^{(a)}$ (emu mol ⁻¹ K)	χT_{exp} (emu mol ⁻¹ K)
Ce	f ¹	² F _{5/2}	6/7	0.80	0.66–0.78
Pr	f ²	³ H ₄	4/5	1.60	1.45–1.62
Nd	f ³	⁴ I _{9/2}	8/11	1.64	1.45–1.53
Pm	f ⁴	⁵ I ₄	3/5	0.90	1.05
Sm	f ⁵	⁶ H _{5/2}	2/7	0.09	0.32
Eu	f ⁶	⁷ F ₀			1.53
Gd	f ⁷	⁸ S _{7/2}	2	7.88	7.61–7.80
Tb	f ⁸	⁷ F ₆	3/2	11.82	11.76–12.01
Dy	f ⁹	⁶ H _{15/2}	4/3	14.17	13.01–14.05
Ho	f ¹⁰	⁵ I ₈	5/4	14.07	13.26–13.78
Er	f ¹¹	⁴ I _{15/2}	6/5	11.48	11.05–11.28
Tm	f ¹²	³ H ₆	7/6	7.15	7.03
Yb	f ¹³	² F _{7/2}	8.7	2.57	2.53

$$^a \chi T_{\text{cal}} = (1/8) g_J^2 [J(J + 1)].$$

sections, different magnetic molecular materials containing lanthanide ions will be introduced in the sequence magnetic coupling, magnetic ordering, and magnetic relaxation.

9.2 Magnetic Coupling in Lanthanide Containing Molecular Materials

From the point of view of magnetic carriers, lanthanide ions not only have possible large spin moments associated with spin unpaired electrons, but also large orbital moments due to unquenched orbital angular momentum, both of which originate from the internal nature of the valence f orbitals. Compared with the transition metals ions, the spin carriers used in many magnetic molecular materials, all paramagnetic lanthanide ions except for Gd(III) and Eu(II) with f⁷ electron configuration have orbitally degenerate ground states, which are split by spin–orbit coupling and ligand field effects. So the magnetic properties of lanthanide containing materials are influenced considerably by the large spin–orbit coupling and the orbital magnetic moment contribution. We divide the introduction to magnetic coupling between lanthanide ions and other paramagnetic centers into two parts: Gd(III) containing systems and other Ln(III) ions with first-order orbital momentum, respectively.

9.2.1 Magnetic Coupling Mechanism of Gd(III) Systems

For a 4f⁷ lanthanide ion such as gadolinium(III), the contribution to its magnetic behavior is only from a pure spin state $S = 7/2$. When interacting with other paramagnetic centers with an orbitally nondegenerate ground state, the HDVV (Heisenberg–Dirac–Van Vleck) spin Hamiltonian will be used to explain the magnetic properties of the system:

$$H = -J S_{\text{Gd}} \cdot S_s \quad (9.3)$$

where

S_{Gd} is the spin operator associated with gadolinium

S_s is the spin operator associated with the other magnetic center

the positive J means ferromagnetic and negative antiferromagnetic coupling in this spin Hamiltonian definition.

The basic model for understanding the magnetic coupling properties was developed by Anderson about 50 years ago. He reduced the complex theory to only take account of simplified magnetic orbitals, which contain one unpaired electron. The magnetic interaction is antiferromagnetic when the two magnetic orbitals on different centers have nonzero overlap. For example, Kahn applied the concept of nature magnetic orbital to analyze a dinuclear system and deduced the approximate magnetic coupling constant

$$J = 2k + 4\beta S \quad (9.4)$$

where

k is two electron exchange integral, which is always positive and favors the ferromagnetic interaction

S is the two electron overlap integral (S is the spin multiplet in other parts of this chapter, but means overlap integral only in this paragraph).

For a molecular magnetic system, S and β are of opposite sign and $4\beta S$ is negative which favors the antiferromagnetic interaction. Hu and coworkers [4] made some further approximations and proposed the linear relationship of J and S^2 , which is the square of the overlap integrals among HOMOs (highest occupied molecular orbitals) with α and β spins. If the magnetic orbitals are orthogonal to each other and the overlap integral S tends to zero, the magnetic interaction will be ferromagnetic and the unpaired electron possesses parallel configuration. There are also some other theoretical models to explain the magnetic properties of different materials, but almost all of the simplified models of magnetic interaction regard the exchange or superexchange interaction as a form of weak bonding between two paramagnetic centers. This general model could understand the mechanism of magnetic coupling interaction between different types of paramagnetic centers, such as 3d transition metal ions, radicals, and lanthanide ions.

9.2.1.1 Magnetic Coupling of Gd(III)-Gd(III) Systems

As compared with the unpaired d electrons of transition metal ions and s, p electrons of organic radicals, the unpaired f electrons of lanthanide ions are highly contracted and energetically deeply shielded by outer 5d, 6s shells. So the directly magnetic interaction between $4f^7-4f^7$ electrons are very weak, the value of coupling constant J is normally less than 1 cm^{-1} [5]. The situation is very different to the indirect pathway involving the 4f localized electrons and conduction electrons responsible for the magnetic ordering of rare earth intermetallic compounds.

For the highly contracted f electrons of Gd(III) type ions, the magnetic interaction is mediated by the spin polarized 5d, 6s valence electrons. To a good approximation, the $4f^7$ exchange field can be viewed as a type of contact effect [6], which only exert its influence on the orbitals centered on the Gd atom. Both the valence 5d and 6s electrons can penetrate to some extent

and experience the $4f^7$ exchange field of the atom core, only the more contracted 5d electrons experience greater exchange interaction with the $4f^7$ core. Consequently, it appears that the valence 5d, 6s electrons are spin polarized and the 5d orbital possesses a larger spin density in *ab initio* or density functional theory (DFT) calculations [5, 6], and controls the magnetic properties of polynuclear compounds containing Gd(III) type ions. This local character of the $4f^7$ exchange field can be treated by a simple perturbative molecular orbital (PMO) model [6] and accounts for the perturbation of the $4f^7$ cores exerted on electrons that reside in molecular orbitals with 5d and 6s characters.

Figure 9.1 illustrates how the potential from the $4f^7$ core affects electrons with 5d and 6s character for the Gd atom. At the left side of this figure, an “unperturbed” system is depicted wherein the valence d electron experiences an average exchange potential from the half-filled 4f shell, so the d electron has no preferred spin orientation. Upon application of the exchange field, the spin aligned with (or against) the 4f spins is stabilized (or destabilized) by an energy δ . For a Gd atom, 2δ is just the difference between the ^9D ground state and the first excited state ^7D . These exchange interactions are intrinsically “ferromagnetic,” favoring parallel alignment of the 4f and 5d spins [6].

Because the energy scale of the magnetic coupling constant J of the $4f^7$ – $4f^7$ system is as small as one wavenumber, it is a very difficult task for any theoretical calculation including *ab initio* and DFT methods. It is only luck that the DFT combined broken symmetry (DFT + BS) method proposed by Noodleman and coworkers [7–9] appears to be not so accurate but is effective for the calculation of the values of magnetic coupling constant, for not only 3d transition metal systems, but also $4f^7$ – $4f^7$ compounds. Roy and Hughbanks calculated the magnetic coupling constants of some oxo-bridged Gd(III) dinuclear complexes using the DFT + BS method [6]. The computational results are fairly consistent with the fit of the experimental results from the magnetic susceptibility data. The calculated magnetic coupling constants are as low as several percent, but are still consistent with the experimental results. This is an amazing success for theoretical calculations. This density functional based method was also used by Ning *et al.* and Pedersen and Ojamae to simulate the magnetic coupling of Gd(III)–Gd(III) in GdO clusters [10, 11]. The results of the calculations can also describe well the magnetic properties of this type of magnetic materials.

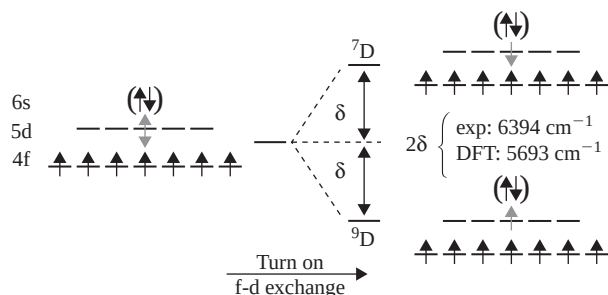


Figure 9.1 Electronic splitting of the Gd atom as a function of 4f–5d exchange perturbation [6]. (Reprinted with permission from L.E. Roy, and T. Hughbanks, “Magnetic coupling in dinuclear Gd complexes,” *Journal of the American Chemical Society*, **128**, no. 2, 568–575, 2006. © 2006 American Chemical Society.)

9.2.1.2 Magnetic Coupling of Gd(III)-3d

Mixed 3d–4f compounds are probably the most studied magnetic complexes that contain lanthanide ions because of their attractive properties in the areas of molecular magnetism and coordination chemistry, such as single-molecule magnets, magnetic ordering materials. Gd(III)-3d systems are widely studied by experimentalists and theoreticians due to the presence of the largest possible magnetic moment $S = 7/2$ and the lack of orbital contribution, which facilitates the analysis of the magnetic properties. Of these clusters, various binuclear and polynuclear complexes containing Gd(III)–Cu(II) units have pronounced magneto-structure correlations and exhibit widespread ferromagnetic coupling between the Gd(III) and the Cu(II) ion with only a few exceptions.

Gatteschi and coworkers [12, 13] proposed a spin polarization mechanism, which is based on the orbital interaction between the 6s orbital of Gd and delocalization tails of the 3d orbital of Cu on the ligand. In this scheme, it is considered that the most important contribution comes from the overlap of the magnetic orbital of Cu(II) with the empty d or s orbitals of Gd(III). Therefore, a fraction of the unpaired electrons are transferred into the empty orbitals and electrons are parallel to each other according to Hund's rule. In fact, this is a generalization of the Goodenough–Kanamori [14] rule for a Gd–Cu system, which suggests ferromagnetic coupling occurs when a magnetic orbital of one site has nonzero overlap with an empty orbital of the other site. This idea is consistent with the theoretical PMO model treatment made by Hughbanks, but the contribution of the 6s orbitals is replaced by the 5d orbitals, which is shown in Figure 9.1.

Also inspired by the general schemes of Goodenough [14], Kahn and coworkers [15] gave an alternative explanation, which attributes the ferromagnetic coupling to the interaction between the Gd(III)–Cu(II) ground state configuration and the excited state configuration arising from the occupied 3d (Cu) → vacant 5d (Gd) electron transfer. They used the extended Hückel approach to check the efficiency of the mechanism by calculation of the electron charge transfer integral β_{5d-3d} , but were limited because they could not offer a proper account for the subtle configuration interaction problems at that time. Yan and Chen [16] reported spin density maps and Mulliken type population analysis based on the DFT + BS calculation, and gave an interpretation of the magnetic coupling as a spin delocalization from the copper center and a spin polarization from the gadolinium center, but gave no discussion about the role of 6s versus 5d polarization mechanisms.

These magnetic coupling mechanisms of the Gd(III)–Cu(II) system were further discussed by Hirao and coworkers based on their state-of-the-art CASSCF (complete active space self-consistent field) and CASPT2 (complete active space with second-order perturbation theory) calculations [17]. They concluded that the ferromagnetic gap is intrinsic to the Cu(II)–Gd(III) pair but appears with a low magnitude for the naked dimer. The pure ligand field (electrostatic and polarization effects, without covalence) slightly increases the ferromagnetic gap. Within an appropriate definition of magnetic orbitals, Kahn's proposal can be proved to be an effective mechanism of ferromagnetic coupling, which involves orbitals that are not genuine Cu (3d) and Gd (5d) AOs (atomic orbitals), but MOs (molecular orbitals) already containing a small tail of Gd-origin on the orbital located mainly on the [CuL] side, in addition to a slight mixing between the 4f and 5d AOs of Gd(III). The spin polarization picture is supported by the computation experiments based on the CASSCF method, involving the ligand and the 5d orbitals of Gd(III). From the point of view of the state-of-the-art calculation, the polarization

mechanisms of Kahn and Gatteschi are not mutually contradictory, but are even interconvertible by appropriate transformations of the magnetic orbitals, thereby adjusting the portion of pure Cu (3d) and ligand tails in the active orbital that interacts with Gd (6s) or Gd (5d). In general, the contribution of the 5d orbitals of Gd(III) is larger than the 6s orbitals and plays a more important role in the magnetic coupling of Gd(III)–Cu(II) compounds. The magnetic orbital analysis shows the orbital orthogonal exchange pathway transmits the ferromagnetic interaction in this type of complex.

The abundance of geometric structures and magnetic measurements stimulated structure–magneto correlation studies on the Gd(III)–Cu(II) complexes. Cirera and Ruiz [18] found that the exchange coupling constant seemed to be directly related to the Cu–O–Gd–O torsion angle based on DFT + BS calculations. Thus the ferromagnetic coupling becomes stronger for planar CuGdO₂ frameworks. The analysis of the overlap integrals for the 3d–4f interactions confirms such magnetostructural correlation due to an increase in the overlap for the nonplanar structures, and consequently a larger antiferromagnetic contribution.

Through reacting tetradentate copper(II) Schiff's bases with Gd(ClO₄)₃, Gatteschi and coworkers obtained the first fully characterized magnetic molecule composed of a Gd(III)–Cu(II) core [19]. Following this example, many Gd(III)–Cu(II) systems have been synthesized and characterized. As it is easier to deduce the magnetic coupling information between Gd(III) and 3d or p spin carriers than other rare earth ions with an unquenched orbital moment, dinuclear Gd(III)–Cu(II) complexes have become a large branch of the family of 3d–4f compounds. Costes and coworkers [20–25] synthesized some Gd(III)–Cu(II) compounds with various coordinations of Cu(II) ions. Magnetic measurements indicate that almost all of the couplings between Gd(III) and Cu(II) are ferromagnetic in the Costes' series. The maximum value of the coupling constant is 12.6 cm^{−1}, which was evaluated on the basis of an HDVV approach [26]. Only one example of a weak antiferromagnetic interaction was observed with a small negative *J* value of −0.49 cm^{−1} [20]. After analyzing the whole series of compounds, Costes and coworkers proposed a correlation between the magnitude of the magnetic interaction and the exponential of the dihedral angle between the two halves (Gd–O–Gd and O–Cu–O) of the bridging core (listed in Table 9.2). This was verified by the theoretical calculations of Cirera and Ruiz [18].

Cu(II) ions can be replaced by other transition metal ions, but this is less documented and characterized. The magnetic couplings have no strong tendency to be ferromagnetic and have no obvious magneto-structure correlation as for Gd(III)–Cu(II) systems. It seems that the magnetic coupling properties are mainly governed by the nature of the chemical linker between the spin carriers, but are not always correct. For example, ferromagnetic couplings occur for Mn(III) [25], Fe(II) [42], Co(II) [43], and Ni(II) [44–46] when the bridges between Gd(III) and TM (transition metal) ions are the oxygen atom of a series of Schiff base derivatives. However, both ferro- and antiferromagnetic interactions were found for the paramagnetic V(IV) ion [47, 48]. If a CN ligand was selected as a bridge, antiferromagnetic interactions were found for Gd(III)–Cr(III) and Gd(III)–Fe(III) compounds [1, 49–51].

For the highly contracted 4f electrons, the magnetic interactions need be mediated by polarized 5d, 6s orbitals, and are typically weak. Gd(III)–Gd(III) systems have been studied less in synthetic chemistry. Some oxygen (from carboxylate, phenoxide ligand, and so on) bridged dinuclear Gd(III) complexes have been reported and exhibit weak antiferromagnetic [52, 53] and ferromagnetic [54, 55] interactions. The exchange coupling constants range from −0.198

Table 9.2 Structural data of the Gd(III)–Cu(II) complexes, Cu–O–Gd–O torsion angle, and experimental J exchange coupling constants.

Complex	Cu–O–Gd–O (degree)	J_{exp} (cm^{-1})	Ref.
CuL1Gd(NO ₃) ₃	38.3	−0.49	[20]
Gd(hfa) ₃ Cu(salen)	32.99	0.4	[27]
Cu(salabza)Gd(hfac) ₃	34.28	0.8	[28]
Cu(salen)Gd(pta) ₃	23.72	1.21	[29]
Cu(acacen)Gd(hfa) ₃	28.46	1.25	[29]
LCuGd(NO ₃) ₃ ·Me ₂ CO	4.05	1.3	[30]
Gd(hfa) ₃ Cu(salen)(Meim)	27.72	1.42	[28]
Cu(acacen)Gd(pta) ₃	29.81	1.47	[30]
Cu(ehphi)Gd(hfac) ₃	30.78	1.91	[31]
CuGd(hmp) ₂ (NO ₃) ₃ (H ₂ O) ₂	15.32	3.36	[32]
[CuGd(ems)(NO ₃) ₃ ·3H ₂ O] Cu(ems)	17.77	3.76	[33]
LCuGd(NO ₃) ₃ ·CH ₃ OH	23.31	4.33	[34]
LCu(C ₃ H ₆ O)Gd(NO ₃) ₃	13.52	4.8	[21]
LCuGd(NO ₃) ₃	14.12	4.98	[22]
LCu(H ₂ O)Gd(NCS) ₃ ·Me ₂ CO	15.44	5.5	[35]
LCuGd(NO ₃) ₃ ·Me ₂ CO	9.6	5.6	[36]
LCu(MeOH)Gd(NO ₃) ₃	10.0	6.8	[21]
LCuGd(NO ₃) ₃ ·Me ₂ CO	10.15	7.0	[23]
LCuGd(NO ₃) ₃ ·Me ₂ CO	10.05	7.3	[37]
LCuGd(NO ₃) ₃ ·Me ₂ CO	9.29	7.4	[38]
LCuGd(NO ₃) ₃	7.45	7.6	[39]
LCuGd(NO ₃) ₃	3.36	8.08	[40]
LCuGd(NO ₃) ₃ ·Me ₂ CO	8.96	8.63	[41]
[LCuCl ₂ Gd(H ₂ O) ₄]Cl·2H ₂ O	1.38	10.1	[24]
LCuGd(NO ₃) ₃	5.5	10.8	[26]
LCuGd(NO ₃) ₃	1.61	12.6	[26]

to 0.21 cm^{-1} and are all much smaller than the values from Gd(III)–TM compounds. It reaches almost zero (0.006 cm^{-1}) in some compounds [56].

9.2.1.3 Magnetic Coupling of Gd(III)–p Systems

Organic radicals are other paramagnetic centers that can couple with the Gd(III) ion. For the direct bonding between the two paramagnetic centers and shorter interacting distances than bridging by diamagnetic ligands, this offers a favorable situation to improve somewhat the strength of the exchange interaction in Ln ion containing compounds. Several Gd(III)–radical compounds have been reported in which the organic parts are mainly nitronyl nitroxide radicals [57, 58], imino nitroxide radicals [59, 60], and semiquinone [61, 62] derivatives. The structures of radicals concerned are depicted in Figure 9.2.

Interestingly, the magnetic coupling properties appear to be influenced greatly by the chemical nature of the organic radicals. For the nitronyl nitroxide radical and derivatives, the exchange interactions are mainly ferromagnetic and can be as large as 6.1 cm^{-1} [63]

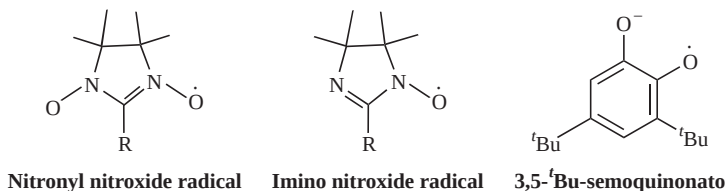


Figure 9.2 The radical structure of nitronyl nitroxide radical, imino nitroxide radical, and semoquinonato.

between the lanthanide ions and the radicals. This coupling intensity can be comparable to the magnetic coupling between Gd(III) and transition metal ions. Accompanied by the strong magnetic couplings between the radicals themselves, Gd(III)–radical complexes can reach magnetic ordering at low temperatures, which are introduced in the next section in this chapter. The anti-ferromagnetic couplings are mainly observed in Gd–R systems when R is the nitronyl nitroxide radical [60, 64], semiquinone or a derivative [61, 62]. For compound Gd(Tp)₂(SQ), where Tp is hydro-trispyrazolyl borate and SQ is 3,5-di-*tert*-butylsemiquinonato, the coupling constant $J = -11.4 \text{ cm}^{-1}$ of the Gd–semiquinone interaction is the maximum value for the magnetic coupling intensity between Gd(III) and other paramagnetic centers, including lanthanide ions, transition metal ions, and organic radicals. This unusually strong interaction has been proposed as reflecting a rather strong chemical link between the two paramagnetic centers. Tetracyanoethylene (TCNE) and tetracyanodimethane (TCNQ) radicals are also effective spin carriers to couple with Gd(III) ion. It is worth mentioning that TCNQ can link the Gd(III) to form an extended structure and behave as a ferrimagnet at low temperatures [65, 66].

9.2.2 Magnetic Coupling in Ln(III) Containing Systems with Orbital Moment Contribution

Besides the spin magnetic moment, the orbital contribution and the ligand field can also clearly affect the magnetic properties of Ln(III) (except for f^7 configuration in this section) containing compounds. For a lanthanide ion with $4f^n$ configuration, the ground state energy is split by interelectronic repulsion in spectroscopic terms, the one with the highest spin multiplicity ($2S + 1$) is the lowest in energy, limited by Hund's rule of maximum spin multiplicity (Figure 9.3). Each of these terms is further split by the spin–orbit interaction into $^{2S+1}L_J$ spectroscopic levels, with $|L - S| \leq J \leq L + S$. For a $4f^n$ configuration with $n < 7$ the ground level has the lowest J value, but for $n > 7$ the ground state has the highest J value. Now J is the good quantum number and should be taken into account when understanding the magnetic properties of Ln(III) containing compounds. Each of these levels can be further split into Stark sublevels by the ligand field effect. Because of the shielding of the $4f$ orbitals, the ligand field splitting is usually only a few hundred per centimeter and is much smaller than for the $3d$ orbitals of the transition metal ions. This energy scale is comparable to the $k_B T$ and changes the population of sublevels from room to low temperature. So the orbital moment has a non-negligible contribution to $\chi_{\text{Ln}} T$ values. Obviously, the temperature dependence of χ_{Ln} deviates from the Curie law in this instance.

This phenomena originates from the intrinsic electron properties of lanthanide ions, and can be modulated by the surrounding ligand field and symmetry of the compound. There is no

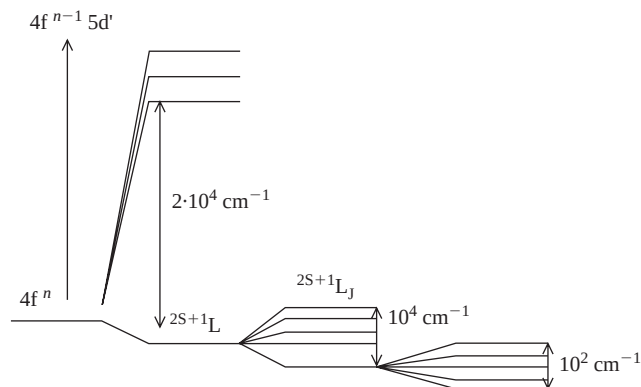


Figure 9.3 Schematic energy diagram showing the relative magnitude of the interelectronic repulsion, the spin–orbit coupling, and ligand-field effects [2]. (Reprinted with permission from J.S. Miller, and M. Drillon, *Magnetism: Molecules to Materials*, vol. V, Copyright Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. © 2005.)

general analytical model to simulate the orbital magnetic contribution of this type of compound. At the same time, the effect of orbital contribution on the magnetic susceptibility is overlapped by the spin moment donation. Thus, it is difficult to analyze the overall magnetic behavior for such a type of compound using a simple theoretical model. However, knowledge of Periodic Table of elements provides a rather simple experimental approach to overcome the problem of the orbital contribution and gives some qualitative insight into the interactions occurring between the Ln(III) ion and other spin carriers. Based on the above discussion, this approach requires two compounds, one is an exchange coupling system including Ln(III) and another spin carrier, and the other molecule is an isostructural compound in which the coordination sphere of the Ln center is identical, but the other spin carrier is replaced by a diamagnetic ion. Then a comparison of the magnetic behaviors of the two compounds reveals the nature of the magnetic interaction taking place in the exchange coupled system.

For instance, a series of Ln(III)–Cu(II) compounds with the chemical formula $[\text{MLLn}(\text{hfac})_2]_2$ have been synthesized and characterized [67] where $\text{H}_3\text{L} = 1$ -(2-hydroxybenzamido)-2-(2-hydroxy-3-methoxybenzylideneamino)ethane and $\text{Hhfac} =$ hexafluoroacetylacetone (Figure 9.4). The electronic structure of the ground state is $^7\text{F}_0$ ($S = 3$, $L = 3$, $J = 0$) for Eu(III), $^7\text{F}_6$ ($S = 3$, $L = 3$, $J = 6$) for Tb(III) and $^6\text{H}_{15/2}$ ($S = 5/2$, $L = 5$, $J = 15/2$) for Dy(III), respectively. These ions with the first-order orbital angular momentum contribute significantly to the overall magnetic properties. The corresponding Ln(III)–Ni(II) compounds are also synthesized as a reference in the study of the magnetic interaction of Ln(III)–Cu(II) compounds.

The magnetic susceptibilities of Eu(III)–Cu(II) and Eu(III)–Ni(II) were measured under an external applied magnetic field of 1 T in the temperature range 2–300 K (Figure 9.5). The value of $\chi_{\text{EuCu}}T$ is found to decrease rapidly as the temperature is lowered. It appears that the coupling between Eu(III) and Cu(II) is antiferromagnetic. However, considering the overlap of the orbital contribution and spin portion, the susceptibility of the reference structure should

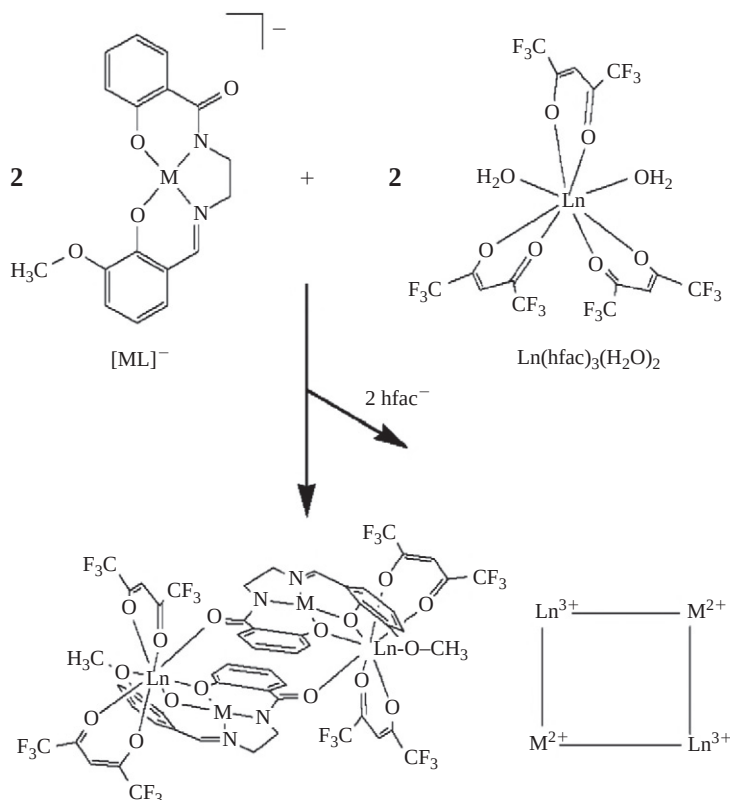


Figure 9.4 $[MLLn(hfac)_2]_2$, $M^{2+} = Cu^{2+}$ (paramagnetic), Ni^{2+} (diamagnetic), $Ln^{3+} = Sm^{3+}$, Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} [67]. (Reprinted with permission from T. Kido, *et al.*, "Nature of copper(II)-lanthanide(III) magnetic interactions and generation of a large magnetic moment with magnetic anisotropy of 3d–4f cyclic cylindrical tetranuclear complexes $[Cu^II L Ln^III(hfac)_2]_2$, ($H_3L = 1$ -(2-hydroxybenzamido)-2-(2-hydroxy-3-methoxybenzylideneamino)ethane and $Hhfac =$ hexafluoroacetylacetonate, $Ln^{III} = Eu, Gd, Tb, Dy$," *Inorganic Chemistry*, **42**, 398–408, 2003. © 2003 American Chemical Society.)

be subtracted from the overall magnetic data. The residual $\Delta\chi(T)$ value is in the range from $0.82 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K to $1.05 \text{ cm}^3 \text{ K mol}^{-1}$ below 75 K. Because $\Delta\chi(T)$ is only slightly larger than the contribution of two non-interacting $Cu(II)$ ions, $0.75 \text{ cm}^3 \text{ K mol}^{-1}$, the magnetic coupling constant J_{EuCu} can be estimated to be slightly positive or almost zero, suggesting that there is no substantial magnetic interaction between the $Cu(II)$ and $Eu(III)$ ions. This is a totally different conclusion from just the overall magnetic susceptibility data.

The magnetic studies on $[NdM(bpm)(H_2O)_4(CN)_6] \cdot 3H_2O$ ($M = Fe, Co$; $bpm = 2,2'$ -bipyrimidine) coordination polymers synthesized by Gao's group [68] gave another example to support this method. The temperature dependences of the $\chi_M T$ for crystalline samples $Nd-Fe(III)$ and $Nd-Co(III)$ measured at 10 kOe and 500 Oe fields are shown in Figure 9.6. To

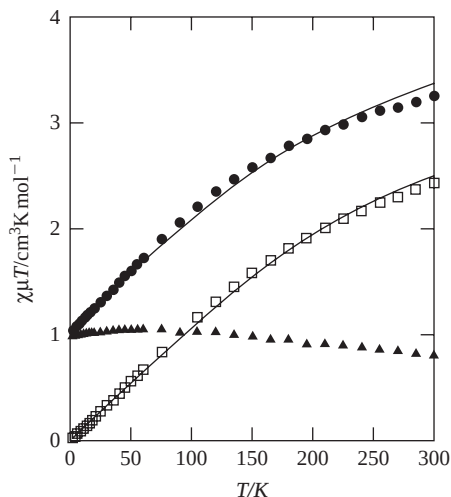


Figure 9.5 Plots of $\chi_M T$ versus temperature for $[\text{CuLEu}(\text{hfac})_2]_2$ (●) and $[\text{NiLEu}(\text{hfac})_2]_2$ (□), and for the difference $\Delta\chi(T) = (\chi_M T)_{\text{Cu}_2\text{Eu}_2} - \chi_M T_{\text{Ni}_2\text{Eu}_2}$ (Δ) [67]. (Reprinted with permission from T. Kido, *et al.*, “Nature of copper(II)-lanthanide(III) magnetic interactions and generation of a large magnetic moment with magnetic anisotropy of 3d-4f cyclic cylindrical tetranuclear complexes $[\text{Cu}^{\text{II}}\text{Ln}^{\text{III}}(\text{hfac})_2]_2$, ($\text{H}_3\text{L} = 1$ -(2-hydroxybenzamido)-2-(2-hydroxy-3-methoxybenzylideneamino)ethane and $\text{Hhfac} = \text{hexafluoroacetylacetone}$, $\text{Ln}^{\text{III}} = \text{Eu, Gd, Tb, Dy}$),” *Inorganic Chemistry*, **42**, 398–408, 2003. © 2003 American Chemical Society.)

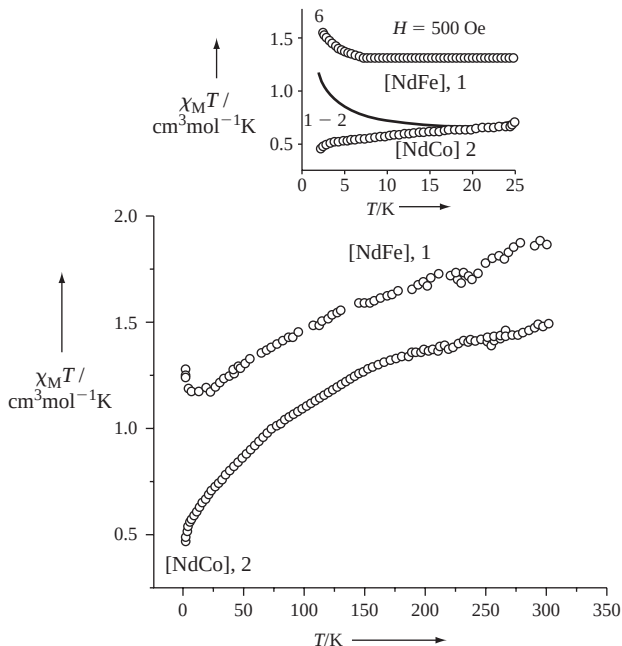


Figure 9.6 Temperature dependence of $\chi_M T$ for $[\text{NdFe}]$ 1 (○) and $[\text{NdCo}]$ 2 (□) at 10 kOe. Inset is the curve of $\chi_M T$ versus T at 500 Oe [68]. (Reprinted with permission from B. Ma, *et al.*, “Cyano-bridged 4f-3d coordination polymers with a unique two-dimensional topological architecture and unusual magnetic behavior,” *Angewandte Chemie International Edition*, 2001, **40**, 434–437 (Figure 3). © Wiley-VCH Verlag GmbH & Co. KGaA.)

exclude the contribution of spin–orbital coupling of the Nd(III) ion, the $\chi_M T$ of Nd–Co(III) was subtracted from that of Nd–Fe(III). It is found that the difference (solid line in the inset of Figure 9.6) increases steadily with cooling, indicative of ferromagnetic interactions between the Nd(III) and Fe(III) ions.

Other examples have been reported for Ln(III)–3d and Ln(III)–radical systems [69–71]. No general magneto-structure correlation relationship has been deduced from the reported compounds for a limited number of studies. These were also restricted by the difficulties of theoretical modeling and calculation for the spin–orbit coupling.

9.3 Magnetic Ordering in Lanthanide Based Molecular Materials

Lanthanide ions with anisotropic magnetic moments are good candidates for building blocks in the construction of magnetic materials with large hysteresis loops [1]. In widely used classical magnetic materials, such as SmCo alloy, or the NdFeB compound, rare earths play an important role in modulating the bulk magnetic properties [72].

In the field of coordination chemistry, rare earth ions are also excellent building blocks in the molecular approach to magnetic materials [2, 73, 74] due to the rather large and anisotropic moments of most of the lanthanide ions and the nature of lanthanide–lanthanide and/or lanthanide–organic radical and/or lanthanide–transition metal interactions. The magnetic orbitals of rare earths are fairly well shielded from the interaction with the ligands, so effects that are usually negligible for transition metal ions become very important for rare earths. A typical example is the polarization effect of the f orbitals determined by the transfer into empty excited orbitals. In 1976, Landolt and coworkers prepared a series of Prussian blue analogs with Ln(III) ions [1], exhibiting 3D-long range magnetic ordering with fairly large hysteresis loops. Since then many lanthanide compounds associated with paramagnetic species, organic radicals or transition metal ions, have been reported [3, 75]. However, with the exception of the spin-only $4f^7$ Gd(III) ion, reports of examples of molecular multi-spin systems involving Ln(III) ions are scarce, which maybe due to the weak interaction between the rare earth ions. So far only a few lanthanide–organic radical compounds and 4f–3d heterometallic compounds have shown long-range ordering, and most of them enter the ordering phase at low temperatures.

9.3.1 Lanthanide–Organic Radical Systems

A successful strategy for preparing molecular magnets is the coordination of organic radicals such as NITR (nitronyl nitrosides, Figure 9.7) [76–78] and organocyanides such as TCNE[−] [79] (TCNE = tetracyanoethylene) and TCNQ[−] (TCNQ = 7,7,8,8-tetracyanoquinodimethane) [80] to paramagnetic metal ions. The presence of both metal spins (typically $S > 1/2$) and organic spin carriers ($S = 1/2$) leads to strong local super-exchange interactions, resulting in typically ferro- or ferrimagnetic ordering. Although molecular magnetic materials based on 3d metals and organic radicals are quite common, analogous 4f element compounds are relatively rare.

The organic radicals NITR have one unpaired electron, which is shared equally by the two NO groups. As far as magnetic exchange is concerned, they behave as a single atom with $S = 1/2$. In addition they are usually employed as organic spin carriers, which can link

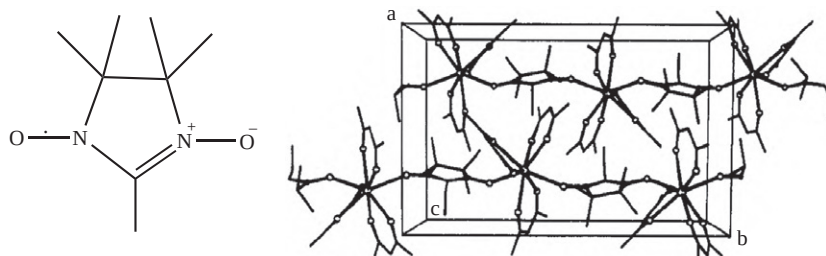


Figure 9.7 The structure of NITR radical and the schematic view of the crystal structure of $\text{RE}(\text{hfac})_3\text{NITet}$ [76]. (Reprinted from A. Caneschi, D. Gatteschi, and R. Sessoli, "Magnetic properties of a layered molecular material comprising manganese hexafluoroacetylacetonate and nitronyl nitroxide radicals," *Inorganic Chemistry* **32**, 4612–4616, 1993. © 1993 American Chemical Society.)

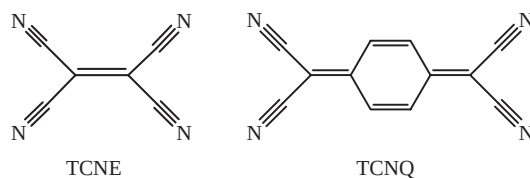
the neighboring metal ions through their two NO groups, forming one-dimensional chains, schematized as:



For transitional metals, when $\text{M} = \text{Cu}(\text{II})$, the materials behave as one-dimensional ferromagnets [81]. When $\text{M} = \text{Ni}(\text{II})$ or $\text{Mn}(\text{II})$ the materials behave as one-dimensional ferrimagnets. The latter exhibit ferromagnetic ordering with critical temperatures in the range 4–9 K, while the former remain paramagnetic down to 1.2 K.

A series of analogous lanthanide–NITR one-dimensional compounds [82] are obtained, which are rather different from those of transition metal ions. The structure of $\text{RE}(\text{hfac})_3\text{NITet}$ compounds ($\text{RE} = \text{Tb}$, Er , Ho ; $\text{hfac} = \text{hexafluoroacetylacetonate}$; $\text{NITet} = 2\text{-ethyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl-3-oxide}$) [82, 83] are illustrated in Figure 9.7. Their unit cell is monoclinic, and the chains develop parallel to the b -axis and are well shielded from each other with the shortest contacts of $10.38\text{\AA}$ between $\text{Gd}(\text{III})$ and $10.95\text{\AA}$ between $\text{Dy}(\text{III})$ ions. The RE ions are eight-coordinated by eight oxygen atoms, six from three hfac ions and two from NITet .

Among these compounds $\text{Dy}(\text{hfac})_3\text{NITet}$ exhibits an overall antiferromagnetic coupling between Dy^{3+} and the NITet radical, but undergoes a magnetic phase transition at about 4 K, ordering as a weak ferromagnet due to spin canting [84, 85]. For comparison, $\text{Mn}(\text{hfac})_2\text{NITR}$ have similar chain structures and a strong intrachain antiferromagnetic coupling of about 400 K, reaching long range magnetic ordering at about 8 K. $\text{Er}(\text{hfac})_3\text{NITet}$ shows magnetic phase transitions at temperatures ranging from 1.2 to 3.2 K. The relatively high critical temperatures for anisotropic $\text{RE}(\text{hfac})_3\text{NITet}$ compounds must essentially be determined by the strong antiferromagnetic exchange between the lanthanide ions mediated through the radical.



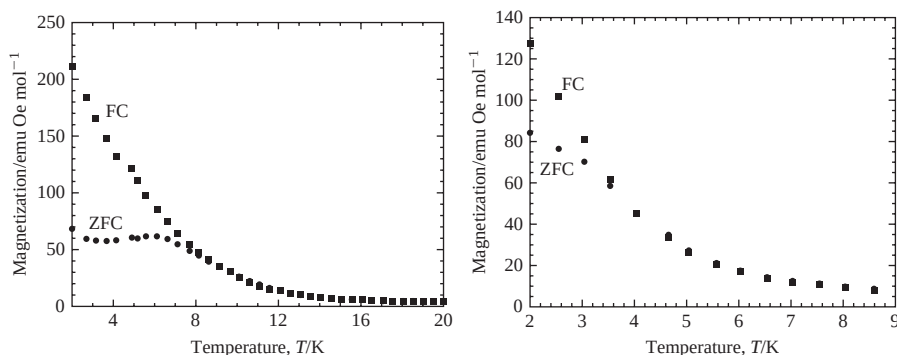


Figure 9.8 Plot of zero-field cooled (ZFC) and field-cooled (FC) magnetization of Dy[TCNE]₃ (left) and Gd[TCNE]₃ (right) measured in a 5 Oe applied field. The low-temperature region is displayed with the bifurcation point at 8.5 and 3.5 K [65]. (Reprinted with permission from J.W. Raebiger, and J.S. Miller, "Magnetic ordering in the rare earth molecule-based magnets, Ln(TCNE)₃ (Ln = Gd, Dy; TCNE = tetracyanoethylene)," *Inorganic Chemistry*, **41**, 3308–3312, 2002. © 2002 American Chemical Society.)

TCNE and TCNQ are organic radicals that are widely employed for constructing lanthanide-based molecular magnetic materials. In 2002 Miller and coworkers provided the first examples Ln[TCNE]₃ through the reaction of LnI₃ · xMeCN (Ln = Gd, Dy) and TCNE in acetonitrile and with thermal annealing [85], without the X-ray structure data, in which 4f elements coordinated to [TCNE][−] [65]. Both Gd[TCNE]₃ and Dy[TCNE]₃ possess $S = 1/2$ [TCNE][−], which weakly antiferromagnetically couples with RE ions and at low temperature exhibits a gradual magnetic phase transition to a ferrimagnetic state with a critical temperature of 8.5 (Dy) and 3.5 (Gd) K (Figure 9.8). The temperatures of the magnetic phase transitions are higher than those reported for the 1D-NITR chains presumably due to the 3D-magnetic interaction of the Ln(TCNE)₃ species.

Slow diffusion of deoxygenated water solutions of GdCl₃ · 6H₂O and Li[TCNQ] (1 : 1 ratio) yields crystals of {[Gd₂(TCNQ)₅(H₂O)₉][Gd(TCNQ)₄ · (H₂O)₃]} · 4H₂O [86], which consist of alternating anionic and cationic layers perpendicular to the *c*-axis, exhibiting different ratios of Gd(III) and TCNQ[−] radicals, both of which are based on a 2D-network of Gd(III) ions coordinated to TCNQ radical anions (Figure 9.9). The different ratios of Gd(III) and TCNQ[−] in the two independent layers leads to the unusual situation of having both cationic and anionic networks.

For this compound, susceptibility data fitting to the Curie–Weiss law for high-temperature gives a Curie constant of 27.1 emu K mol^{−1}, consistent with the expected value for three isolated Gd(III) ions ($S = 7/2$) and nine TCNQ[−] radical anions ($S = 1/2$) (27 emu K mol^{−1} for $g = 2$). The Weiss constant ($\theta = -5.07$ K) is small and negative, indicative of antiferromagnetic interactions between spin carriers. It is actually magnetically three-dimensional with multiple interactions: in addition to the intralayer interactions, including direct exchange (Gd–TCNQ) and superexchange (between TCNQ groups through the Gd bridges, and vice versa), there are also strong magnetic interactions between layers through the short p–p contacts between TCNQ units in adjacent layers. It is known that the latter type of interaction

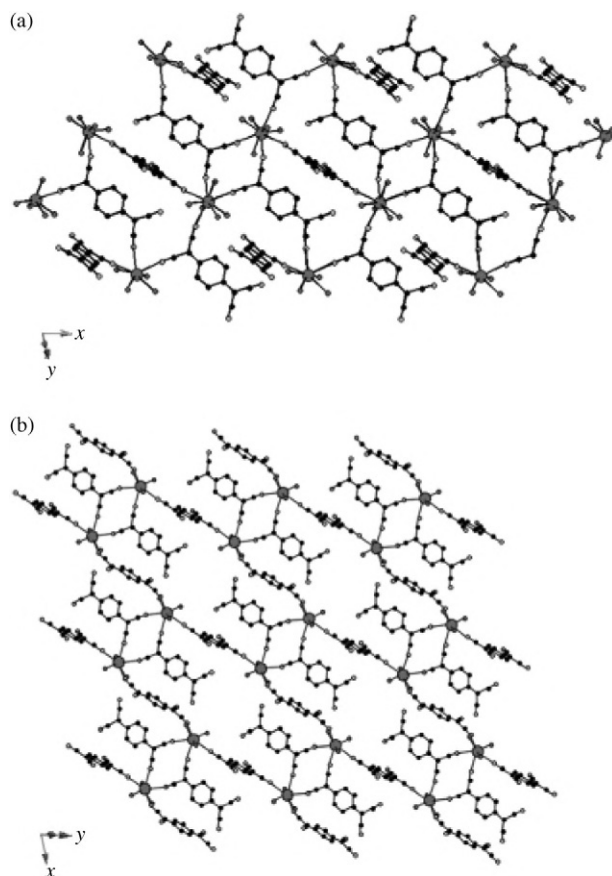


Figure 9.9 (a) Top view of the tetrameric chains and (b) the 2D-anionic network (terminal TCNQ have been omitted for clarity) in $\{[\text{Gd}_2(\text{TCNQ})_5(\text{H}_2\text{O})_9][\text{Gd}(\text{TCNQ})_4 \bullet (\text{H}_2\text{O})_3]\} \cdot 4\text{H}_2\text{O}$. [86]. (Reprinted with permission from H. Zhao, *et al.*, “A rare-earth metal TCNQ magnet: synthesis, structure, and magnetic properties of $\{[\text{Gd}_2(\text{TCNQ})_5(\text{H}_2\text{O})_9][\text{Gd}(\text{TCNQ})_4(\text{H}_2\text{O})_3]\} \cdot 4\text{H}_2\text{O}$,” *Angewandte Chemie International Edition*, 2003, **42**, 1015–1018 (Figure 2). © Wiley-VCH Verlag GmbH & Co. KGaA.)

is antiferromagnetic. It can be clearly seen from AC magnetic susceptibility measurements (Figure 9.10) that the material exhibits an out-of-phase signal at $T_c \sim 3.5$ K. This material is a ferrimagnet and behaves as a soft magnet without an obvious hysteric at 1.8 K. It is the third example of a lanthanide–organic radical based magnet and the first lanthanide–TCNQ magnet.

9.3.2 4f–3d Heterometallic Systems

Another type of lanthanide-containing magnetic materials are 4f–3d/4d heterometallic complexes, which have attracted much attention as part of the tremendous development of molecular magnetism [2, 3].

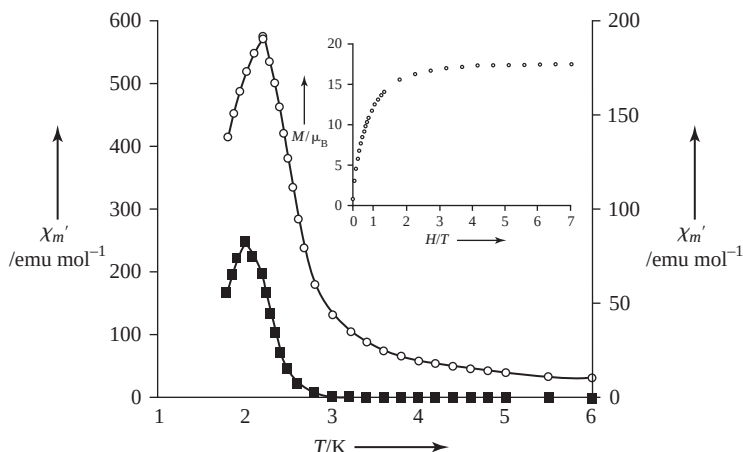


Figure 9.10 AC susceptibility data for $\{[\text{Gd}_2(\text{TCNQ})_5(\text{H}_2\text{O})_9][\text{Gd}(\text{TCNQ})_4 \cdot (\text{H}_2\text{O})_3]\} \cdot 4\text{H}_2\text{O}$, in-phase (empty circle), out-of-phase (solid square). Inset: plot of $M-H$ performed at 1.8 K [86]. (Reprinted with permission from H. Zhao, *et al.*, “A rare-earth metal TCNQ magnet: synthesis, structure, and magnetic properties of $\{[\text{Gd}_2(\text{TCNQ})_5(\text{H}_2\text{O})_9][\text{Gd}(\text{TCNQ})_4(\text{H}_2\text{O})_3]\} \cdot 4\text{H}_2\text{O}$,” *Angewandte Chemie International Edition*, 2003, **42**, 1015–1018 (Figure 2). © Wiley-VCH Verlag GmbH & Co. KGaA.)

On the borderline of molecular magnets, Prussian blue type derivatives can be cited [1]. $[\text{SmFe}(\text{CN})_6] \cdot 4\text{H}_2\text{O}$ and $[\text{TbCr}(\text{CN})_6] \cdot 4\text{H}_2\text{O}$ have a three-dimensional structure, which gives important magnetic properties. In fact, the former orders as a ferrimagnet at about 3.5 K with a strong coercive field, the latter has a critical temperature as high as 11.7 K. These compounds are a clear indication that provided the appropriate conditions are developed, interesting magnetic properties can be observed in compounds containing rare earth and transition metal ions [3].

A large family of heterometallic 4f–3d/4d coordination polymers have been constructed by using anionic polycyano complexes as building blocks [87], the most interesting systems of which are paramagnetic $[\text{M}(\text{CN})_6]^{3-}$ ($\text{M} = \text{Fe}, \text{Cr}$) [88] and $[\text{M}(\text{CN})_8]^{3-}$ ($\text{M} = \text{Mo}, \text{W}$) [89] tectons. Hexacyanometallates ($[\text{M}(\text{CN})_6]^{3-}$, $\text{M} = \text{Fe}, \text{Co}, \text{Cr}$, and so on) are the simple and direct building blocks for constructing cyano-bridged heterometal complexes, because the N ends of cyanide are strong donor atoms for linking two metal ions. A rational strategy for the synthesis of networks is the suitable combinations of cyanide-containing precursors and other coligands and adjusting their stoichiometries.

Adding DMF to the reaction system of $\text{Ln}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ and $\text{K}_3[\text{Cr}(\text{CN})_6]$, two 2D-iso-structural bimetallic complexes $[\text{Ln}(\text{DMF})_2(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_6] \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Gd}, \text{Sm}$) are obtained [50, 51], which consist of brick-wall type neutral layers with slightly distorted Cr_3Ln_3 rectangles (Figure 9.11a). In $[\text{Gd}(\text{DMF})_2(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_6] \cdot \text{H}_2\text{O}$, for instance, each $[\text{Cr}(\text{CN})_6]^{3-}$ unit uses three cyanide groups in the meridional arrangement to connect with three $[\text{Gd}(\text{DMF})_2(\text{H}_2\text{O})_3]^{2+}$ units. Each $[\text{Gd}(\text{DMF})_2(\text{H}_2\text{O})_3]^{2+}$ unit links three $[\text{Cr}(\text{CN})_6]^{3-}$ ions, with the bridging cyanides and the bridged metal ions lying in a plane. This local molecular disposition extends to generate a flat brick-wall type structure, which is the first cyano-bridged 3d–4f complex with such a topology. For the two compounds, the adjacent Ln(III) and Cr(III)

ions are AF (antiferromagnetic) coupled. In general, the compounds behave as metamagnets (Figure 9.11b), which is the first observation of the two-dimensional cyano-bridged 3d–4f complexes. Owing to the AF interaction between the ferrimagnetic layers, they reach a long-range antiferromagnetic ordering at 3.5 and 4.2 K, respectively.

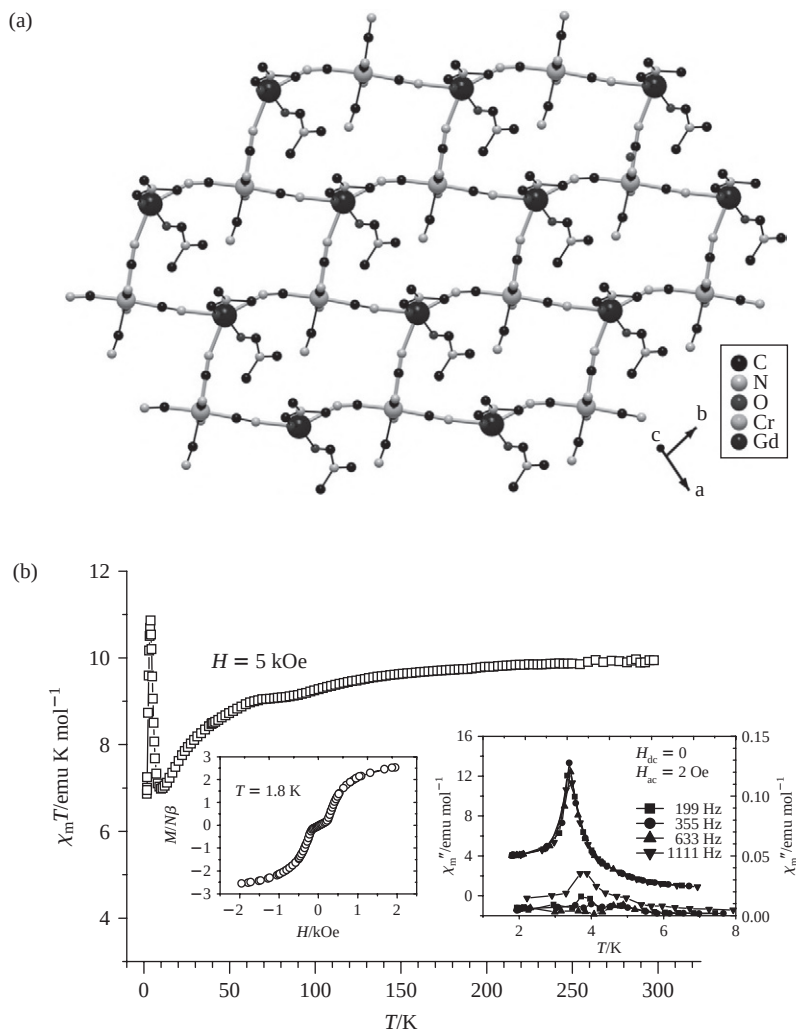


Figure 9.11 (a) Brick-wall-like structure of $[\text{Gd}(\text{DMF})_2(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_6] \cdot \text{H}_2\text{O}$. (b) Temperature dependence of $\chi_M T$ for $[\text{Gd}(\text{DMF})_2(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_6] \cdot \text{H}_2\text{O}$. Inset: left, isothermal magnetization at 1.8 K; right, real and imaginary AC susceptibilities in zero applied DC field and an AC field of 2 Oe at different frequencies [49]. (Reprinted with permission from H. Kou, *et al.*, “Metamagnetism of the first cyano-bridged two-dimensional brick-wall-like 4f-3d array,” *Chemistry of Materials*, **13**, 1431–1433, 2001. © 2001 American Chemical Society.)

Using 4,4'-bipyridine *N,N'*-dioxide (bpdo) as the bridging ligand, with polycyanometalate, six 2D-cyano-bpdo bridged 3d-4f compounds $[\text{Ln}(\text{III})(\text{bpdo})(\text{H}_2\text{O})_2\text{M}(\text{III})(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}$ with $\text{M} = \text{Fe}$; $\text{Ln} = \text{Nd}, \text{Sm}$ with $\text{M} = \text{Co}$) have been obtained [90]. They have the same 2D-corrugated grid-like layer structures (Figure 9.12), where each $[\text{M}(\text{CN})_6]^{3+}$ unit uses four coplanar cyanide groups to connect with four square anti-prism Ln^{3+} ions, and accordingly, each Ln^{3+} ion links four $[\text{M}(\text{CN})_6]^{3+}$ units. Simultaneously, the next nearest Ln^{3+} ions are bridged by bpdo in the diagonal direction from the same layer but not from two different layers, which play a special role in stabilizing the grid-like layer. Magnetic studies showed that the $\text{Ln}^{3+}-\text{Fe}^{3+}$ interaction is ferromagnetic for NdFe, antiferromagnetic for SmFe and GdFe, while negligible for TbFe. In particular, SmFe and GdFe compounds exhibit ferromagnetic orderings below 2.9 and 1.9 K, respectively. Meanwhile an NdCo compound shows an unusual field-induced magnetization relaxation.

A series of 1D-3d-4f complexes were prepared with $\text{M}(\text{CN})_6^{3-}$, Ln ions and 2,2'-bpy (bpy = bipyridyl) ligands, $\text{trans}-[\text{Ln}(\text{H}_2\text{O})_4(\text{bpy})(\mu-\text{CN})_2\text{M}(\text{CN})_4]_n \cdot X_n\text{H}_2\text{O} \cdot 1.5nbpy$ ($\text{M}^{3+} = \text{Fe}$ and $\text{Ln}^{3+} = \text{Sm}, \text{Dy}$; $\text{M}^{3+} = \text{Co}$ and $\text{Ln}^{3+} = \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$; $n = 4$ or 5) [91, 92].

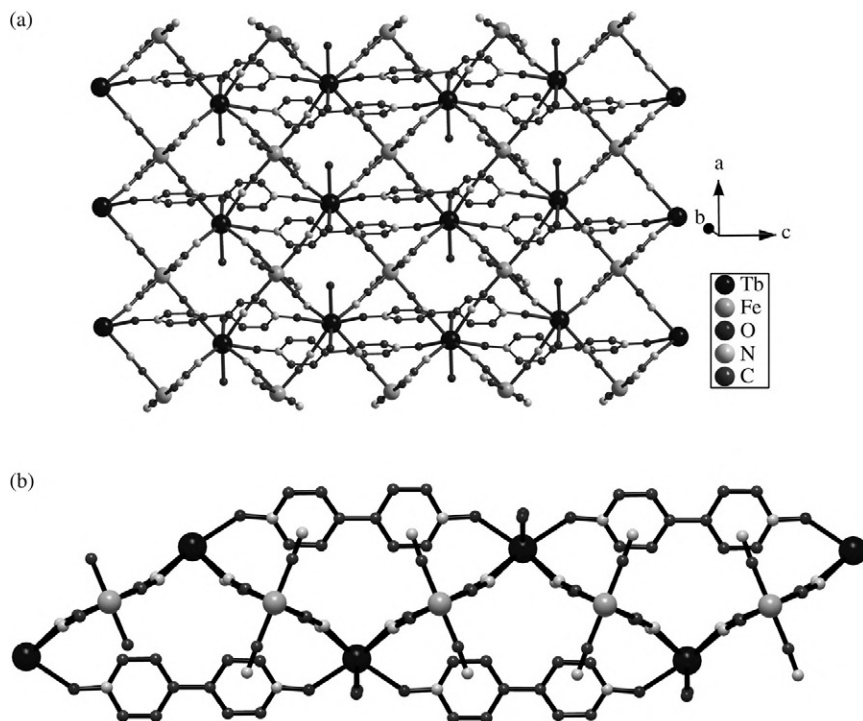


Figure 9.12 (a) The view of 2D grid-like $\text{Tb}^{3+} - \text{Fe}^{3+}$ layer mixed-bridged by cyanide and bpdo in the *ac* plane; (b) a projection of the corrugated layer.

All compounds confine isomorphous 1D-polymers (Figure 9.13a), which show an alternation of $\text{Ln}(\text{H}_2\text{O})_4(\text{bpy})$ and $\text{M}(\text{CN})_6$ ($\text{M}^{3+} = \text{Fe}, \text{Co}$) units linked by cyanide bridges in the *trans* geometry. A supramolecular 3D-network is given by hydrogen bonds and π - π interaction. Among these compounds, *trans*- $[\text{Sm}(\text{H}_2\text{O})_4(\text{bpy})(\mu\text{-CN})_2\text{Fe}(\text{CN})_4]_n \cdot 5n\text{H}_2\text{O} \cdot 1.5n\text{bpy}$ show weak ferromagnetic 3D-ordering. Susceptibility measurements were carried out in a range of low magnetic fields (Figure 9.13b). When the magnetic field decreased from 1000 to 10 Oe, the maximum susceptibility increased from 2.5 to 33 $\text{cm}^3 \text{mol}^{-1} \text{K}$. Zero-field cooling (ZFC) and field cooling (FC) measurements at 50 Oe indicate the onset of weak ferromagnetic 3D-ordering at 3.5 K (Figure 9.13c). The isothermal magnetization at 2.5 K (Figure 9.13c, inset) shows an obvious hysteresis, with the coercivity field $H_c \approx 137$ Oe, and the remnant magnetization $M_r = 0.08 \text{ N}\beta$. For the *trans*- $[\text{Dy}(\text{H}_2\text{O})_4(\text{bpy})(\mu\text{-CN})_2\text{Fe}(\text{CN})_4]_n \cdot 1.5n\text{bpy} \cdot 4n\text{H}_2\text{O}$ complex, the $\chi_M T$ value presents a maximum at 2.5 K in a low magnetic field. When the magnetic field decreases from 400 to 20 Oe, the maximum value of $\chi_M T$ increases from 11.36 to 12.63 $\text{cm}^3 \text{mol}^{-1} \text{K}$. And ZFC-FC measurements at 20 Oe show a bifurcation point at 2.5 K, which indicates the onset of weak ferromagnetic 3D ordering. The AC susceptibility shows a small frequency dependence of the peaks, attributed to the glassy behavior of the magnetically ordered state.

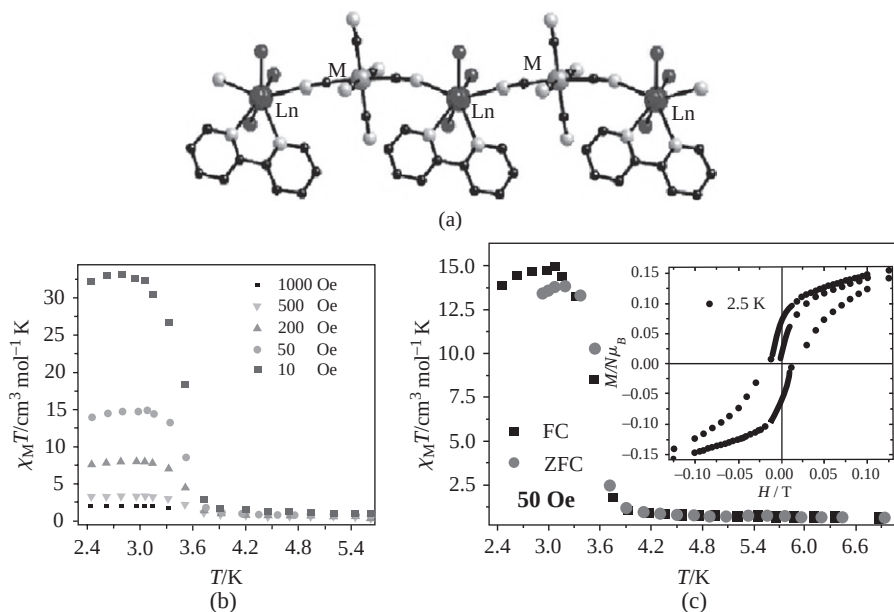


Figure 9.13 (a) The alternative chain structure of *trans*- $[\text{Ln}(\text{H}_2\text{O})_4(\text{bpy})(\mu\text{-CN})_2\text{M}(\text{CN})_4]_n \cdot Xn\text{H}_2\text{O} \cdot 1.5n\text{bpy}$; (b) thermal dependence at different low fields (from 1000 to 10 Oe) of $\chi_M T$ for $[\text{Sm}(\text{H}_2\text{O})_4(\text{bpy})(\mu\text{-CN})_2\text{Fe}(\text{CN})_4]_n \cdot 5n\text{H}_2\text{O} \cdot 1.5n\text{bpy}$; and (c) thermal dependence of $\chi_M T$ for $[\text{Sm}(\text{H}_2\text{O})_4(\text{bpy})(\mu\text{-CN})_2\text{Fe}(\text{CN})_4]_n \cdot 5n\text{H}_2\text{O} \cdot 1.5n\text{bpy}$, cooled in zero field (ZFC) and in a field of 50 Oe (FC). Inset: hysteresis cycle at 2.5 K [91]. (Reprinted with permission from A. Figuerola, *et al.*, "Magnetism of cyano-bridged hetero-one-dimensional $\text{Ln}^{3+} - \text{M}^{3+}$ Complexes ($\text{Ln}^{3+} = \text{Sm}, \text{Gd}, \text{Yb}$; $\text{M}^{3+} = \text{FeLS}, \text{Co}$)," *Inorganic Chemistry*, **42**, 5274–5281, 2003. © 2003 American Chemical Society.)

Isomorphous complexes *trans*-[Sm(H₂O)₄(bpy)(μ-CN)₂Cr(CN)₄]_n·3.5nH₂O·1.5nbpy [93, 94] were obtained using [Fe(CN)₆]³⁻ instead of [Cr(CN)₆]³⁻. For this complex, susceptibility measurements at low temperature were carried out at a range of low magnetic fields (Figure 9.14). When the magnetic field decreased from 1000 to 50 Oe, the $\chi_M T$ value increased from 14.32 to 37.53 cm³ mol⁻¹ K at 2 K, which indicates the onset of a weak ferromagnetic 3D-ordering. The magnetic transition temperature, T_c , is lower than 2 K, because a signal of χ' appears in a plot of the temperature dependency of the AC susceptibility, but a maximum in the χ'' versus T curve is not observed.

Inserting [M(CN)₆]³⁻ ions to the 3d–4f compounds, a few 3d–3d'–4f coordination polymers constructed from oligonuclear 3d–4f complexes as nodes are obtained [95–97]. One of these compounds, [Co(II)₂Gd(III)L₂(H₂O)₄{Cr(III)(CN)₆}]·2H₂O [H₂L = 2,6-di(acetoacetyl)pyridine], is a 3D-network exhibiting 3D-ferromagnetic ordering with T_c = 15.4 K. This is the highest critical temperature among PB (Prussian Blue) analogs incorporating lanthanide ions [95].

Using *N,N*-dimethylacetamide (DMA) as a hybrid ligand, three cyano-bridged lanthanide complexes {[Sm(DMA)₂(H₂O)₄Fe(CN)₆]·5H₂O}_n, [(Gd(DMA)₃(H₂O)₄)₂Fe(CN)₆]·[Fe(CN)₆]·3H₂O and [Ho(DMA)₃(H₂O)₃Fe(CN)₆]·3H₂O were synthesized by the reaction of K₃Fe(CN)₆, Ln(NO₃)₃·6H₂O, and DMA [98]. Only the SmFe compound shows long range ordering.

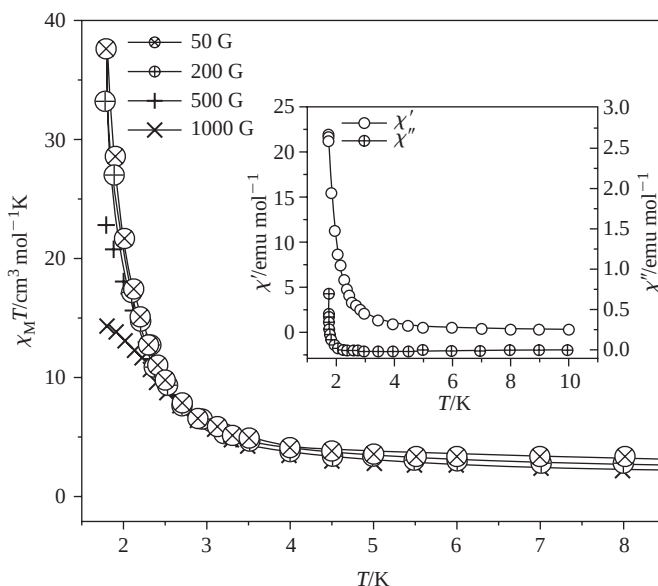


Figure 9.14 Thermal dependence at different fields of $\chi_M T$ for [Sm(H₂O)₄(bpy)(μ-CN)₂Cr(CN)₄]_n·3.5nH₂O·1.5nbpy. Inset: plot in the in-phase and out of phase components of the AC susceptibility at 1500, 1000, 750, 500, 100, and 50 Hz [93]. (Reprinted with permission from M. Estrader, *et al.*, "Crystal structure, and magnetic studies of one-dimensional cyano-bridged Ln³⁺ – Cr³⁺ complexes with bpy as a blocking ligand," *Inorganic Chemistry*, **45**, 8239–8250, 2006. © 2006 American Chemical Society.)

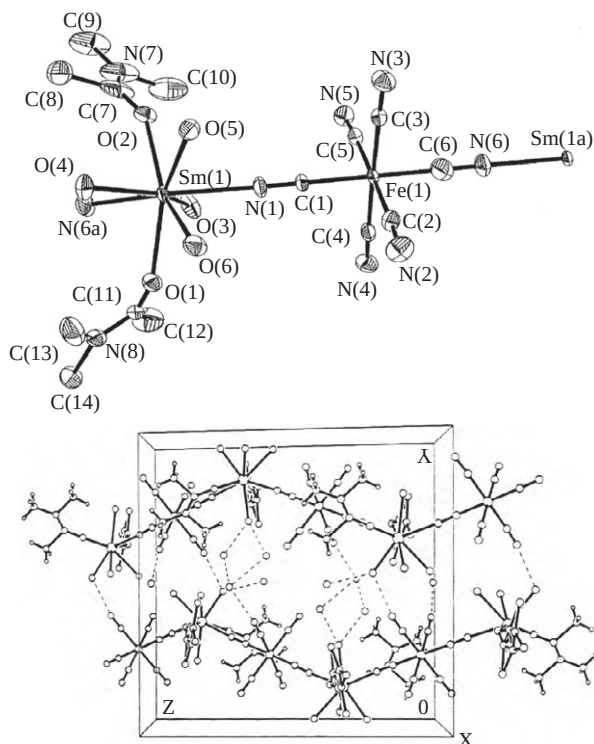


Figure 9.15 ORTEP plot (upper) and unit-cell packing diagram of the complex $[\text{SmFe}]_n$ [99]. (Reprinted with permission from B. Yan, and Z. Chen, “Cyano-bridged aqua(*N,N*-dimethylacetamide)(cyanoiron)lanthanides from samarium, gadolinium, or holmium nitrate and potassium hexacyanoferrate: crystal structures and magnetochemistry,” *Helvetica Chimica Acta*, 2001, **84**, 817–829 (Figures 1 and 2). © Wiley-VCH Verlag GmbH & Co. KGaA.)

Compound $\{[\text{Sm}(\text{DMA})_2(\text{H}_2\text{O})_4\text{Fe}(\text{CN})_6 \cdot 5\text{H}_2\text{O}]_n\}$ has a one-dimensional chain structure with approximately parallel *trans*-positioned bridging CN ligands between the Sm and Fe atoms (Figure 9.15). The Sm atom is eight-coordinate, bound by six O atoms of the two DMA molecules and four H_2O molecules as well as by two N atoms from the two bridging CN ligands. The geometry of the $\text{Fe}(\text{CN})_6^{3-}$ group is an approximate octahedron with the coordination of six CN ligands. The SmFe chains are stacked to form a 3D extended structure through two types of H-bonding. One is the intramolecular H-bond between the coordinated H_2O molecule in one complex unit and the CN of another complex unit. Another is the intermolecular H-bond involving an uncoordinated H_2O molecule present in the space within the unit cell of the complex. The O-atom of the uncoordinated H_2O molecule forms the H-bond with the coordinated H_2O molecule, while the uncoordinated H_2O molecule forms the other H-bond with the terminal CN group, thus representing an intermolecular H-bond tetrahedron.

The $\chi_{\text{M}}T$ value of $[\text{SmFe}]_n$ decreases from $1.632 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K to $0.533 \text{ cm}^3 \text{ K mol}^{-1}$ at 8.85 K, then sharply increases. The temperature dependent susceptibility of the $[\text{SmFe}]_n$, ranging from 1.8 to 9 K (Figure 9.16), suggests a weak ferrimagnetic behavior,

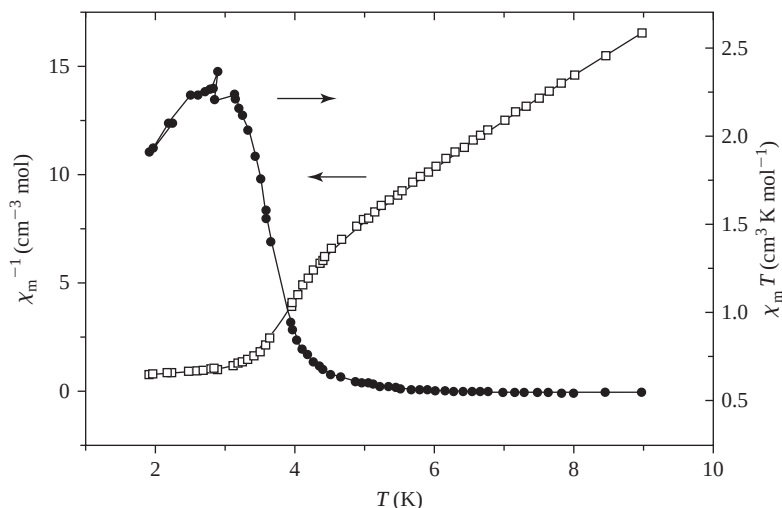


Figure 9.16 Variable low-temperature (1.8–9 K) susceptibility of the complex $[\text{SmFe}]_n$ under external field $H = 1000$ Oe [99]. (Reprinted with permission from B. Yan, and Z. Chen, “Cyano-bridged aqua(*N,N*-dimethylacetamide)(cyanoiron)lanthanides from samarium, gadolinium, or holmium nitrate and potassium hexacyanoferrate: crystal structures and magnetochemistry,” *Helvetica Chimica Acta*, 2001, **84**, 817–829 (Figure 6). © Wiley-VCH Verlag GmbH & Co. KGaA.)

which indicates the onset of three-dimensional magnetic ordering. The temperature dependence of AC susceptibility shows that both in-phase, and out-of-phase components exist in the temperature range 2.2–5.5 K (Figure 9.17). The observation of χ'' is due to a long-range magnetic ordering to a certain extent. The best determination of T_c is 3.5 K through the first χ' (T) peak maximum. The hysteresis loop reveals a stronger coercive field H_c of 1400 Oe and a remnant magnetization M_R of $0.11 N\beta \text{ mol}^{-1}$.

Reaction of $\text{K}_3\text{Mn}(\text{CN})_6$, DMF, and $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{Tb}$, Dy or Er) affords cyano-bridged complexes, $\text{Ln}(\text{DMF})_4(\text{H}_2\text{O})_2\text{Mn}(\text{CN})_6 \cdot \text{H}_2\text{O}$ (TbMn , DyMn , and ErMn , respectively) [99]. In particular, among these compounds $\text{Er}(\text{DMF})_4(\text{H}_2\text{O})_2\text{Mn}(\text{CN})_6 \cdot \text{H}_2\text{O}$ is the only compound that exhibits long-range magnetic ordering.

The DC temperature dependent magnetic behavior (Figure 9.18) of compound ErMn is similar to that of compound $[\text{SmFe}]_n$. The critical temperature is determined to be 17.5 K by the $\chi'(T)$ peak maximum. Figure 9.19 provides the field-dependent magnetization hysteresis data for the ErMn complex under the applied magnetic field from -2000 to $+2000$ Oe at 5.7 K, which reveals a stronger coercive field H_c of 980 Oe and a remnant magnetization M_R of $0.03 N\beta \text{ mol}^{-1}$.

Thus, so far not many 3D-magnetic ordered lanthanide-based molecular materials have been obtained. However, the existing examples, including the lanthanide–radical systems and lanthanide–transition metals, provide us with much experimental and theoretical knowledge and experience. The research into 3D-magnetic ordered lanthanide-based molecular materials is still an open subject for chemists and physicists.

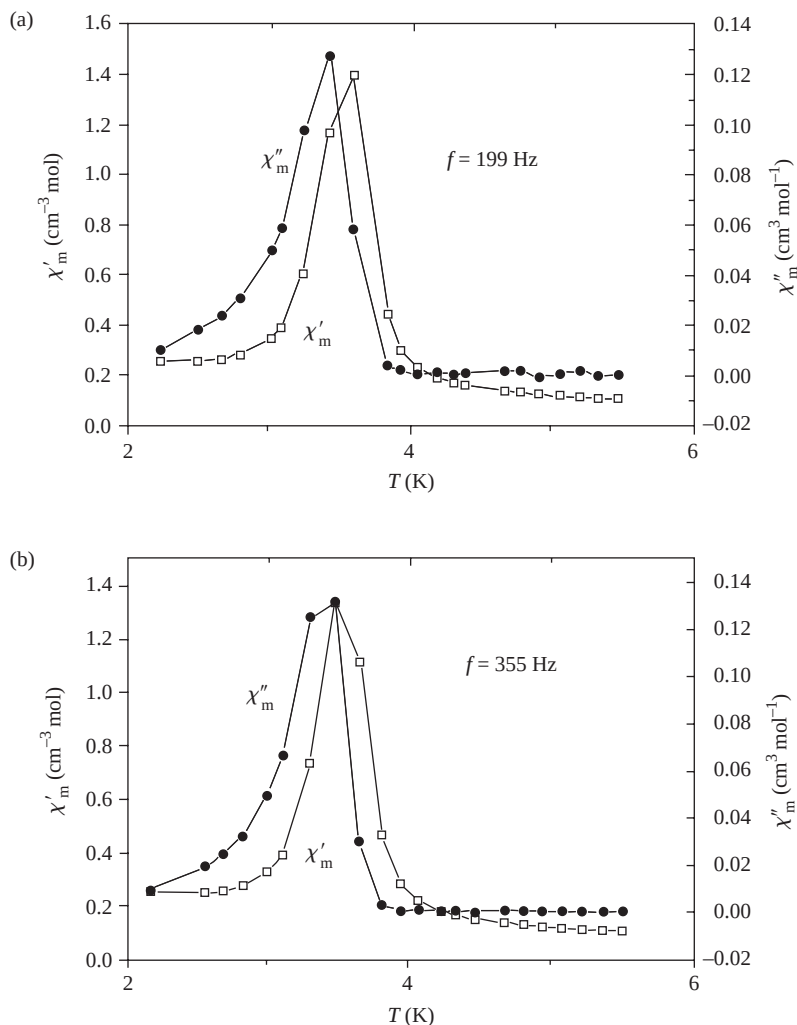


Figure 9.17 Plot of the in-phase and out-of-phase AC magnetic susceptibility for the complex $[\text{SmFe}]_n$ at driving frequency of 199 Hz and 355 Hz [98]. (Reprinted with permission from B. Yan, and Z. Chen, “Cyano-bridged aqua(*N,N*-dimethylacetamide)(cyanoiron)lanthanides from samarium, gadolinium, or holmium nitrate and potassium hexacyanoferrate: crystal structures and magnetochemistry,” *Helvetica Chimica Acta*, 2001, **84**, 817–829 (Figure 7). © Wiley-VCH Verlag GmbH & Co. KGaA.)

9.4 Magnetic Relaxation in Lanthanide Containing Molecular Materials

9.4.1 Introduction to Magnetic Relaxation

Relaxation is the process involved when a system in an equilibrium state is perturbed and moves to a new equilibrium state. The time between the two equilibrium states is called the relaxation time. In a magnetic relaxation, the perturbation is a change in the magnetic field.

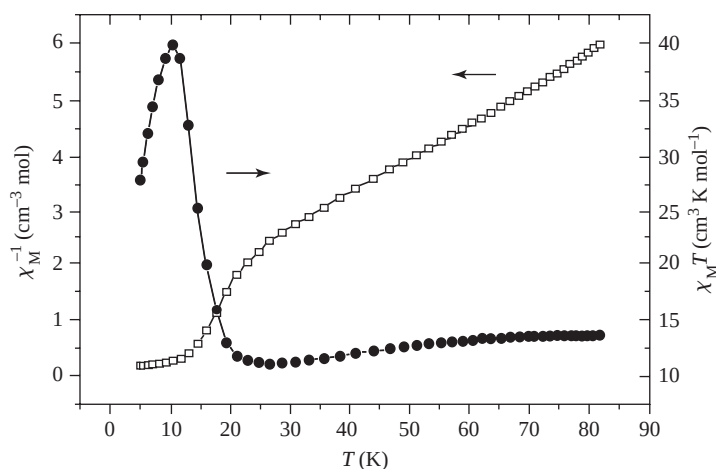


Figure 9.18 Variable temperature (4–82 K) susceptibility for ErMn [99]. (With kind permission from Springer Science+Business Media: *Transition Metal Chemistry*, “The magnetochemistry of novel cyano-bridged complexes $\text{Ln}(\text{DMF})_4(\text{H}_2\text{O})_2\text{Mn}(\text{CN})_6 \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{Tb}, \text{Dy}, \text{Er}$),” **26**, © 2001, 287–289, B. Yan, and Z. Chen.)

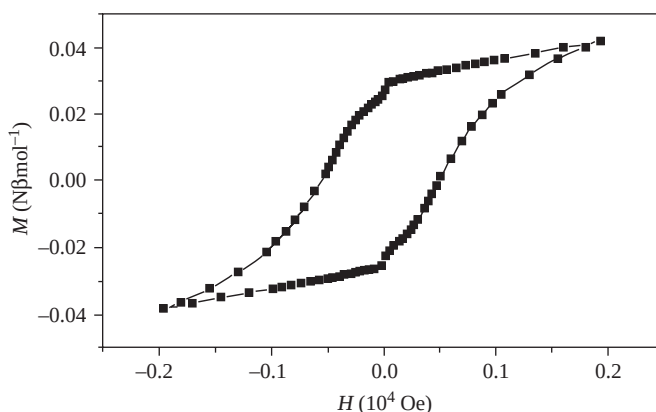


Figure 9.19 Hysteresis loop for ErMn at 5.7 K [99]. (With kind permission from Springer Science + Business Media: *Transition Metal Chemistry*, “The magnetochemistry of novel cyano-bridged complexes $\text{Ln}(\text{DMF})_4(\text{H}_2\text{O})_2\text{Mn}(\text{CN})_6 \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{Tb}, \text{Dy}, \text{Er}$),” **26**, © 2001, 287–289, B. Yan, and Z. Chen.)

Magnetic relaxation time τ , is the parameter that describes the magnetic relaxation process, during which the magnetization M_t will reach a new equilibrium value M_0 after a change of the magnetic field from H to $H + \Delta H$, as shown in Equation 9.5:

$$\frac{dm_z}{dt} = \frac{M_0 - M_z}{\tau} \quad (9.5)$$

9.4.1.1 AC Susceptibility

Alternating current susceptibility [100, 101] (AC susceptibility), χ_{AC} , is the most widely used parameter to characterize the dynamic behavior of the relaxation system. The AC susceptibility is a function of the frequency of the alternating field, where the static field (which may be zero) is parallel to the AC field. χ_{AC} is a complex value, combined from two parts, in-phase and out-of-phase.

$$\text{For an alternating field: } H(t) = H_0 + h \cos(\omega t) \quad (9.6)$$

where

H_0 is a constant (which may be zero) on behalf of the static field

h is the amplitude of the oscillating field

$$\omega = 2\pi f$$

f is the frequency of the oscillating field.

Any harmonic function with the form $A(t) = a \cos(\omega t + \alpha)$ can be rewritten in a complex form $A(t) = ae^{i(\omega t + \alpha)}$, which can be expanded as $A(t) = a \cos(\omega t + \alpha) + ia \sin(\omega t + \alpha)$. So the complex form of the oscillating field can be written as:

$$\begin{aligned} H_{AC}(t) &= H_0 + h \cos(\omega t) + ih \sin(\omega t) \\ &= H_0 + he^{i\omega t} \end{aligned} \quad (9.7)$$

The magnetization related to the oscillating field is delayed because of the relaxation. The delay, which is a function of the frequency, is described by phase angle as follows:

$$M(t) = M_0 + m \cos(\omega t - \theta) \quad (9.8)$$

Its complex form is:

$$\begin{aligned} M_{AC}(t) &= M_0 + m \cos(\omega t - \theta) + im \sin(\omega t - \theta) \\ &= M_0 + me^{i(\omega t - \theta)} \end{aligned} \quad (9.9)$$

AC susceptibility is also known as dynamic or differential susceptibility, which is defined as response of the magnetization to a small change in the AC field: $\chi_{AC} = dM/dH$, then one obtains:

$$\chi_{AC}(\omega) = \frac{me^{i(\omega t - \theta)}}{he^{i\omega t}} = \frac{m}{h} e^{-i\theta} = \frac{m}{h} \cos \theta - i \frac{m}{h} \sin \theta \quad (9.10)$$

Taking

$$\chi' = \frac{m}{h} \cos \theta \text{ and } \chi'' = \frac{m}{h} \sin \theta \quad (9.11)$$

the AC susceptibility can be expressed as:

$$\chi_{AC}(\omega) = \chi'(\omega) - i\chi''(\omega) \quad (9.12)$$

χ' is the in-phase response with the driven field $H(t)$, which is known as magnetic dispersion, and χ'' is the out-of-phase one, which describes the energy absorption from the field, and is always referred to as magnetic absorption.

AC susceptibility is a function of frequency, which means that, at a certain temperature, a series of in-phase and out-of-phase susceptibilities can be obtained by scanning the frequency. A plot of a series of χ'' versus χ' is an Argand diagram [102], which is a semicircle if only one relaxation process occurs. This type of plotting is referred to as Colo-Colo analysis.

9.4.1.2 Spin–Lattice Relaxation and Spin–Spin Relaxation

A magnetic relaxation process is always involved in energy exchange, and the exchange of energy between the spin centers is much faster (by several orders) than that between spin and the crystal lattice. The energy exchange between spin centers is called spin–spin relaxation and that between spin and the crystal lattice vibrations is called spin–lattice relaxation.

The spin–lattice relaxation is enabled via spin–orbital coupling involving a phonon process. Spin–lattice relaxation time (τ_{SL}) is temperature dependent. Generally speaking, τ_{SL} becomes smaller on increasing the temperature. One can distinguish three types of spin–lattice relaxation processes [103]:

- 1) **Direct process:** the spin center transfer to another energy level by absorption or emission of one phonon.
- 2) **Raman process:** the spin center transfer to another energy level via a virtual state involving two phonons and this is called non-resonance scattering process.
- 3) **Orbach process:** the spin center transfer to another energy level via a real intermediate state involving two phonons through a resonant process.

In the following equations the temperature and field dependence of the spin–lattice relaxation time are given. One must realize that these relationships are over simplified.

$$\frac{1}{\tau_{\text{SL}}} = A_1 H^2 T + B_1 T^7 + C_1 \exp(-\Delta/k_B T) \quad (9.13)$$

$$\frac{1}{\tau_{\text{SL}}} = A_2 H^4 T + B_2 T^9 + C_2 \exp(-\Delta/k_B T) \quad (9.14)$$

$$\frac{1}{\tau_{\text{SL}}} = A_3 H^2 T + B_3 T^5 \quad (9.15)$$

The first equation refers to non-Kramer ions; the second refers to Kramer ions where the energy between doublets is sufficiently large compared with $k_B T$; the third refers to Kramer ions' doublets where the energy gap is small compared with $k_B T$. The term in the equations with the coefficient A is the direct process part; the terms with coefficients B and C refer to Raman and Orbach process, respectively.

Spin–spin relaxation time (τ_{SS}) is much smaller than τ_{SL} and it is temperature independent. The τ_{SL} is of the order of 10^{-10} s, because of the fast rate of the spin-spin relaxation, one can only observe it at very low temperatures and with a high frequency oscillating field.

9.4.2 Magnetic Relaxation in Lanthanide Containing Complexes

The magnetic relaxation phenomena in lanthanide containing complexes covers a wide range, among which the single-molecule magnets (SMMs) and single-chain magnets (SCMs) are the two most important families.

9.4.2.1 Single-Molecule Magnets Including Lanthanide Ions

A single-molecule magnet [104] is an object composed of molecules each of which behaves as a superparamagnet. Different from traditional magnets, SMMs cannot participate in long-range ordering, which means that in SMMs, the unpaired spins cannot align parallel to each other in domains spontaneously. In contrast, the interaction between clusters in SMMs can be negligible. We consider SMMs as a type of magnet because they possess the capability of holding the spin state under blocking temperature (T_B) just as traditional magnets do under Curie (T_C , for ferromagnet) or Neel (T_N , for antiferromagnet) temperature. SMM clusters possess a high spin ground state (S_T) and a high negative zero field splitting value (D) due to high uniaxial magnetic anisotropy. Owing to the two properties above, a large energy barrier (ΔE) between the two possible ground spin states exists [$\Delta E = |D|S_T^2$ for integer S_T , and $\Delta E = |D|(S_T^2 - 1/4)$ for half integer S_T], which give rise to SMMs holding the spin state under T_B . SMMs exhibit stair like magnetization hysteretic loops under T_B , where the step substructures arise from the quantum-tunneling effect between degenerate spin states under certain magnetic fields. Under T_B , with thermal perturbation, SMMs can relax to another ground spin state, and this relaxation time (τ) obeys the thermally activated Arrhenius law:

$$\tau(T) = \tau_0 \exp(\Delta E/k_B T) \quad (9.16)$$

It can be easily found that, with a larger energy barrier, the relaxation time will be longer and the blocking temperature will be higher. In order to make use of the extraordinary properties of SMMs, it is very important to increase the ground state spin value and uniaxial magnetic anisotropy. Because of the heavier weight of lanthanide atoms, the relativistic effect is more apparent, which make the spin-orbit coupling stronger, resulting in the stronger anisotropy. It is believed that introducing lanthanide ions into the molecules will enhance the properties of the SMM, and some lanthanide containing compounds were discovered to behave as SMMs.

To design SMMs, the most frequently used lanthanide ions are heavy rare earth ions: terbium (Tb^{3+} , f^8 , ground state $^7F_6$), dysprosium (Dy^{3+} , f^9 , ground state $^6H_{15/2}$), and holmium (Ho^{3+} , f^{10} , ground state $^5I_8$), because of their large uniaxial anisotropy and large ground state.

The first example of a lanthanide containing SMM is the $[Cu-L-Ln(hfac)_2]_2$ cluster [105], where $H_3L = 1-(2\text{-hydroxybenzamido})-2-(2\text{-hydroxy-3-methoxy-benzylideneamino})\text{-ethane}$, $Hhfac = \text{hexafluoroacetylacetone}$, and $Ln = Tb^{3+}$ and Dy^{3+} . For the $[Cu-L-Tb(hfac)_2]_2$ cluster, at a 3 Oe oscillating field in the frequency range from 20 to 1000 Hz at a zero static field, the out-of-phase susceptibility shows frequency-dependent peaks (Figure 9.20), which indicates the slow relaxation of the magnetization. By varying the frequency, the χ_M'' curves reach peaks at different temperatures. The relaxation rate at the peak temperature is equal to the frequency. Through Arrhenius analysis, the energy barrier is 21 K and relaxation time constant is 2.7×10^{-8} s. For the $[Cu-L-Dy(hfac)_2]_2$ cluster, the χ_M'' signal shows frequency dependence but, unfortunately, no peak is observed down to 2 K.

Another example of SMM including a dysprosium ion is $[Dy(hfac)_3]_2Cu(dpk)_2$ [106], where $dpk = \text{di-2-pyridyl ketoximate}$. On taking the alternating current susceptibility measurements at from 2 to 17 K at 50–10000 Hz, both the in-phase and out-of-phase susceptibilities are found to be frequency dependent (Figure 9.21). On cooling from 12 to 8 K, the increment of χ_M'' is found together with the decrement of χ_M' . The energy barrier is found to be 47 K and τ_0 is 1.1×10^{-7} s. Additionally, these workers plotted χ_M'' against χ_M' as shown in Figure 9.21b, at

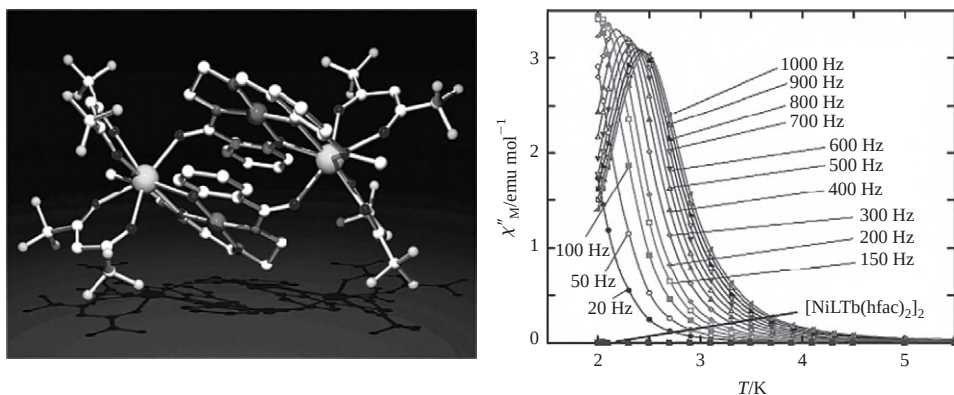


Figure 9.20 The structure of the [Cu-L-Tb(hfac)₂]₂ cluster and its relaxation behavior [106]. (Reprinted with permission from S. Osa, *et al.*, “A tetranuclear 3d-4f single molecule magnet: [Cu^{II}LTb^{III}(hfac)₂]₂,” *Journal of the American Chemical Society*, **126**, 420–421, 2004. © 2004 American Chemical Society.)

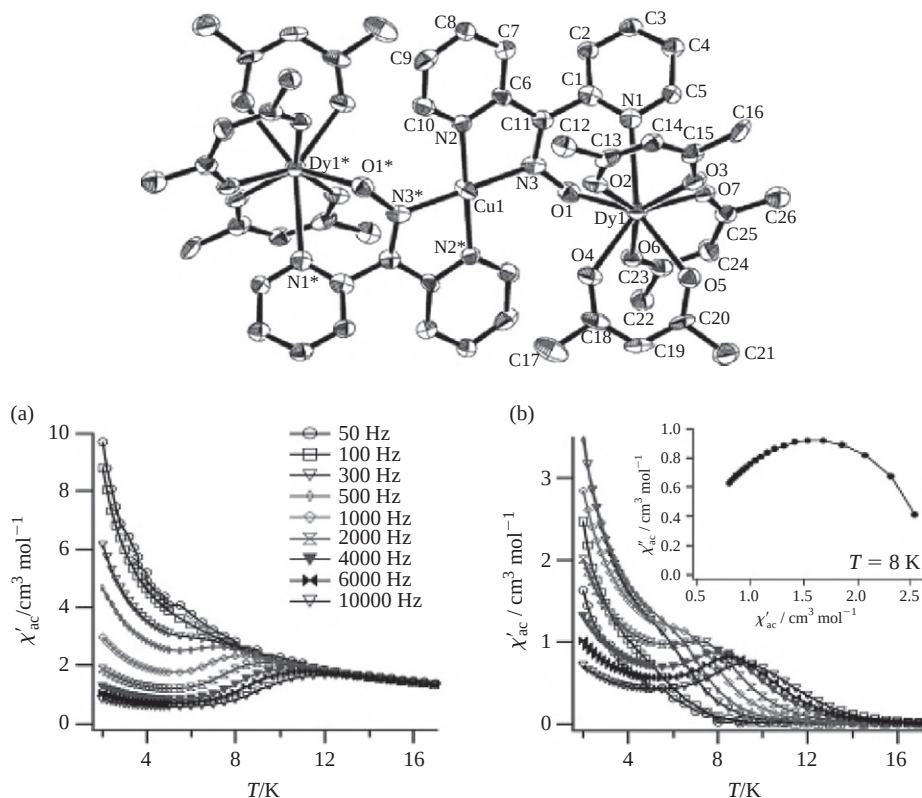


Figure 9.21 The structure of [Dy(hfac)₃]₂Cu(dpk)₂ and the frequency dependence of its AC susceptibility [106]. (Reprinted with permission from F. Mori, *et al.*, “Oximate-bridged trinuclear Dy-Cu-Dy complex behaving as a single-molecule magnet and its mechanistic investigation,” *Journal of the American Chemical Society*, **128**, 1440–1441, 2006. © 2006 American Chemical Society.)

8 K and from 50 to 10 000 Hz, and a semicircle was found, which indicates a single relaxation process. Another increment of χ_M'' and χ_M' is found below 6 K, and this type of increment is also found in other systems [107–109]. It is suggested that intermolecular interactions in such low temperature regions may give rise to the phenomena.

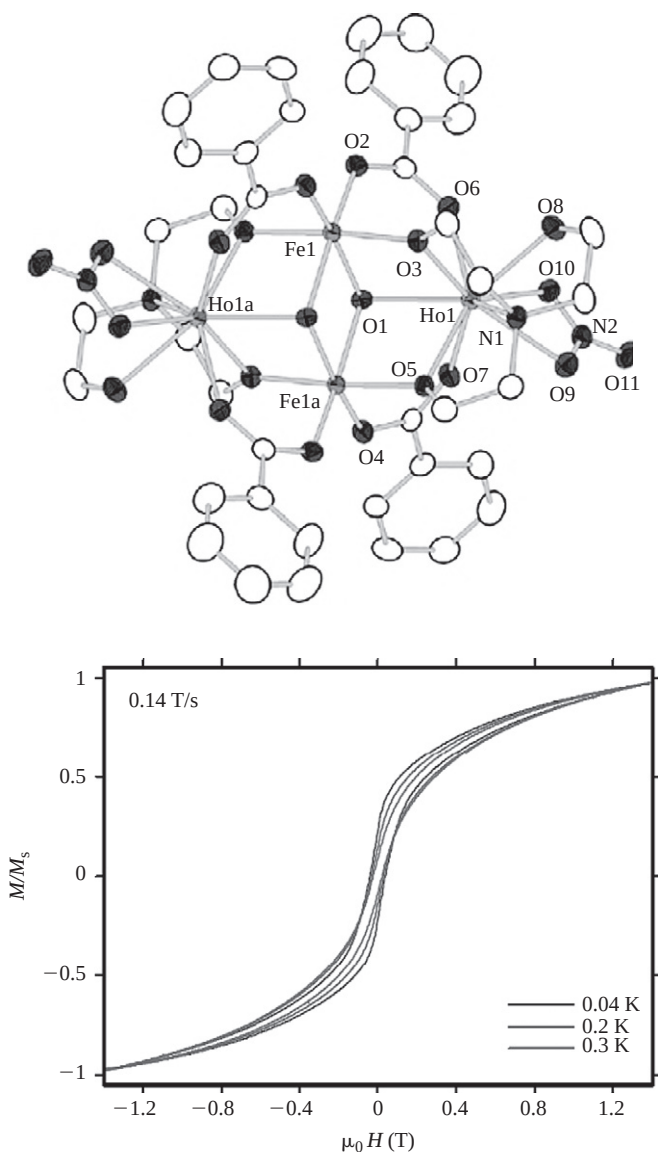


Figure 9.22 The structure of $[\text{Fe}_2\text{Ho}_2(\text{OH})_2(\text{teaH})_2(\text{O}_2\text{CPh})_4(\text{NO}_3)_2] \cdot 6\text{CH}_3\text{CN}$ and its hysteresis loops measured in micro-SQUID [110]. (Reprinted from *Polyhedron*, **25**, M. Murugesu, *et al.*, “Mixed 3d/4d and 3d/4f metal clusters: tetranuclear image and image complexes, and the first Fe/4f single-molecule magnets,” 613–625, 2006, with permission from Elsevier.)

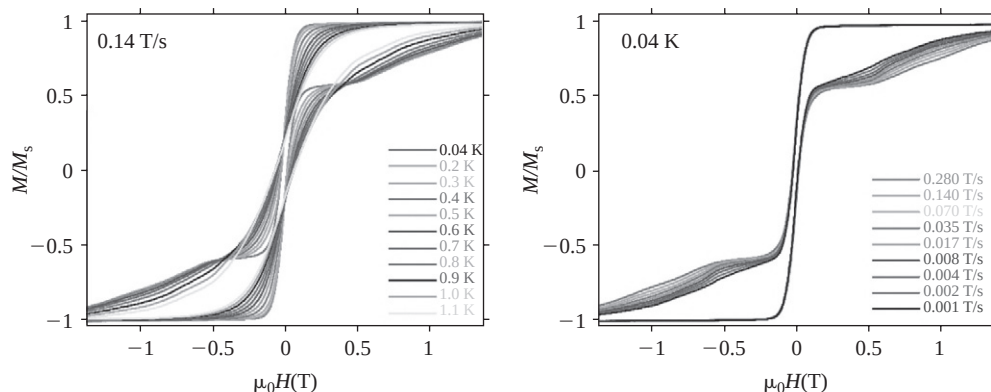


Figure 9.23 The hysteresis loops of $[\text{Fe}_2\text{Dy}_2(\text{OH})_2(\text{teaH})_2(\text{O}_2\text{CPh})_6]$ [110]. (Reprinted from *Polyhedron*, 25, M. Murugesu, *et al.*, “Mixed 3d/4d and 3d/4f metal clusters: tetranuclear image and image complexes, and the first Fe/4f single-molecule magnets,” 613–625, 2006, with permission from Elsevier.)

A tetranuclear Fe_2Ho_2 complex $[\text{Fe}_2\text{Ho}_2(\text{OH})_2(\text{teaH})_2(\text{O}_2\text{CPh})_4(\text{NO}_3)_2] \cdot 6\text{CH}_3\text{CN}$ can be used as an example of a holmium ion included SMM [110], where teaH = triethanolamine. AC susceptibility measurements were taken in the 1.8–10 K range using a 3.5 Oe oscillating field at 50–1000 Hz. The results indicate that the magnetic moment of this compound cannot relax fast enough to keep up with the AC field, and as a result, no clear χ_M'' signal is found. These workers chose a single crystal to take a micro-SQUID (Superconducting Quantum Interference Device) measurement down to milli-Kelvin temperatures. At temperatures of 0.3 K and below and a 0.14 T s^{-1} applied field sweep rate, hysteresis loops are observed, which are slightly temperature dependent (Figure 9.22), and with lower temperatures, the coercivity is larger. However, after studying the crystal structure of the complex in detail, it was considered that the hysteresis loop resulted from the ordering. Intermolecular π – π stacking overlaps ($3.7 \text{ \AA}$) between the aromatic rings of benzoate groups might be the pathway for intermolecular exchange interactions. For this reason, this compound could be regarded as an exchange-biased SMM at best, although it is clearly difficult to separate the intermolecular interactions and the SMM behavior.

By changing the Ho^{3+} to Dy^{3+} a similar structure complex $[\text{Fe}_2\text{Dy}_2(\text{OH})_2(\text{teaH})_2(\text{O}_2\text{CPh})_6]$ was obtained. Similarly, AC susceptibility measurements revealed no clear χ_M'' signal. However, a series of stair-like hysteresis loops were observed below 1.1 K at 0.14 T s^{-1} by micro-SQUID measurement (Figure 9.23). By changing field increasing rate from 0.001 to 0.280 T s^{-1} , two clear steps can be found at 0 and 0.5 T, respectively, where the fast quantum tunneling of magnetization occurs, and this can be considered as the evidence for SMM. From this example we know that the intermolecular interaction which may induce ordering must be avoided.

Gadolinium ions possess an f^7 configuration and an $^8S_{7/2}$ singlet ground state. In principle, the orbit angular momentum is zero and no spin–orbit coupling occurs, which means the gadolinium ion is an isotropic ion. However, some examples of SMMs including Gd^{3+} have been found [111, 112]. Gd–Mn will be used as an example

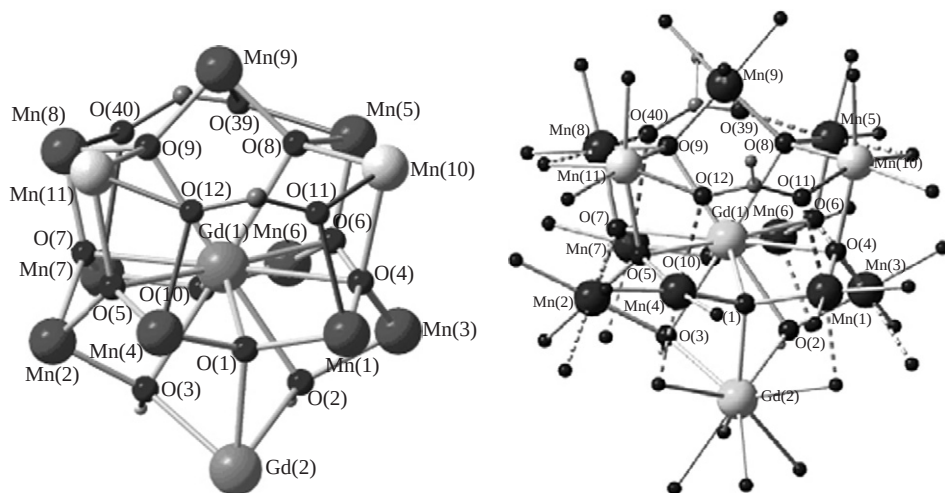


Figure 9.24 The structure of $\text{Mn}_{11}\text{Gd}_2$ cluster [111]. (Reprinted with permission from V.M. Mereacre, *et al.*, “A bell-shaped $\text{Mn}_{11}\text{Gd}_2$ single-molecule magnet,” *Journal of the American Chemical Society*, **129**, 9248–9249, 2007. © 2007 American Chemical Society.)

[111]. This compound is a high-nuclearity complex with the formula $[\text{Mn}(\text{III})_9\text{Mn}(\text{II})_2\text{Gd}(\text{III})_2\text{O}_8(\text{OH})_2(\text{piv})_{10.6}(\text{fca})_{6.4}(\text{NO}_3)_2(\text{H}_2\text{O})] \cdot 13\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$, where $\text{pivH} = t\text{-BuCOOH}$, $\text{fcaH} = 2\text{-furan-carboxylic acid}$. The 13-nuclei complex can be described as bell-shaped and the two Gd ions are the bell’s clapper (Figure 9.24).

The DC magnetic susceptibility of the complex measured at 1000 Oe from 1.8 to 300 K revealed a room temperature $\chi_{\text{M}}T$ value of $46.9 \text{ cm}^3\text{K mol}^{-1}$ (Figure 9.25). $\chi_{\text{M}}T$ decreased and reached $35.2 \text{ cm}^3\text{K mol}^{-1}$ at 37 K and then increased to a maximum value at 1.81 K of $74.5 \text{ cm}^3\text{K mol}^{-1}$. The fact that the $\chi_{\text{M}}T$ value begins to saturate at 1.81 K suggests that below this temperature a well-defined high-spin ground state is almost exclusively thermally populated. The Curie–Weiss fitting result of $\chi_{\text{M}}T$ versus T above 30 K indicates dominant antiferromagnetic interactions between the spin carriers.

By taking AC susceptibility of the complex over 1–1500 Hz from 1.8 to 3 K, the out-of-phase susceptibility displays frequency dependence (Figure 9.26), however, none of the curves reaches a peak at 1.8 K. The DC magnetization decay method (Figure 9.26) [113, 114] determined effective barrier to be 18.4 K and a relaxation time constant of $2 \times 10^{-12} \text{ s}$. As discussed above, Gd^{3+} is a pure spin ion; the major anisotropy contribution is the Mn^{3+} ion, which is the most well known anisotropy source in the design of SMM and SCM.

Another example of SMM including Gd^{3+} is $[\text{L}_2\text{Co}_2\text{Gd}][\text{NO}_3] \cdot 2\text{CHCl}_3$ [112], where $\text{LH}_3 = (\text{S})\text{P}[\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-2\text{-OH}-3\text{-OCH}_3]_3$. The out of phase AC susceptibility curves of the linear compound show peaks below 4 K on 1–1500 Hz measurement, which indicates the magnetization relaxation property. Arrhenius analysis gives the energy gap of the SMM as 27.2 K and a relaxation constant of $1.7 \times 10^{-7} \text{ s}$. This Gd–Co compound is similar to the Gd–Mn compound above, Gd^{3+} is an isotropy ion and Co^{2+} , just as with Mn^{3+} , is the major anisotropy source for the SMM (Figure 9.27).

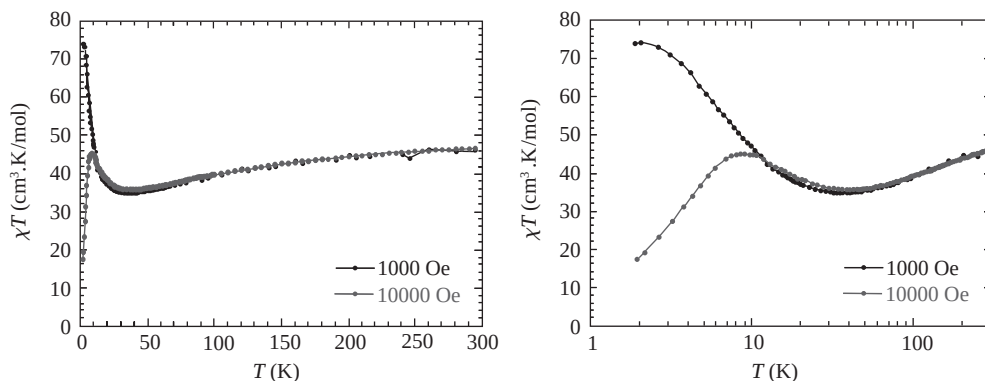


Figure 9.25 $\chi_M T$ versus T in 1000 and 10 000 Oe fields [111]. (Reprinted with permission from V.M. Mereacre, *et al.*, “A bell-shaped $\text{Mn}_{11}\text{Gd}_2$ single-molecule magnet,” *Journal of the American Chemical Society*, **129**, 9248–9249, 2007. © 2007 American Chemical Society.)

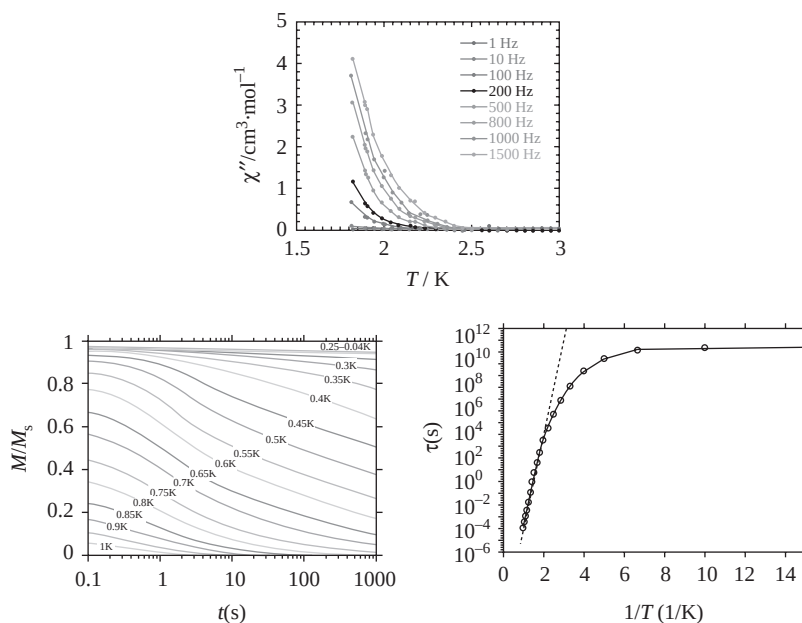


Figure 9.26 The relaxation behavior of $\text{Mn}_{11}\text{Gd}_2$ cluster [111]. (Reprinted with permission from V.M. Mereacre, *et al.*, “A bell-shaped $\text{Mn}_{11}\text{Gd}_2$ single-molecule magnet,” *Journal of the American Chemical Society*, **129**, 9248–9249, 2007. © 2007 American Chemical Society.)

The above examples are SMMs of the 3d–4f series. In some of the 3d–4f SMMs, the major anisotropy comes from the 3d ions, such as Mn^{3+} , Co^{2+} or Fe^{3+} [111, 112]. There are some pure 4f clusters that behave as SMMs [115, 116]. Powell and coworkers reported two pure lanthanide SMMs in 2006 [116], both of which are dysprosium clusters and they share a similar

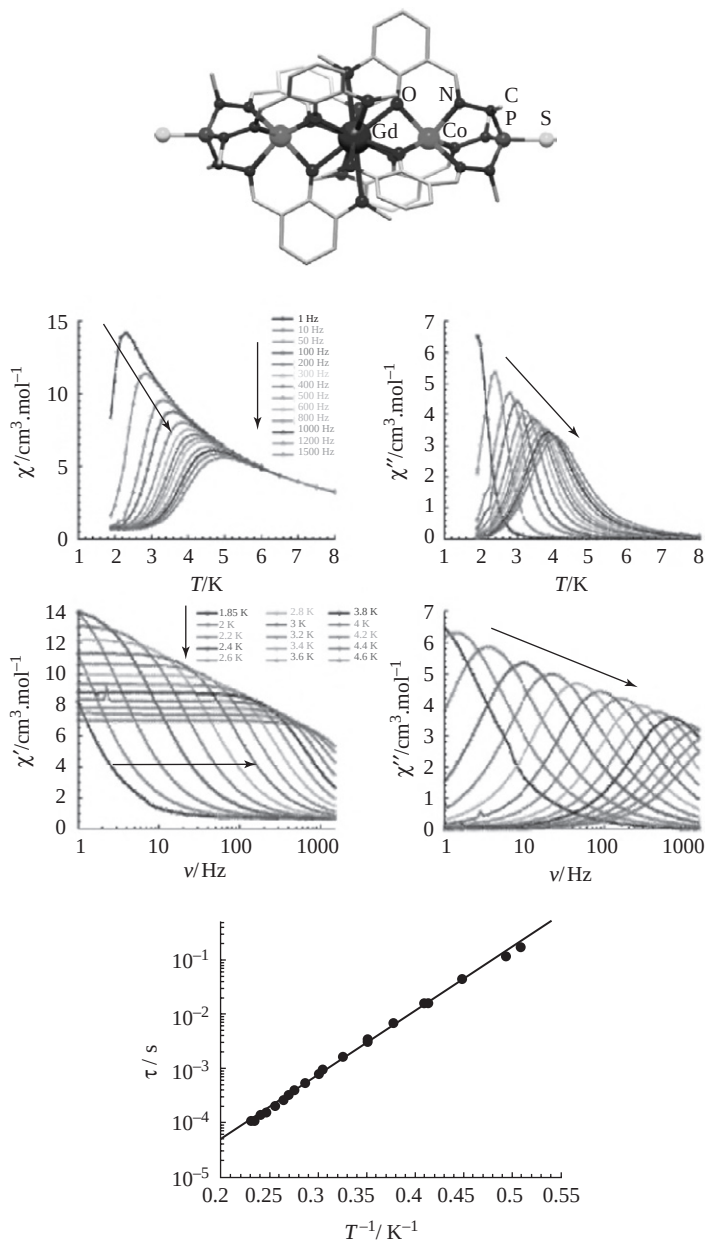


Figure 9.27 The structure of the GdCo₂ cluster and its magnetic relaxation behavior [112]. (Reprinted with permission from V. Chandrasekhar, *et al.*, “Linear trinuclear mixed-metal Co^{II} – Gd^{III} – Co^{II} single-molecule magnet: [L₂Co₂Gd][NO₃]₂·2CHCl₃ (LH₃ = (S)P[N(Me)NCH–C₆H₃-2-OH-3-OMe]₃),” *Inorganic Chemistry*, **46**, 5140–5142, 2007. © 2007 American Chemical Society.)

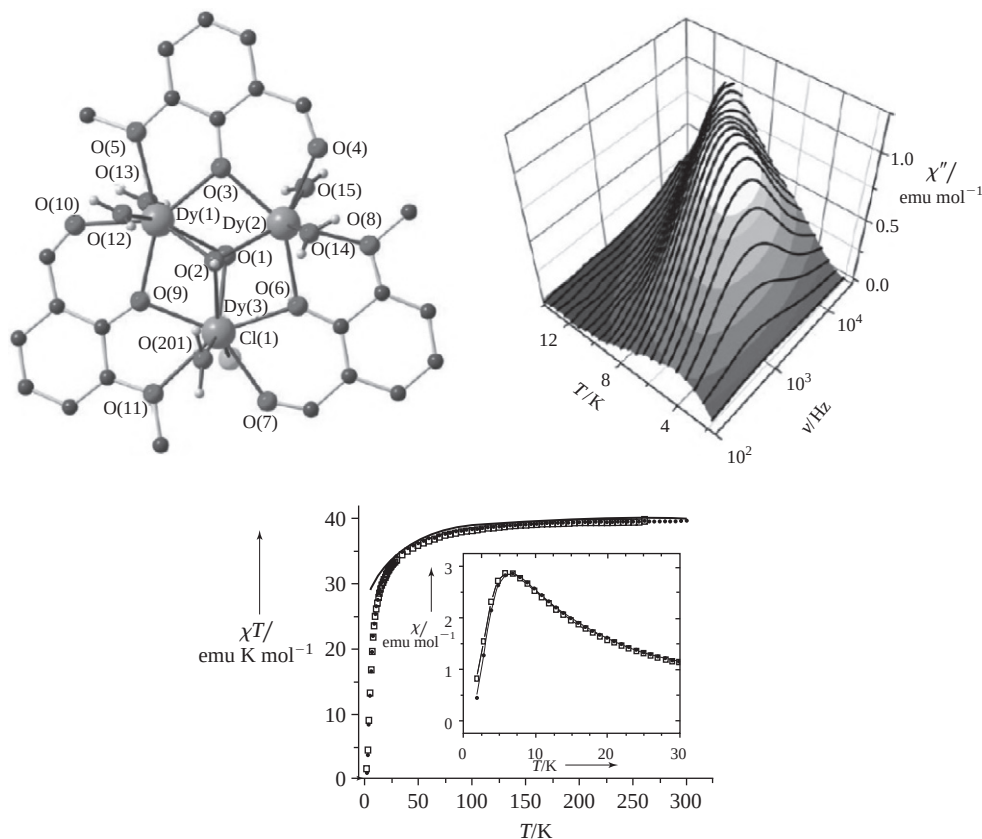


Figure 9.28 The structures of Dy_3 and its relaxation behavior [116]. (Reprinted with permission from J. Tang, *et al.*, “Dysprosium triangles showing single-molecule magnet behavior of thermally excited spin states,” *Angewandte Chemie International Edition*, 2006, **45**, 1729–1733 (Figures 1, 4 and 5). © Wiley-VCH Verlag GmbH & Co. KGaA.)

structure to Dy_3 . The two compounds are $[\text{Dy}_3(\mu_3\text{-OH})_2\text{L}_3\text{Cl}_2(\text{H}_2\text{O})_4][\text{Dy}_3(\mu_3\text{-OH})_2\text{L}_3\text{Cl}(\text{H}_2\text{O})_5]\text{Cl}_5 \cdot 19\text{H}_2\text{O}$ and $[\text{Dy}_3(\mu_3\text{-OH})_2\text{L}_3\text{Cl}(\text{H}_2\text{O})_5]\text{Cl}_3 \cdot 4\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH} \cdot 0.7\text{CH}_3\text{CN}$, where $\text{HL} = o\text{-vanillin}$. Both the structures consist of triangles of Dy^{3+} centers capped by two μ_3 -hydroxy bridges and both the compounds are almost a plane (Figure 9.28, top left). The DC susceptibilities of the two compounds are similar, showing antiferromagnetic coupling between intratrimer spin centers, similar to the gadolinium analogs. Dynamics of the magnetization studies were undertaken for both compounds. The AC susceptibilities of the complexes show strong frequency dependence below 20 K. χ_M'' reaches peaks below 8 K, the positions of which are frequency dependent as is typically observed for SMMs. However, the peaks are quite distorted with a shoulder structure (Figure 9.28, top right). Plotting the relaxation time versus the inverse temperature reveals that the behavior is only linear at very high temperature, and the energy barrier is 61.7 K with a relaxation time constant is 2.2×10^{-8} s (Figure 9.28, bottom).

9.4.2.2 Single-Chain Magnet Including Lanthanide Ions

The 2005 Nobel Prize winner in physics, Roy J. Glauber from Harvard University, predicted 40 years ago that slow relaxation can be observed in one-dimensional ferromagnetic Ising chains at low temperature [117], and this prediction became true when the first SCM was found [118]. In principle, a one dimensional Ising chain is paramagnetic state at all finite temperature ranges, and the long range ordering can only be reached at zero Kelvin. However, if the magnetic coupling between spin centers within the chain is large enough, magnetic interaction between chains can be negligible and there is uniaxial anisotropy, then the magnetic behavior of the chain is similar to SMMs: stair-like magnetization hysteretic loops under T_B , and slow relaxation in a zero static magnetic field. Usually, the T_B of SCMs could be higher than SMMs because of their larger ground spin state value. It should be noted that to design an SCM, one should avoid interchain interactions [119, 120]. Although the 3d–4f or 4f–4f magnetic interaction is weaker than that of 3d–3d, lanthanide ions are always considered to be introduced into the SCMs because of which large uniaxial magnetic anisotropy.

The first reported SCM using rare earth ions as the anisotropic source was $(\text{LCu})_2\text{Tb}(\text{NO}_3)$ [121], where $\text{H}_3\text{L} = 2\text{-hydroxy-}N\text{-}[(2\text{-hydroxyethyl})\text{amino}]\text{ethylbenzamide}$. The frequency dependency of the χ_M'' is observed below 5 K for frequencies ranging from 1 to 1000 Hz. Through Arrhenius analysis the energy barrier is calculated to be 28.5 K and relaxation time constant is 3.8×10^{-8} s. It should be noted that these workers failed to obtain the crystal structure of the compound and the formula was determined based on elemental analysis.

A rare earth and radical based SCM is $[\text{Dy}(\text{hfac})_3\text{NIT}(\text{C}_6\text{H}_4p\text{-OPh})]$ [122], where $\text{NIT}(\text{C}_6\text{H}_4p\text{-OPh})$ is a radical as shown in Figure 9.29. Actually, the similar compound $[\text{Dy}(\text{hfac})_3\text{NITC}_2\text{H}_5]$ displays a transition to three-dimensional ordering at 4.8 K although the inter-chain interaction is relatively weak [84, 85, 123]. The shortest Dy–Dy inter-chain distance is 10.76 Å, and only the dipolar inter-chain interaction is active. By changing the ethyl into a biphenyl substituent, the free volume between the chains is alternatively occupied by the biphenyl substituent of two different chains, which is surrounded by the fluorine atoms to minimize any weak magnetic interactions between the radicals. In this way, the average volume taken up by each metal center increases from 881 to 1001 Å³ and, more importantly, all distances between different chains are well separated. The shortest distance between two Dy centers increases from 10.76 to 11.35 Å (Figure 9.29).

The DC magnetic susceptibility measurement for a powder sample shows that $\chi_M T$ reaches a minimum at 8.6 K and a rounded peak of 68.5 emu·K mol^{−1} at 3.6 K, which is a typical 1D-behavior, while the cusp found in the 3D-ordered compound is not observed (Figure 9.30). The AC magnetic susceptibility measurements show that χ_M'' reaches peaks below 4.2 K and ranges from 2.5 to 20 000 Hz. The Arrhenius plot extracted from AC measurements, shows the presence of a crossover between two different activated regimes, both of which give best-fits with physical τ_0 values (5.6×10^{-10} and 1.9×10^{-12} s for the low- and high-temperature regimes, respectively) and two different barriers (42 and 69 K, respectively) (Figure 9.30). The two different activated regimes of SCMs could be due to finite-size effects [119, 120].

9.4.2.3 Single Lanthanide Ion Relaxation Systems: Single-Ion Magnet and Field Dependent Relaxation

The magnetic relaxation phenomena can be considered in certain classes; magnetic relaxation has been discovered in ferromagnets, spin glass, superparamagnetic particles including SMM

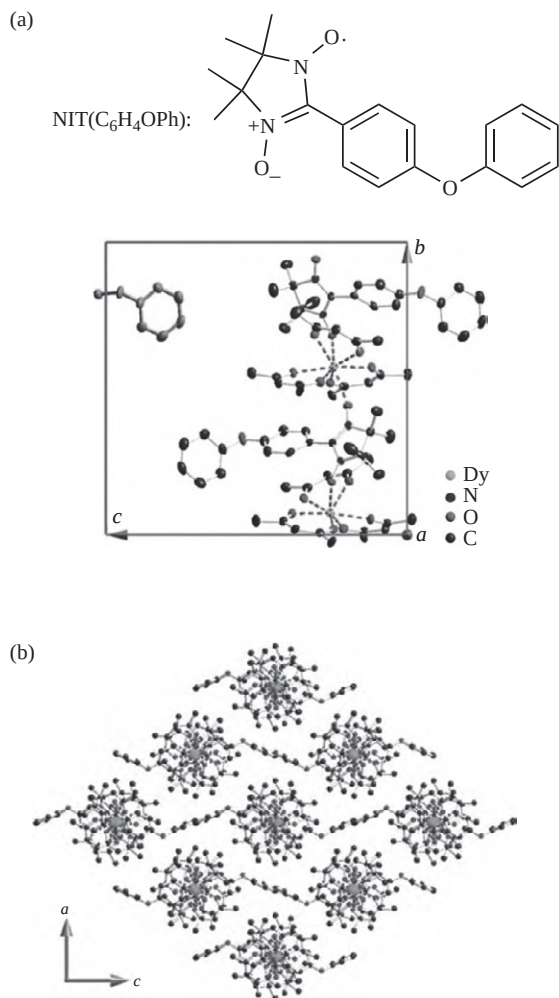


Figure 9.29 Structures of the compound [Dy(hfac)₃NIT(C₆H₄*p*-OPh)] and ligand NIT(C₆H₄*p*-OPh) [122]. (Reprinted with permission from L. Bogani, *et al.*, “Molecular engineering for single-chain-magnet behavior in a one-dimensional dysprosium-nitronyl nitroxide compound,” *Angewandte Chemie International Edition*, 2005, **44**, 5817–5821 (Figure 1). © Wiley-VCH Verlag GmbH & Co. KGaA.)

and SCM. There is always intramolecular (SMM, SCM), long-range (3D-ordering magnets) or short-range (spin glass) interaction between spin centers. However, in 2003 Ishikawa and coworkers discovered that some of lanthanide phthalocyanine complexes exhibit an extremely slow relaxation rate so that the electronic magnetic moment of the system is fixed in a certain direction, without magnetic ordering, due to intermolecular interactions [108, 124] This type of molecules is defined as a single-ion magnet (SIM). In 2001, Gao *et al.* discovered a DC field dependent relaxation phenomena in isolated lanthanide systems, which is very different from the one in normal spin glass and superparamagnets [69]. The above two types of relaxation,

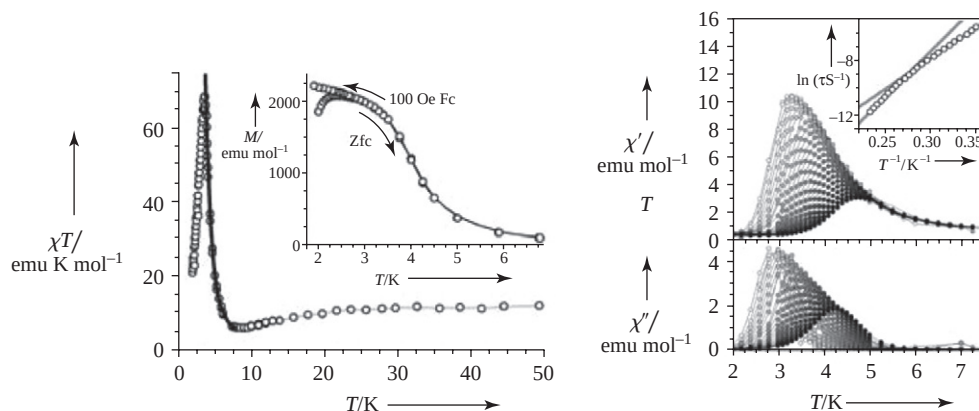


Figure 9.30 The DC and AC magnetic susceptibility of $[\text{Dy}(\text{hfac})_3\text{NIT}(\text{C}_6\text{H}_4p\text{-OPh})]$ [122]. (Reprinted with permission from L. Bogani, *et al.*, “Molecular engineering for single-chain-magnet behavior in a one-dimensional dysprosium-nitronyl nitroxide compound,” *Angewandte Chemie International Edition*, 2005, **44**, 5817–5821 (Figures 2 and 3). © Wiley-VCH Verlag GmbH & Co. KGaA.)

one in a zero DC field and the other in a non-zero DC field are attributed to single lanthanide ion relaxation systems.

The first SIM was a bis(phthalocyaninato) terbium or dysprosium anion complex having a double-decker structure. AC susceptibilities as a function of temperature were measured on polycrystalline powder sample of $[\text{Pc}_2\text{Tb}]^- \cdot \text{TBA}^+$ where $\text{TBA}^+ = (\text{C}_4\text{H}_9)_4\text{N}^+$. The χ_M''/χ_M reach maxima at 15, 32, and 40 K with frequencies of 10, 100, and 997 Hz, respectively (the white plots in Figure 9.31). The measurements for a diluted sample in a diamagnetic isostructural yttrium complex $[\text{Pc}_2\text{Y}]^- \cdot \text{TBA}^+$ showed that the χ_M''/χ_M peaks remained (the solid plots in Figure 9.31). This clearly proves that the slow magnetization relaxation is the single molecular property of $[\text{Pc}_2\text{Tb}]^-$, rather than resulting from intermolecular interactions and magnetic order.

Similar experiment was made on $[\text{Pc}_2\text{Dy}]^- \cdot \text{TBA}^+$, and the peaks of χ_M''/χ_M plot are at 4.5, 7, and 11.5 K with an AC frequency of 10, 100, and 997 Hz, respectively (Figure 9.31, right). It should be noted that the temperature ranges in which the magnetization relaxations are observed here are significantly higher than any of the 3d metal cluster SMMs and that the SMM behavior was not observed for the Pc double-decker complexes with other heavy lanthanides (Ho, Er, Tm, and Yb). By measuring with a micro-SQUID, the quantum tunneling effect was discovered in the Tb, Dy [125], and Ho [126] system (Figure 9.32).

Further investigation by determining the electronic structure [127, 128] revealed that slow magnetization relaxation comes from the ligand field induced electron substructures splitting, making Orbach relaxation processes possible. In the Tb complex, the lowest substates are assigned to $J_z = \pm 6$, which are the maximum and minimum values and correspond to the “spin-up” and “spin-down” states in the $J = 6$ ground multiplet. In the Dy complex, the lowest substates are characterized as $J_z = \pm 13/2$, the second largest in the $J = 15/2$ ground state (Figure 9.33, top left). This means the two complexes have strong uniaxial magnetic anisotropy, which is a requirement for an SMM. Arrhenius analysis showed that a two-phonon Orbach

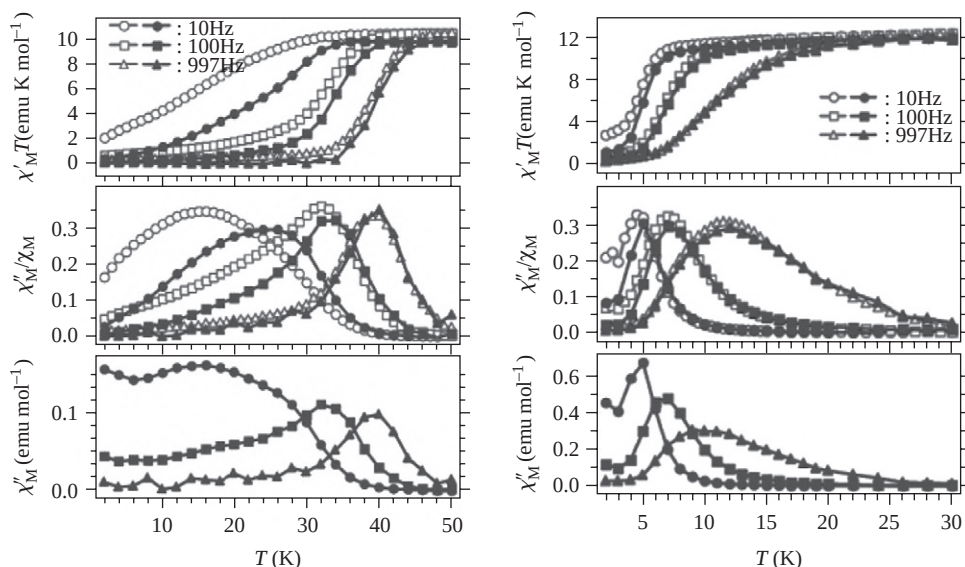


Figure 9.31 Frequency dependence of $[\text{Pc}_2\text{Ln}]^+\cdot\text{TBA}^-$, where $\text{Ln}=\text{Tb}$ (left), and Dy (right) [124]. (Reprinted with permission from N. Ishikawa, *et al.*, “Lanthanide double-decker complexes functioning as magnets at the single-molecular level,” *Journal of the American Chemical Society*, **125**, 8694–8695, 2003. © 2003 American Chemical Society.)

process was dominant in the temperature range 25–40 K in the Tb complex, and 3–12 K in the Dy complex. The energy barrier through which the Orbach process occurs was estimated to be 2.6×10^2 and $3.1 \times 10^1 \text{ cm}^{-1}$ for the Tb and Dy complexes, respectively (Figure 9.33, top right and bottom). These values are close to the energy differences between the lowest and the second lowest sublevels, supporting the dominance of the Orbach process.

Generally, a stronger ligand field leads to larger electron structure splitting, which will result in a higher temperature χ_M''/χ_M peak. This has been verified by oxidation of $[\text{Pc}_2\text{Tb}]^-$ to $[\text{Pc}_2\text{Tb}]$, the peak of χ_M''/χ_M against temperature of the new compound shifting from 40 to 52 K [129–131]. The quantum tunneling effect can be attributed to the coupling of electron spin and orbit angular moments with the nuclei spin moments through the disturbance of the hyperfine interaction term $A_{\text{hf}} \mathbf{J} \cdot \mathbf{I}$, and the nuclear quadrupole interaction term $P\{I_z^2 - 1/3I(I+1)\}$ [125, 126].

The anisotropy of the double-decker lanthanide compound comes from the ligand field, which is different from regular SMMs and SCMs. It should be noted that the coordination polyhedron is anti-square, and the relaxation phenomena in single lanthanide ions has also been discovered in some other systems with the coordination polyhedron of anti-square [107, 132, 133].

In 2001, Gao and coworkers synthesized $[\text{NdCo}(\text{bpym})(\text{H}_2\text{O})_4(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, where $\text{bpym} = 2,2'$ -bipyrimidine [69]. By measuring DC susceptibilities down to 2 K, no evidence of long range magnetic order is observed. However, unexpectedly the compound showed a puzzling behavior of the AC susceptibility measured in the presence of an applied field of

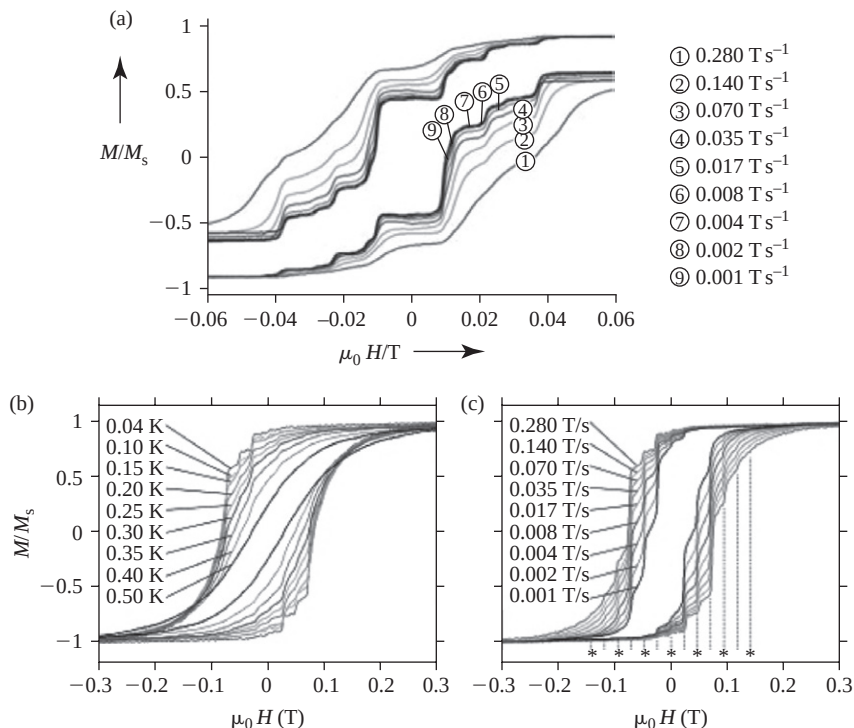


Figure 9.32 The quantum tunneling effect for compound $[\text{Pc}_2\text{Ln}] \cdot \text{TBA}^+$, where (a) $\text{Ln}=\text{Tb}$ [125] (Reprinted with permission from N. Ishikawa, *et al.*, “Quantum tunneling of magnetization in lanthanide single-molecule magnets: bis(phthalocyaninato) terbium and bis(phthalocyaninato)dysprosium anions,” *Angewandte Chemie International Edition*, 2005, **44**, 2931–2935 (Figure 1). © Wiley-VCH Verlag GmbH & Co. KGaA); and (b and c) Ho [126] (Reprinted with permission from N. Ishikawa, *et al.*, “Nuclear spin driven quantum tunneling of magnetization in a new lanthanide single-molecule magnet: bis(phthalocyaninato)holmium anion,” *Journal of the American Chemical Society*, **127**, 3650–3651, 2005. © 2005 American Chemical Society.)

2000 Oe (Figure 9.34). In fact, while measurements at a zero field showed normal paramagnetic behavior without slow relaxation, those in the presence of a field showed evidence of slow paramagnetic relaxation. This behavior was tentatively attributed to spin frustration, which is incrementally unveiled by the external magnetic field [134]. However, because the coupling between the Nd^{3+} ions (1 nm separation) should be very weak, it is essentially an “isolated ion” or “isolated ion-like” system. In this respect, an explanation for the origin of DC-field induced relaxation might be the lifting of the Kramer’s degeneracy by the magnetic field. However, this seems to be a rather general phenomenon in many weak-coupled or isolated magnetic molecular systems [90, 135], and the question is still open and more efforts devoted to this are expected.

Ishikawa and coworkers discovered similar field induced magnetic relaxation in isolated lanthanide ions [136]. Through a series of measurements of the susceptibility of $[\text{N}(\text{C}_2\text{H}_5)_4]^{3+}[\text{Ln}(\text{dipic})_3]^{3-}$, where $\text{dipic} = \text{pyridine-2,6-dicarboxylate}$, $\text{Ln} = \text{Tb, Dy, Ho, Er}$,

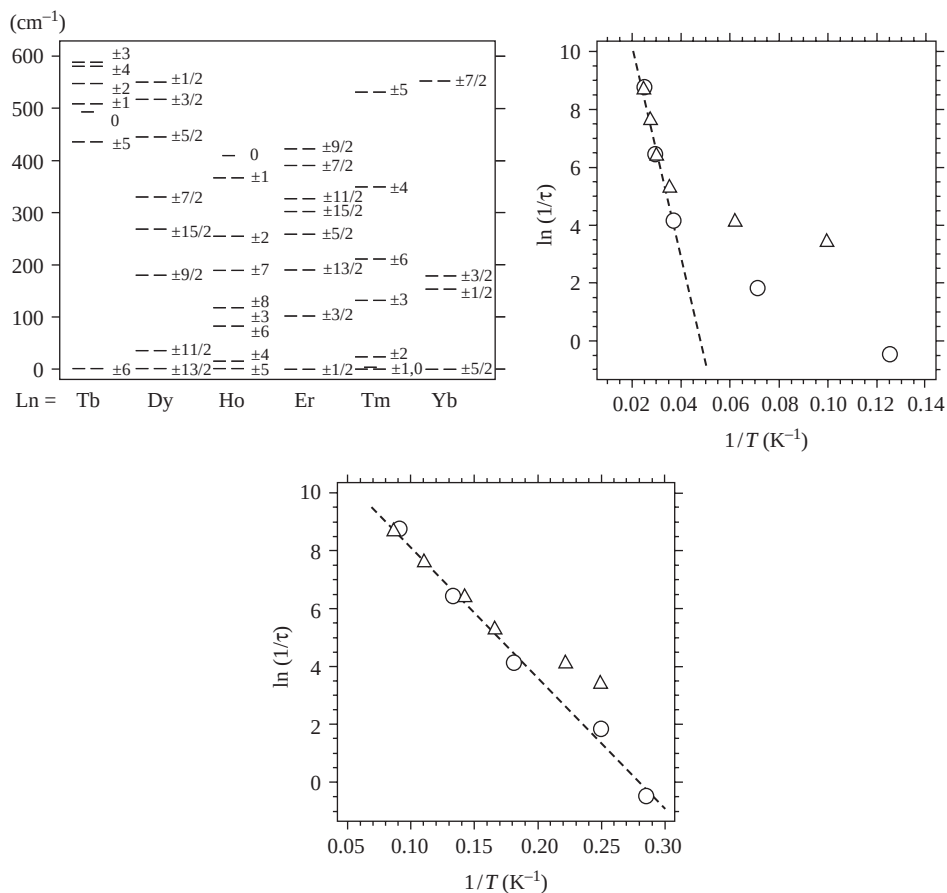


Figure 9.33 The structure configurations of $[\text{Pc}_2\text{Ln}]^-\cdot\text{TBA}^+$, where Ln = Tb, Dy, Ho, Er, Tm, Yb; and Arrhenius analysis for $[\text{Pc}_2\text{Ln}]^-\cdot\text{TBA}^+$, where Ln = Tb (top right), Dy (bottom) [108]. (Reprinted with permission from N. Ishikawa, *et al.*, "Mononuclear lanthanide complexes with a long magnetization relaxation time at high temperatures: a new category of magnets at the single-molecular level," *Journal of Physical Chemistry B*, **108**, 11265–11271, 2004. © 2004 American Chemical Society.)

Tm, and Yb, none of the six complexes showed a magnetization relaxation range of $10\text{--}10^3$ Hz above 1.8 K at a zero DC field. However, while applying a Dc field of 1000 Oe, the Dy, Er, and Yb compounds showed a slow relaxation. This phenomenon has been explained to be caused by the elimination of a fast relaxation path, which is only effective for the Kramer's doublet ground states in a near-zero field. At higher static fields, the remaining paths, such as Orbach and/or direct processes, govern the dynamics of the two-level systems comprised of spin-up and spin-down states. The non-Kramer's complexes were found to have a nondegenerate ground state with large energy gaps from higher states, which is consistent with their fast magnetization relaxation.

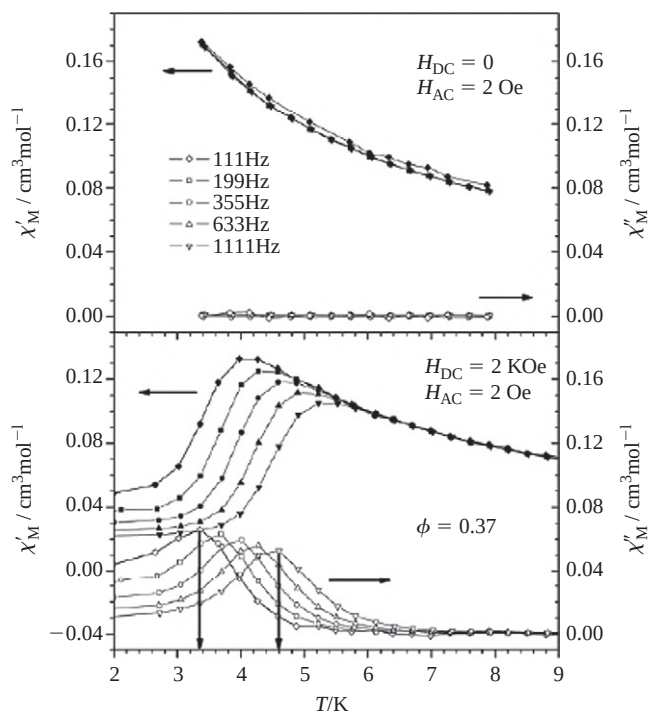


Figure 9.34 Frequency dependence of AC susceptibility at 0 and 2 kOe DC bias field for compound $[\text{NdCo}(\text{bpy})(\text{H}_2\text{O})_4(\text{CN})_6] \cdot 3\text{H}_2\text{O}$. The filled symbols are for the in-phase component χ'_M ; the open symbols are for the out-of-phase component χ''_M [68]. (Reprinted with permission from B. Ma, *et al.*, “Cyano-bridged 4f-3d coordination polymers with a unique two-dimensional topological architecture and unusual magnetic behavior,” *Angewandte Chemie International Edition*, 2001, **40**, 434–437 (Figure 3). © Wiley-VCH Verlag GmbH & Co. KGaA.)

9.5 Outlook

For the complicated electronic structures of ground and low excited states, lanthanide ions are good spin carriers from which to compose magnetic molecular materials. Various magnetic compounds with 4f–3d, 4f–p, 4f–4f exchange coupling interactions have been synthesized and exhibit diverse magnetic phenomena, such as magnetic ordering, single-molecule magnets, and single-chain magnets. In addition, the presence of the single-ion magnets and field-dependent relaxations originating from the intrinsic properties of the lanthanide ions show these distinct functions, which is different to the transition metal ions, in the construction of magnetic molecular materials. However, the studies on magnetic molecular materials containing lanthanide ions are far from developed and plenty of questions and opportunities still exist.

Firstly, besides the spin magnetic moment, the magnetic properties of lanthanide ions are also affected by the orbital contribution and the ligand field. The large spin–orbit interaction complicates the properties of ground and low excited states of lanthanide ions, and makes the magnetic properties of lanthanide ions more confused. Although the compensation method can study the magnetic coupling of 4f systems indirectly, it is still not convenient and clear for

aiding in the understanding of the mechanism of the interactions between 4f electrons and other spin carriers. Thus, comprehending the spin–orbit effect and the orbital moment contribution to the magnetic properties, especially controlling the resulting magnetic anisotropy of lanthanide ions, is one of the biggest challenges in magnetic molecular materials from the point of view of both the theoretical and the experimental. For example, why do most of the SMMs, SCMs, and single-ion magnets contain the Dy(III) ion? Is it possible to control the magnetic anisotropy through tuning up the symmetry and the strength of the ligand field?

Secondly, the critical temperatures of magnetic ordering reported so far are all in the low temperature range, although magnetic ordering does exist in some lanthanide ion containing systems, such as 4f–3d, 4f–4d, 4f–p complexes. This tendency is attributed to the weak exchange coupling between lanthanide ions and transition metal ions or an organic radical. Therefore, how to enhance the strength of magnetic coupling interactions is another appealing field in the molecular-magnetism research into lanthanide containing systems. For example, searching for new bridge ligands that can transmit stronger magnetic coupling, increasing the efficiency of the linker when constructing magnetic compounds from low dimension to high dimension, and utilizing the character of spin frustration systems are all effective methods to obtaining higher critical temperatures of magnetic ordering systems, or to finding new phenomena. In particular, the power of the strongly delocalized, even conducting electrons in transmitting magnetic exchange coupling should be considered as one of the most important factors in designing magnetic materials with high ordering temperatures, such as the situation in mixed valence systems.

Finally, with the aim of industrial applications, assembling the magnetic molecules onto various substrates is another important field, but one that has been less studied. The application potential of magnetic molecular materials in the manufacture of molecular based memory devices, quantum computing, and spintronics devices, requires an understanding of the interactions between the material and substrate in order to manipulate the spin and electronic states of the target system to realize the desired specific properties [137].

Acknowledgments

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10

Gadolinium Complexes as MRI Contrast Agents for Diagnosis

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10.1 Clinical Magnetic Resonance Imaging (MRI) Contrast Agents

Magnetic resonance imaging (MRI) is a powerful modality in medicine for the non-invasive imaging of human bodies. It has a high spatial resolution and offers great contrast between soft tissues. It is therefore used globally in clinical diagnosis and the staging of diseases, and more importantly, in making advances in clinical research by assessing the therapeutic effects of drug, gene, and cell therapies and by elucidating the physiology of diseases. Currently, more than 60 million MRI scans are performed each year.

MRI stems from nuclear magnetic resonance (NMR), which has an indispensable role in chemistry for the characterization of compounds. Bloch and Purcell, Nobel Laureates in Physics in 1952, developed the technique in 1944 based on Rabi's earlier discovery of NMR. They found a precise way to identify elements by using magnetic fields and radiofrequencies. Damadian later observed a difference in NMR relaxation times between tumors and normal tissues, which inspired Lauterbur to work out a way to reconstruct two-dimensional images [1]. Lauterbur and Mansfield later revolutionized imaging by linking NMR to potential clinical applications, which earned them the Nobel Prize for Physiology/Medicine in 2003.

Protons (^1H) of water molecules are the most important type of NMR-active nuclei, but other nuclei such as ^{13}C , ^{14}N , ^{15}N , ^{17}O , ^{19}F , and ^{31}P are also NMR active. These nuclei exhibit magnetic resonance under an external magnetic field and a radiofrequency pulse. Human bodies are composed of more than 60% water, and this abundance of water protons generates MRI images with excellent soft tissue discrimination that give detailed anatomical information. However, the inherent contrast between tissues may not be sufficient for the diagnosis of all types of diseases, and thus contrast agents (CAs) were developed. CAs are paramagnetic compounds that are introduced into the body to enhance the contrast between tissues, organs, or a

particular physiological status. The first gadolinium-based MRI CA was gadopentetate dimeglumine (gadolinium diethylenetriaminepentaacetic acid, Gd-DTPA), which was introduced into patients in 1983 and approved for clinical use in 1988 [2]. Since its introduction, there has been enormous growth in this unique field of diagnostic medicine in the last 20 years [1].

10.1.1 Development of Clinical Contrast Agents

The story of MRI CAs began with X-ray CAs. DTPA (diethyltriaminepentaacetic acid) was widely used as a chelate for the detoxification and solubilization of bismuth, which is a metal ion in X-ray CAs [3]. DTPA attracted the attention of scientist, who developed Gd-DTPA as the first paramagnetic complex in MRI clinical studies [4]. It was initially applied to image the central nervous system (CNS). However, owing to its superior anatomical contrast enhancement, it was later applied to the imaging of cardiovascular and neurovascular systems, and in oncology [5].

DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid) is another chelate that is commonly found in clinical CAs. Gd-DOTA has been approved for body imaging, including CNS and vascular imaging [6]. Osmolality is a measure of osmoles of solute per kilogram of solvent. Both Gd-DTPA and Gd-DOTA are hyperosmolar agents because of their negative charge. However, hyper- or hypoosmolar agents are not preferred in clinical situations, because the typical administration pathway of CAs is intravenous injection. A low-osmolality agent can minimize tissue damage at the site of injection, which allows the dose to be increased [7, 8]. Hence, Gd-DTPA derivatives, such as Gd-DTPA-BMA [BMA = bis(methylamide)] and Gd-DTPA-BMEA [BMEA = bis(methoxyethylamide)], were developed as neutral complexes to improve osmolality. Gd-HP-DO3A [HP-DO3A = 10-(2-hydroxypropyl)-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid] is another neutral complex and is a Gd-DOTA analog with a low osmolality [9].

Gd-based MR CAs can be classified as extracellular fluid space (EFS) or tissue specific agents, according to their *in vivo* properties. The first generation of EFS agents have no specific targeted site. They are hydrophilic, and are excreted rapidly from the intravascular space via capillaries into the interstitial space. Over 95% of unaltered CAs are excreted via glomerula filtration. These CAs give good anatomical information, but limited physiological information. There was thus a need to develop tissue- or cell-specific CAs. The second generation tissue-specific CAs include two DTPA derivatives, Gd-BOPTA [BOPTA = 4-carboxy-5,8,11-tris(carboxymethyl)-l-phenyl-2-oxa-5,8,11-triazatridecan-13-oic acid] and Gd-EOB-DTPA [EOB-DTPA = (4S)-4-(4-ethoxybenzyl)-3,6,9-tris(carboxylatomethyl)-3,6,9-triazaundecanedioic acid], that are hepatobiliary agents that target hepatocytes and improve the delineation of liver lesions [10]. The details of these CAs are discussed in Section 10.3.2. MS-325 [(trisodium-[(2-(R)-[(4,4-diphenylcyclohexyl)phosphonooxymethyl]-diethylenetriaminepentaacetato)(aquo)gadolinium (III)]] is another tissue-specific agent belonging to the DTPA family, and has recently been approved as a blood pool agent for clinical use due to its high affinity for human serum albumin (HSA). A more detailed description of MS-325 is given in Section 10.3.1. In general, there are three major areas in which tissue-specific CAs are required to improve the diagnosis for advanced therapy: MR angiography, liver disease, and oncology.

The development of Gd and lanthanide (Ln) complexes for uses as MRI CAs has given rise to a rich lanthanide chemistry. However, the multidisciplinary field of monitoring physiological changes remains a challenge, as *in vivo* parameters such as pH, partial oxygen pressure (pO_2),

and enzyme activity are all closely related to diseases. The physiological information acquired from contrast-enhanced images not only enables a non-invasive and accurate diagnosis, but also a pre-symptomatic diagnosis or diagnosis at an early stage that can greatly enhance the curability of diseases. This has led MRI CAs into the era of diagnosis at the molecular level.

10.1.2 Clinical Contrast Agents

Gd-based clinical CAs can be divided into two groups according to their structure. The two groups are acyclic complexes and cyclic complexes, the structures of which are shown in Figures 10.1 and 10.2, respectively, and the properties of which are summarized in Table 10.1.

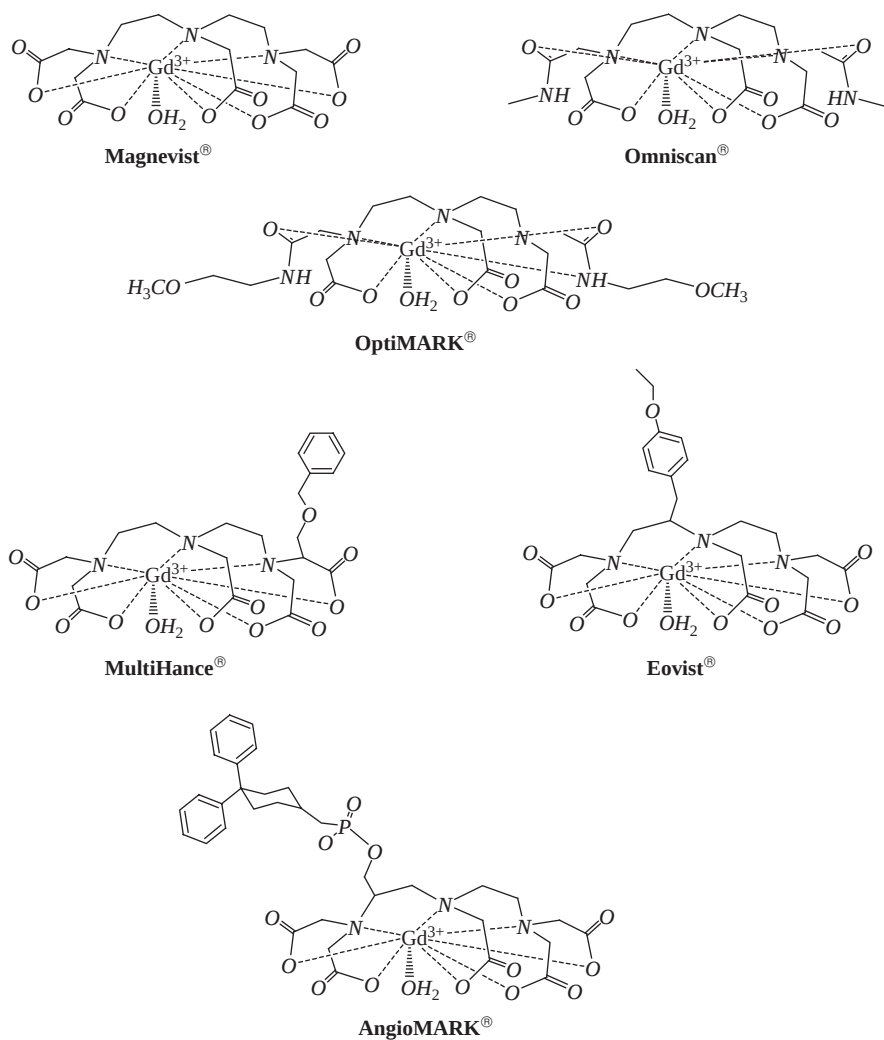


Figure 10.1 Clinical contrast agents with acyclic chelates.

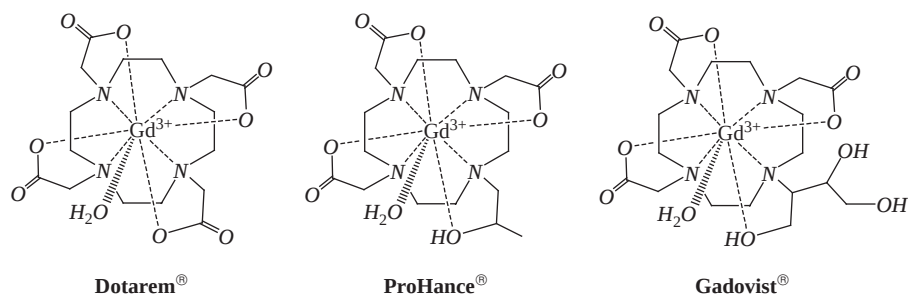


Figure 10.2 Clinical contrast agents with cyclic chelates.

Table 10.1 Nomenclature, charge, hydration number, and relaxivity of clinical contrast agents.

Generic name	Chemical name/ brand name	Acyclic (A)/ cyclic (C)	Charge	Hydration number	Relaxivity (r_1)/ $\text{mM}^{-1}\text{s}^{-1}$ ^a
Gadopentetate dimeglumine	Gd-DTPA/Magnevist [®]	A	2–	1	3.3
Gadodiamide	Gd-DTPA-BMA/ Omniscan [®]	A	0	1	3.3
Gadoversetamide	Gd-DTPA-BMEA/ OptiMARK [®]	A	0	1	3.6
Gadobenate dimeglumine	Gd-BOPTA/ MultiHance [®]	A	2–	1	3.8
Gadoxetic acid disodium	Gd-EOB-DTPA/ Eovist [®]	A	2–	1	4.6
Gadophostriamine trisodium	MS-325/AngioMARK [®]	A	2–	1	5.0
Gadoterate meglumine	Gd-DOTA/Dotarem [®]	C	1–	1	3.0
Gadoteridol	Gd-HP-DO3A/ ProHance [®]	C	0	1	2.9
Gadobutrol	Gd-DO3A-butrol/ Gadovist [®]	C	0	1	3.3

^aAt 1.5 T and 310 K [11].

Gd(III) is the best candidate for application as an MRI CA because of its seven unpaired electrons and symmetric S-state, which is favorable for electron spins and results in a slow electronic relaxation rate. As a mid-member of the Ln family, Gd(III) has a coordination number of nine. In clinical CAs, chelates have a denticity of eight, and thus in Gd(III) occupy eight of the coordination sites, leaving the ninth for a coordinated water molecule. Gd(III) prefers hard donor atoms, such as N and O. The N and O of the carboxylate in DTPA and DOTA are coordinated to the metal center. The solid-state structure of Ln(III) DTPA was reported in 1984 [12], and that of Gd-DOTA was reported in 1993 [13]. Gd(III) coordinates with

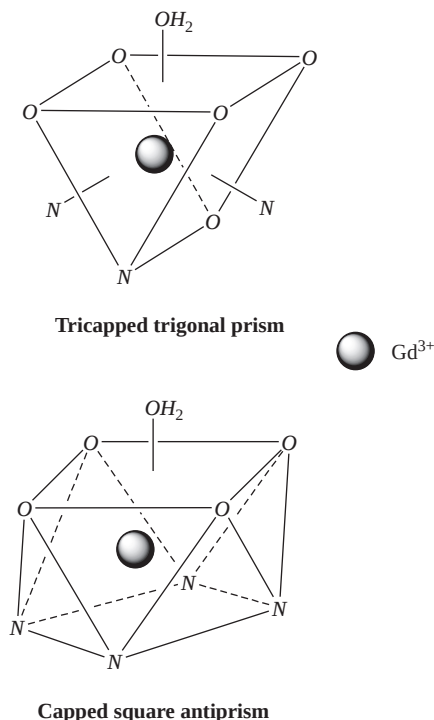


Figure 10.3 Coordination geometry of a tricapped trigonal-prism (TTP) and a capped square-antiprism (CSAP) form of Gd-DTPA and Gd-DOTA, respectively [14].

three nitrogen and five carboxylate oxygen DTPA, and with four nitrogen and four carboxylate oxygen DOTA. The theoretical geometry of the chelates is a tricapped trigonal-prism (TTP), and a capped square-antiprism (CSAP) in the absence of steric effects (as shown in Figure 10.3). Caravan *et al.* described both the solid and solution states of various Gd(III) complexes [14]. In the CSAP geometry, isomers with different twisted angles between the basal plane and the capped plane have been observed.

Image contrast depends on three proton factors, namely, the proton density, longitudinal relaxation (T_1), and transverse relaxation time (T_2). CAs increase both the longitudinal and transverse relaxation rate (that is, $1/T_1$ and $1/T_2$) but to different extents depending on their nature and the applied magnetic field strength. CAs that cause a relatively large increase in the longitudinal relaxation rate are regarded as T_1 -agents, whereas those that significantly increase the transverse relaxation rate are regarded as T_2 -agents. Signal intensity increases for T_1 -agents, but decreases for T_2 -agents. T_1 is larger than T_2 in tissues, and thus the relative effect of CAs on T_1 is larger than the effect on T_2 . T_1 -agents give a better contrast than T_2 -agents in regions that have a strong T_2 effect. Gd-based CAs are T_1 -agents and appear as a bright spot in T_1 -weighted images, and are thus easier to visualize in the regions in which they are localized. Clinical T_1 -agents have a relaxivity (r_1) of $3\text{--}5\text{ mM}^{-1}\text{ s}^{-1}$ at 1.5 T, where r_1 is the longitudinal relaxation rate normalized by concentration.

10.2 Chemistry of Gadolinium Based Contrast Agents

Gd complexes of MRI CAs have contributed significantly to lanthanide chemistry. In the past two decades, scientists have designed a vast number of complexes to improve the relaxivity and selectivity of CAs. Understanding the chemistry of CAs not only gives information about the pharmacological properties of these substances, but also forms the basis for their improvement.

Today, nearly half of all MR examinations are contrast enhanced. CAs are a distinctive class of pharmaceuticals, in that they are applied to improve the contrast between normal and diseased tissues, or at the site of interest, but are not intended to cause unnecessary biological activity. The development of MRI CAs from bench to patient is a multi-step process that can take more than 10 years [5].

A new Gd complex must fulfill three main physiochemical criteria before being considered as a potential MRI CA. Firstly, it should have a reasonably high relaxivity so that it generates an observable contrast enhancement *in vivo*. A high relaxivity can be expected if the complex has at least one bound water molecule and a fast water exchange rate for the effective propagation of paramagnetism to its surroundings. Secondly, the chelates should firmly coordinate with the Gd(III) and at the same time should not interfere with or limit the relaxivity. They should also prefer Gd(III) to Zn(II) or Ca(II), especially *in vivo*, to prevent the release of toxic free Gd(III). The third criterion is that the complex should not be highly charged, as charged complexes might lead to non-specific interactions with physiological biomolecules, such as proteins. Neutrality is thus a factor for selectivity, as is low osmolality. Chelates govern the physiochemistry of the complexes, and should be designed to overcome the weaknesses of current clinical CAs so that new complexes can have improved relaxivity, pharmacokinetics, biodistribution, protein selectivity, and safety profiles.

10.2.1 Relaxivity

The motion of the protons in the proximity of Gd-based CAs contributes to the relaxivity, which is defined as the relaxation rate at a 1 mM concentration. Paramagnetic compounds, such as Gd complexes, increase the $1/T_1$ and $1/T_2$ of solvent nuclei. The observed relaxivity $(1/T_i)_{\text{obs}}$ is composed of the diamagnetic relaxation $(1/T_i)_{\text{d}}$ and the paramagnetic relaxation $(1/T_i)_{\text{p}}$, which refer to the solvent relaxation in the absence and presence of paramagnetic compounds, respectively, as shown in Equation 10.1.

$$(1/T_i)_{\text{obs}} = (1/T_i)_{\text{d}} + (1/T_i)_{\text{p}} \quad i = 1 \text{ or } 2 \quad (10.1)$$

where

$i = 1$ is the longitudinal relaxation

$i = 2$ is the transverse relaxation

Interactions of water protons account for an alteration of the local magnetic field surrounding a paramagnetic center. The observed relaxivity depends on the distance and time of these interactions and the translational diffusion. The interactions are classified as either inner-sphere, which describes protons of water molecules that are bound to the metal center, or outer-sphere, which describes bulk solvent molecules that experience a paramagnetic effect when they diffuse around the metal center. The diamagnetic contribution has a linear relationship

with the concentration of paramagnetic compounds provided that there is no solvent–solvent interaction (Equation 10.2).

$$\left(\frac{1}{T_i}\right)_p = \left(\frac{1}{T_i}\right)_{\text{inner-sphere}} + \left(\frac{1}{T_i}\right)_{\text{outer-sphere}} = r_i[\text{Gd}] + \left(\frac{1}{T_i}\right)_{\text{outer-sphere}} \quad i = 1 \text{ or } 2 \quad (10.2)$$

where $[\text{Gd}]$ is the concentration of the Gd complex.

More precisely, the paramagnetic contribution of the longitudinal relaxation rate is composed of the inner-sphere relaxation, the second-sphere relaxation, and the outer-sphere relaxation. The model used to describe these interactions is shown in Figure 10.4. The various parameters that influence the observed longitudinal relaxivity will be discussed using Gd-based CAs as illustrative examples.

The inner-sphere relaxation refers to the contribution from the water molecules that are directly bound to the gadolinium, and is expressed by the Solomon–Bloembergen equations (Equations 10.3–10.6) [15, 16].

$$\left(\frac{1}{T_1}\right)_{\text{inner-sphere}} = \frac{[\text{Gd}]q}{55.6(T_{1M} + \tau_m)} \quad (10.3)$$

$$\frac{1}{T_{1M}} = \frac{1}{T_1^{DD}} + \frac{1}{T_1^{SC}} \quad (10.4)$$

$$\frac{1}{T_1^{DD}} = \frac{2}{15} \left[\frac{\gamma_I^2 g^2 \mu_B^2 S(S+1)}{r_{\text{GdH}}^6} \right] \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{7\tau_{c2}}{1 + \omega_s^2 \tau_{c2}^2} + \frac{3\tau_{c1}}{1 + \omega_I^2 \tau_{c1}^2} \right) \quad (10.5)$$

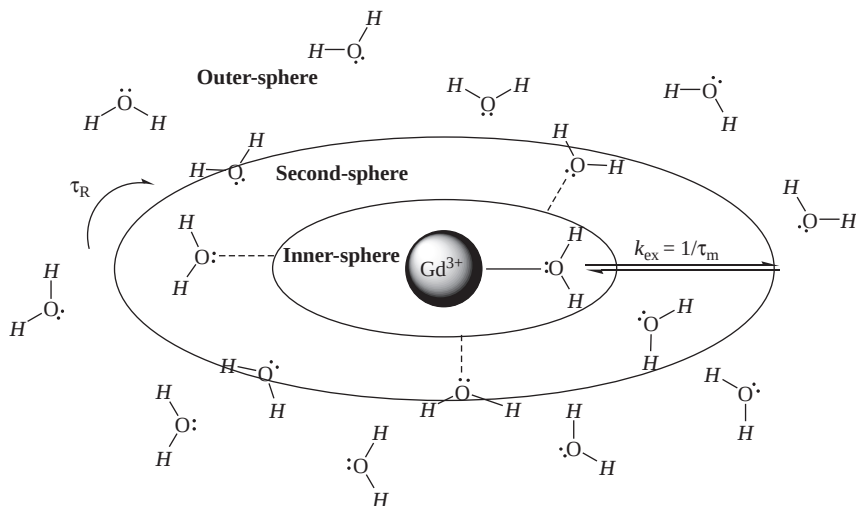


Figure 10.4 Schematic diagram of the three types of relaxation mechanisms and the major parameters in the relaxation, which are the number of coordinated water molecules, water exchange rate (k_{ex}), and reorientational correlation time (τ_R).

$$\frac{1}{T_1^{SC}} = \frac{2S(S+1)}{3} \left(\frac{A}{\hbar} \right)^2 \left(\frac{\tau_{e2}}{1 + \omega_s^2 \tau_{e2}^2} \right) \quad (10.6)$$

where

$[M]$ is the molar concentration of the paramagnetic ions

q is the number of coordinated water molecules per Gd

τ_m is the residence lifetime of the bound inner-sphere water molecules

τ_{ci} and τ_{ei} are the correlation times that define dipole–dipole and scalar relaxation, respectively

$1/T_{1M}$ is the longitudinal proton relaxation rate

γ_I is the nuclear gyromagnetic ratio [$\gamma(H) = 42.6 \text{ MHz T}^{-1}$]

S is 7/2 for gadolinium ions

g is the electron g -factor

μ_B is the Bohr magneton

r_{GdH} is the electron spin–proton distance

ω_I and ω_s are the nuclear and electron Larmor frequencies, respectively

$A/\hbar$ is the hyperfine or scalar coupling constant between the electron of the paramagnetic center and the proton of the coordinated water

DD refers to a dipole–dipole mechanism

SC refers to a scalar mechanism.

The relationship between the correlation times is shown in Equations 10.7 and 10.8.

$$\frac{1}{\tau_{c1}} = \frac{1}{\tau_R} + \frac{1}{T_{1e}} + \frac{1}{\tau_m} \quad (10.7)$$

$$\frac{1}{\tau_{e1}} = \frac{1}{T_{1e}} + \frac{1}{\tau_m} \quad (10.8)$$

where

τ_R is the reorientational correlation time (or the rotational correlation time)

T_{1e} is the longitudinal electron spin relaxation time of the metal ion.

As relaxation is also field dependent, Bloembergen and Morgan developed a theory for the field dependence of T_{1e} (Equation 10.9) that accounts for the discrepancies for ions with $S > 1/2$ [17, 18].

$$\frac{1}{T_{1e}} = B \left[\frac{\tau_v}{(1 + \omega_s^2 \tau_v^2)} + \frac{4\tau_v}{(1 + 4\omega_s^2 \tau_v^2)} \right] \quad (10.9)$$

where

τ_v is a correlation time for the modulation of this transient zero-field splitting (ZFS).

The outer-sphere relaxation originates from the translational diffusion of solvent molecules around the metal center, and consists of the outer-sphere relaxation and the second-sphere relaxation. As there is no chemical interaction or electron transfer between the solvent molecules and the metal center, it is more difficult to rationalize. A hard sphere diffusion

model can be applied, in which the outer-sphere mechanism can be described by Equations 10.10–10.12.

$$\left(\frac{1}{T_1}\right)_{\text{outer-sphere}} = C[3j(\omega_I) + 7j(\omega_S)] \quad (10.10)$$

$$C = \left(\frac{32\pi}{405}\right) \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \frac{N_A [\text{Gd}]}{1000aD} \quad (10.11)$$

$$j(\omega) = \text{Re} \left\{ \left[1 + \frac{1}{4} \left[i\omega\tau_D + \left(\frac{\tau_D}{T_{1e}} \right) \right]^{1/2} \right] / \left[1 + \left[i\omega\tau_D + \left(\frac{\tau_D}{T_{1e}} \right) \right]^{1/2} + \frac{4}{9} \left[i\omega\tau_D + \left(\frac{\tau_D}{T_{1e}} \right) \right] + \frac{1}{9} \left[i\omega\tau_D + \left(\frac{\tau_D}{T_{1e}} \right) \right]^{3/2} \right] \right\} \quad (10.12)$$

where

N_A is Avogadro's number

$[\text{Gd}]$ is the concentration of the complex

a is the distance of the closest approach of the water molecule and the complex

D is the sum of the diffusion constants of water and the complex

τ_D is a diffusional correlation time given by $\tau_D = a^2/D$.

The second-sphere relaxation is the motion of the water molecules that are hydrogen bonded to the metal center. These water molecules have a longer residence time around the paramagnetic center with respect to the outer-sphere water molecules. Three parameters of relaxation mechanism that may increase the relaxivity have been intensely studied, namely, the number of coordinated water molecules (q), the water exchange rate ($k_{\text{ex}} = 1/\tau_m$) in Equation 10.3, and the reorientational correlation time (τ_R) in Equation 10.7.

Clinical CAs have one inner-sphere water molecule, and thus an increase in q will directly increase the inner-sphere relaxivity. However, this leads to a trade-off in stability by decreasing the coordination number. Desirable modifications of Gd–DTPA or Gd–DOTA to optimize the relaxivity would be to use octadentate or heptadentate chelates. Scientists have designed many different chelates to increase q [19–21]. Raymond and coworkers reported a novel class of chelate, HOPO (tris[(3-hydroxy-1-methyl-2-oxo-1,2-didehydropyridine-4-carboxamido)-ethyl]amine), which can accommodate two or more inner-sphere water molecules and have a good thermodynamic stability and relaxivity [22–25]. The observed r_1 of some HOPO–Gd complexes can be as high as $11.1 \text{ mM}^{-1} \text{ s}^{-1}$ at 298 K and 20 MHz [26]. The q value of Gd complexes in solution can be estimated by luminescence lifetime studies of Eu or Tb analogs, according to the Horrocks equation.

An increase in q does not always lead to an increase in the relaxivity [27]. The q value changes from one to two in an MS-325 derivative that has a carboxylate group replaced by a methyl group. However, its thermodynamic stability decreases, and the modification drastically decreases the water exchange rate by more than an order of magnitude. The observed relaxivity of the derivative upon biomacromolecule binding is lower than that of MS-325, although the r_1 of the derivative is slightly higher than that of MS-325, because a slow water exchange limits relaxivity in a system with a slow tumbling rate. Clearly, both the q and $1/\tau_m$ need to be considered in chelate designs.

Gd-based clinical CAs are small molecular agents with a molecular weight of around 700 Da. Their τ_R is 50–90 ps at 310 K [9]. Relaxivity has a linear relationship with the molecular weight of complexes at a given q value, provided that k_{ex} is not a limiting factor [41]. Strategies applied to lengthen τ_R include increasing the molecular dimension via either covalent or non-covalent interactions.

The covalent linkage of two DOTA type structures results in a τ_R of 130–190 ps, which is relatively longer than that of clinical CAs [42]. An increase in τ_R leads to an increase in r_1 . The relaxivity of a dimeric phosphinate analog of DOTA has a value of $8.2 \text{ mM}^{-1} \text{ s}^{-1}$, which is higher than that of the monomeric analog ($5.2 \text{ mM}^{-1} \text{ s}^{-1}$ at 298 K and 20 MHz) [43].

Non-covalent macromolecular binding is also favorable for a long τ_R . The interaction between CAs and cyclodextrin (CD) has been studied [44]. The first Gd complex that binds non-covalently to CD has been found to have BOM groups (BOM = benzyloxymethyl), for example $\text{Gd}\{\text{DOTA}(\text{BOM})_3\}$ and $\text{Gd}\{\text{DO3A}(\text{BOM})_3\}$ [45]. The CD-bound complex has a relaxivity of $25 \text{ mM}^{-1} \text{ s}^{-1}$, which changes to $49 \text{ mM}^{-1} \text{ s}^{-1}$ upon binding to poly- β -CD at 298 K and 20 MHz, due to the τ_R of the CD non-bound complex increasing by an order of magnitude upon binding. Several methodologies are available to estimate τ_R , one of which is to perform ^{17}O T_1 measurements. As Gd(III) does not favor the T_1 relaxation of ^{17}O , this method can be used to ascertain τ_R in the complex [14].

The relaxivity of complexes is governed by the interplay of the parameters and features of their chelates. Hence, an integrative approach that combines nuclear magnetic resonance dispersion (NMRD), ^{17}O NMR, and EPR (electron paramagnetic resonance) improves the consistency of relaxivity determinations. NMRD is good at predicting parameters in low fields in which electronic relaxation dominates. However, it offers weak predictions in high fields in which rotational relaxation dominates. Uncertainties in the outer-sphere relaxivity contribute about 50% of the observed relaxivity. ^{17}O NMR gives a good estimation of the water exchange rate, which has a negligible contribution from the outer-sphere, and the EPR depends only on the transverse relaxivity, and thus both methods can function alongside NMRD. This integrative approach refines the parameters that influence relaxivity [28].

High relaxivity improves the contrast of images and the response of CAs to physiological environments, such as oxygen, enzyme, protein, and pH in the regions in which they operate. $p\text{O}_2$ -responsive CAs are interesting because this parameter is related to several pathologies, such as stroke, ischemic diseases, and tumors. The designs of such CAs are based on the response of the metal center to redox reactions in their surroundings [46, 47].

CAs that respond to the presence of enzymes have enzymatic cleavable bonds. A well known example is EgadMe [48], which is a modified analog of Egad [49]. EgadMe is a DOTA derivative with β -galactopyranose, and has a β -galactosidase cleavable bond. After cleavage by this enzyme, the Gd center is relatively more exposed to water molecules and the r_1 increases. Another analog of EgadMe has β -glucuronic acid attached and is activated by β -glucuronidase [50].

Numerous Gd–DOTA derivatives show pH responsiveness. This phenomenon derives from mobile protons of coordinated water molecules or chelates. The exchange can be an acid- or base-catalyzed prototropic exchange, and is expressed as follows (Equation 10.13).

$$k = k_{\text{ex}}^{\text{H}_2\text{O}} + k^{\text{H}}[\text{H}^+] + k^{\text{OH}}[\text{OH}^-] \quad (10.13)$$

The deprotonation, protonation, or change in the number of coordinated water molecules of complexes results in a change in relaxivity [51, 52]. The difference in relaxivity of a

DOTA derivative containing a nitrophenolic group at pH 5 and pH 9 is due to the change in the prototropic exchange rate [53]. A DOTA derivative with phenolic and pyridyl protons has an enhanced relaxivity at a low and high pH. This is because of the prototropic exchange of coordinated water molecules at a low pH and the deprotonation of amide that forms intramolecular acid–base pairs at a high pH. In addition, the pyridyl group is able to form hydrogen bonding and prolongs the residence time of water molecules in the second-sphere [54]. Gd–DOTA-4Amp (DOTA-4Amp = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetamidomethylene phosphonic acid dihydrobromide in Figure 10.5) has a novel relaxivity profile at different pH because of rapid prototropic exchange between the phosphonate groups and the coordinated water molecule [55, 56]. The possibility of *in vivo* pH mapping using MRI has been successfully demonstrated [57, 58].

Chemical exchange saturation transfer (CEST) is another means of assessing pH in MRI, and involves the application of saturation pulses to exchangeable protons. The CEST signal comes from exchangeable protons, such as protons of –OH or –NH groups. Gd–DOTA-4Amp is also an efficient CEST agent [59], and is a sensitive pH CEST agent due to the presence of Ln–OH and Ln–NH. Sugars and amino acids can also be CEST CAs for the detection of signal changes at physiological pH and temperatures [60, 61]. Recently, a lanthanide complex, europium DOTAM–Gly, showed a change in CEST signal between pH 6 and 8 [62].

The percentage change in contrast enhancement must be significantly large for imaging physiological environments at the molecular level, otherwise the signal changes may not be observable in the MR images. The development of CAs will continue to focus on the improvement of relaxivity, and in particular agents that have a sensitive response toward *in vivo* environments.

10.2.2 Biomolecular Interactions

MRI CAs meet a variety of biomolecules in physiological environments, and may interact with proteins, human serum albumin (HSA), enzymes, and receptors. The binding of CAs to HSA is widely studied because it is the most abundant protein in blood plasma. HSA has a molecular weight of 66 kDa, a concentration of approximately 0.64 mM, and with two major binding sites, which are subdomains of IIA and IIIA [63].

Receptor-induced magnetization enhancement (RIME) describes the binding of CAs to biomolecules, such as proteins or receptors. This leads to an increase in the concentration and retention time of CAs in a particular region. It also results in an increase in τ_R and has a tremendous effect on increasing the relaxivity [64].

The binding affinity (K_A) (Equation 10.14) and relaxivity (r_1^b) of the adducts that form between complexes and macromolecules can be measured by the proton relaxation enhancement (PRE) method [65, 66]. PRE is based on the titration of complexes against the binding substrate of macromolecules, such as HSA. The binding of complexes to HSA influences the τ_R , τ_m , T_{1e} , and T_{1M} of complexes. If a Gd complex (GdL) binds to HSA, then adducts form and r_1^b is usually higher than r_1 .

$$K_A = [\text{GdL} - \text{HSA}]/[\text{GdL}][n\text{HSA}] \quad (10.14)$$

Ibuprofen and warfarin are ligands that strongly bind to the sub-domains IIA and IIIA, respectively, of HSA. The identity of the HSA binding site can be determined through competitive binding assays with known binding substrates, such as ibuprofen, warfarin, bilirubin, linolenic acid, and 1,3,5-triiodobenzoic acid.

Gd(III) complexes that show preferential binding to HSA have hydrophobic moieties. The hydrophobic phenyl group of Gd{DOTA(BOM)₃} is responsible for HSA binding. It has an r_1^b of $53.2 \text{ mM}^{-1} \text{ s}^{-1}$ at 298 K and 20 MHz [67], although the binding affinity ($K_A = 1.7 \times 10^3 \text{ M}^{-1}$) is weaker than that of Gd-DTPA(BOM)₃ ($K_A = 4.0 \times 10^4 \text{ M}^{-1}$) [68]. Other Gd-DO3A derivatives that have phenyl moieties also show HSA binding properties [69]. However, their r_1^b is not close to $100 \text{ mM}^{-1} \text{ s}^{-1}$, which is the maximum relaxivity predicted theoretically in low fields. One of the reasons for this is the displacement of the inner-sphere water molecules upon HSA binding. According to a docking study, a coordination cage that is further away from the water layer on the protein surface causes a high relaxivity [70]. This is because carboxylate groups on the protein surface cannot displace the bound water molecules, which means that the inner-sphere water molecules and k_{ex} of the complex will not be interfered with or quenched. Moreover, dianions, such as phosphate, can also displace water molecules and form ternary adducts, which will limit the r_1^b . The geometry of complexes with two inner-sphere water molecules leads to this dianionic displacement [71].

MS-325 is a clinical HSA binding CA that is suitable for magnetic resonance angiography (MRA). It has a strong HSA binding affinity and its r_1^b undergoes a ninefold increase upon binding. MS-325 has a favorable r_1^b as the τ_R lengthens by 100 times, and because it binds to a fast water exchange site II region of HSA [72]. The r_1^b of its two isomers is $42 \text{ mM}^{-1} \text{ s}^{-1}$ and $38.3 \text{ mM}^{-1} \text{ s}^{-1}$ at 20 MHz and 310 K, respectively. Differences in observed relaxivity between isomers are small because of their similar water exchange rates [73, 74]. The physiochemical properties of MS-325, such as the k_{ex} , are changed upon binding [75]. Moreover, the r_1^b of serum albumin adducts is species dependent. MS-325 has an r_1^b of $46.3 \text{ mM}^{-1} \text{ s}^{-1}$ when it binds to HSA, and of $30.5 \text{ mM}^{-1} \text{ s}^{-1}$ when it binds to serum albumin of rabbit at 308 K and 20 MHz [76]. This is because the k_{ex} binding of HSA is faster than that of serum albumin of rabbit.

HSA binding not only interferes with the inner-sphere water molecules, but also the outer-sphere. DOTP(1,4,7,10-tetraazacyclododecane-*N'*,*N''*,*N'''*,*N''''*-tetrakis(methylenephosphonic acid) derivatives have no inner-sphere water molecule, and rely on the outer-sphere mechanism. This property allows the study of how HSA binding sites affect relaxivity, which shows that differences in r_1^b are solely due to the nature of the binding sites [77, 78].

Enzymes are common biomolecules. Gd complexes that have specific enzyme responsiveness favor generating signals *in vivo*, as discussed in the previous section. The percentage relaxivity change can be magnified in various ways. One Gd-DTPA derivative shows binding toward carbonic anhydrase, after which the observed relaxivity increases seven times [79]. Gd-DTPA or Gd-DOTA derivatives with enzyme cleavable linkage have been studied to amplify the percentage change in relaxivity. In general, relaxivity increases when CAs bind to enzymes or when specific groups are removed from CAs in the presence of an enzyme. A different strategy makes use of a change in binding affinity. A Gd-DTPA derivative is activated by a human carboxypeptidase B known as the thrombin-activatable fibrinolysis inhibitor (TAFI). After cleavage, this complex shows improved HSA binding and an increased r_1^b [80]. Bond formation can also be employed in hydrolysis or cleavage to generate changes in the relaxivity. In this process, the enzyme catalyzes oligomerization *in situ*. A Gd-DOTA derivative acts as an enzyme substrate of myeloperoxidase to probe atherosclerosis or E-selectin on the surface of endothelial cells, which polymerize in the presence of enzymes [81, 82]. Receptor targeting has attracted attention because it involves cell signaling pathways, such as progesterone receptors. Relaxivity responses to gene transcription activation have also been

observed. Upon receptor binding, a specific endogeneous gene expression pathway is activated and the r_1^b increases [83]. Analogs have been tested as CAs for cancer prognostication [84].

In general r_1^b depends on the inner-sphere of water molecules, the formation of ternary adducts, the binding affinity, the site of binding, the number of binding sites, and the water exchange rate upon biomolecular binding. These factors also influence and are observed in enzyme binding. The percentage relaxivity increase can be further enhanced by designing complexes with a specific mode of binding. An example of this is multilocus binding, which maintains the rigidity of complexes by having two anchorage points on biomolecules that leads to an increase in the percentage change in relaxivity [85]. Biomolecular interactions are another strategy for maximizing relaxivity *in vivo*, and the percentage change of these interactions can reveal certain physiological conditions. This is worth noting for new chelate designs, and especially those for clinical applications.

10.2.3 Toxicity and Safety Issues

Safety is a prime concern in the development of pharmaceutical products. A drug that has an excellent therapeutic effect cannot be released to the market if it has serious adverse effects. Extensive pharmacologic studies and strict evaluations of CAs are required before gaining approval from the Food and Drug Administration (FDA). Factors assessed include the formulation, hemodynamic effect, toxicity, adverse effects, viscosity, osmolality, and immunogenicity of the agent [86].

Clinical CAs are generally safe in clinical use, but there is always some concern about their toxicity, which originates from the dissociation of the complexes. Both chelates and metal ions are acutely toxic in terms of lethal dose (LD_{50}) [87]. Dechelated Gd(III) is highly toxic and will deposit in the liver, spleen, kidney, and bone marrow [88]. It can also disturb calcium-dependent processes, such as muscle contraction, coagulation, enzyme function, phagocytosis, and signal transmission in the nerves. This is caused by transmetallation with Ca(II) [89]. Cyclic complexes have a lower percentage of Gd(III) in tissues compared with acyclic complexes because of their greater stability [90, 91].

The likelihood of dechelation depends on both the thermodynamic and the kinetic stability. A complex with a low thermodynamic stability will be dechelated easily when there is a change in pH. A low kinetic stability implies that Ca(II) or other endogeneous cations can easily free Gd(III) from its chelates. Clinical CAs are thermodynamically stable with a $\log K_{eq}$ of 17–26 (Table 10.2), and the kinetic stability of cyclic CAs is higher than that of acyclic CAs. Among the clinical CAs, Gd-DOTA has the highest thermodynamic and kinetic stability.

Nephrogenic systemic fibrosis (NSF) is a sclerosing disorder found in patients with impaired renal function. It was recognized in 1997 and first reported in 2000 [92]. The majority of reported cases are associated with acyclic Gd-based clinical CAs, such as Gd-DTPA-BMA, in patients with renal deficiency. CAs will usually be excreted within 2 h in patients with normal renal function. However, the half-life is prolonged in patients with renal failure, and can be between 30 and 120 h [93]. The persistence of CAs increases the risk of dechelation and increases the tissue exposure to Gd(III). Certainly, this risk also depends on the strength of the chelations. A recent clinical study showed the association of NSF with Gd-DTPA and Gd-DTPA-BMA [94]. However, no validated mechanism has been established for NSF. The association with CAs is still controversial, and many questions remain unanswered.

Table 10.2 Physiochemical properties of clinical CAs.

Property	Gd– DTPA	Gd– DTPA– BMA	Gd– DTPA– BMEA	Gd– BOPTA	Gd– EOB– DTPA	MS-325	Gd– DOTA	Gd– HP– DO3A	Gd– DO3A– butrol
Osmolality, Osm kg ^{−1} at 310 K	1.96	0.65	1.11	1.97	0.69	0.83	1.35	0.63	1.60
Viscosity, mPa s at 310 K	2.9	1.4	2.0	5.4	1.2	2.1	2.0	1.3	5.0
Thermodynamic stability, log <i>K</i> _{eq}	22.1	16.9	16.6	22.6	22.6	22.1	25.8	23.8	21.8
Kinetic stability ^a	Low	Low	Low	Medium	Medium	Medium	High	High	High
Lethal dose, mmol kg ^{−1}	6.4	34	26	7.9	>10	5–6	10.6	12	23

^aLow: long-time index < 0.30. Medium: long-time index = 0.30–0.95. High: long-time index > 0.95, where the long-time index is the long time and ratio indexes of Zn(II) transmetallation [9, 89, 95–98].

Potential complexes with special functionalities and improved relaxivity should be biocompatible and safe *in vivo*, and the chelates must be designed to circumvent the toxicity of Gd(III) to give complexes with a high safety profile. Gd complexes containing cyclic chelates are preferred in this regard.

10.3 Contrast Enhanced MRI for Disease Diagnosis

The choice of CAs and imaging protocols in MRI depends on the organ to be imaged and the pathology of the disease in question. Clinical Gd-based CAs can be classified as ECF (extracellular fluid) agents, blood pool agents, or hepatobiliary agents [99], and are usually administered intravenously by bolus injection. ECF CAs disperse throughout the body and have similar contrast enhancement patterns, as observed *in vivo*. They also have a low incidence of adverse effects and are used for imaging the vascular system, the central nervous system (CNS), and renal and hepatic function. Blood pool agents are used in magnetic resonance angiography (MRA) for vascular imaging, whereas dynamic contrast-enhanced (DCE) and delayed-phase MRI are both commonly used for the imaging of lesions. DCE-MRI can image the region of interest (ROI) before and after injection of CAs at different time points, and allows the distribution half-life, region of distribution, excretion half-life, and excretion pathway of CAs to be observed. Delayed-phase MRI describes the imaging after a certain period of time post-injection, such as 10–40 min, and is thus efficient for diagnosis with tissue-specific CAs. Tissue-specific CAs have a high local concentration in tissues, and provide a persistent signal for tissue identification. For example, hepatobiliary CAs have a better contrast enhancement than ECF agents in the liver.

SNR and CNR are terms that describe the contrast of MR images. SNR is the signal-to-noise ratio and is equal to SI_{ROI}/SD , where SI is the signal intensity and SD is the standard deviation. SNR describes the signal from the ROI. The contrast-to-noise ratio [CNR = $(SI_{ROI} - SI_{background})/SD$] is used to describe the difference between the ROI and the background.

The use of specific CAs improves the quality of images and provides additional physiological information. For example, HSA-binding CAs provide a wide window for MRI scans, and

hepatocyte-targeted CAs can improve the liver-to-lesion CNR. Thus, with the aid of suitable CAs and imaging protocols, physicians can achieve an accurate and confirmative diagnosis.

10.3.1 Magnetic Resonance Angiography (MRA)

Magnetic resonance angiography (MRA) is a method of imaging blood vessels in the presence of certain diseases, such as angiogenesis, tumors, atherosclerosis, coronary arteries [100], myocardium infarction, vascular injury, and blood flow reduction. Blood pool CA enhanced MRA increases the vessel-to-background ratio [101]. Blood pool CAs can be classified into two types, namely, low molecular weight Gd-based CAs and macromolecular CAs.

MS-325 is a low molecular weight blood pool CA, and was the first Gd-based CA approved for clinical use. The complex is both thermodynamically and kinetically stable [102]. It binds strongly but reversibly to HSA, and stays in the blood pool for a longer time than EFS CAs [103]. About 80 to 96% of the dose binds to HSA [104], which ensures the availability of free MS-325 to achieve equilibrium binding, and hence a relatively slow and efficient renal excretion (Figure 10.6).

The percentage binding of MS-325 is species dependent [105]. It has a binding range of 64–91%, but preferentially binds to human > pig > rabbit > dog > rat > mouse [106]. Its *in vitro* relaxivity is 53.5, 32.5, 28.0, and 22.6 mM⁻¹ s⁻¹ at 20 MHz in human plasma, rabbit plasma, rat plasma, and mouse plasma, respectively [104]. The first clinical trial demonstrated MS-325 to have a good CNR for DCE-MRI at a dose of 0.05 mmol kg⁻¹ [107]. Its excretion half-life is 2–3 h [105].

DCE-MRA using MS-325 displays a long blood pool retention and allows steady-state imaging, which improves the vascular, arterial, and venous contrast enhancement [108]. This combination has been used for imaging the whole heart [109] and for cardio-venous imaging [110]. The pattern of contrast enhancement for cardiovascular imaging also depends on the type of CA used [111].

Among the macromolecular CAs, P792 is a Gd-DOTA derivative that has a molecular weight of 6.47 kDa. Its high molecular weight gives a high relaxivity because of the heightened τ_R . It has a limited diffusion through the endothelium and is rapidly excreted by the kidneys. It does not cross the blood–brain barrier (BBB) and hence remains in the blood pool. It has been used for the assessment of cardiac function. Although other macromolecular CAs have a prolonged blood circulation, their slow renal excretion excludes them from clinical use [112, 113].

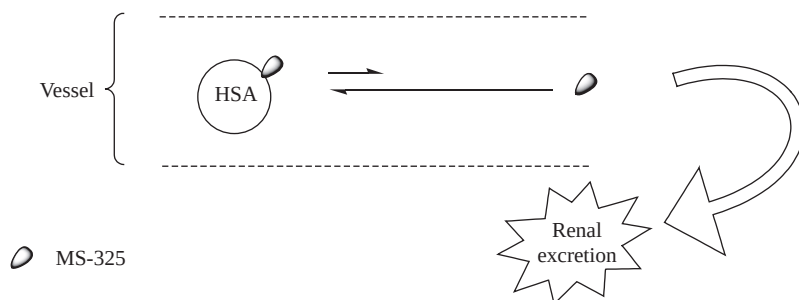


Figure 10.6 The mechanism of HSA binding of MS-325 in the blood pool. An equilibrium is established between the HSA bound form and the free form, which leads to a slow renal excretion.

The differences between low molecular weight Gd-based CAs and macromolecular CAs stem mainly from their pharmacodynamic and pharmacokinetic properties, that is, what the CA does to the body, and vice versa. In addition to the observed relaxivity, the dynamic relaxivity is another parameter that is used in contrast-enhanced MRA in the presence of different types of CAs. The dynamic relaxivity describes the relaxivity results from both bound and non-bound complexes. For example, a comparison of the strongly HSA-bound MS-325 with the non-HSA-bound P792 in rabbit showed P792 to have a more constant dynamic relaxivity [114]. A constant pharmacokinetics profile is also favorable for MRA analysis.

Ideal blood pool agents display moderate HSA binding and a good dynamic relaxivity, a reasonably long blood residence time, no diffusion via the endothelium or reduced interstitial diffusion, a smaller dose and injection volume requirement, and efficient excretion. These qualities enable high-resolution MRA and an increase in vessel-to-background contrast, and thus a better visualization of smaller vessels and vascular pathology.

10.3.2 Liver Disease

Clinical hepatobiliary CAs have preferential uptake in the liver, or specifically in hepatocytes. Gd-BOPTA and Gd-EOB-DTPA are both hepatocyte-targeted CAs for liver imaging. These hepatobiliary agents enter hepatocytes via ATP-dependent organic anion transporter polypeptides (OATPs), and are excreted in non-metabolized forms to the bile canaliculi via canalicular multispecific organic anion transporters. These transporters are similar to glutathione-S-transferase, an enzyme with many functions, including reduction, oxidation, and substitution. The pathways of these hepatobiliary agents can be inhibited by bromosulphothalein or bilirubin [115, 116]. As they target hepatocytes, the degree of contrast enhancement and biliary excretion of these CAs depends on the liver function. For compounds to be excreted via organic anion transporters, they should have both hydrophilic and hydrophobic parts and a molecular weight of 300–1000 Da [117].

The degree of biliary excretion is species dependent. Generally, mice, rats, and dogs have a better biliary excretion than rabbits, monkeys, and humans [118]. Gd-BOPTA has a 0.6–4% biliary excretion in humans, the remainder being excreted in urine [119]. Gd-EOB-DTPA has a biliary excretion of 43.1–53.2%, a renal excretion of 41.6–51.2%, and an extrahepatic recirculation of about 4% in humans [120]. In various animals, excretion is slightly different. For example, the biliary excretion of Gd-BOPTA in rats is 55% and in rabbits is 25% [121]. Gd-EOB-DTPA has a 63–80% biliary excretion in rats and a 32–34% excretion in monkeys [122].

Hepatobiliary CAs also show good contrast enhancement in the liver parenchyma. The recommended dose of Gd-BOPTA is $0.05 \text{ mmol kg}^{-1}$ in humans [119], and it has a plasma half-life of 15 min [123]. Its hepatic contrast enhancement is prominent at the delayed phase of 40–120 min post-injection. The estimated relaxivity in the liver is $16.6 \text{ mmol}^{-1} \text{ s}^{-1}$, and the percentage improvement relative to the non-enhanced image is 44.5% versus 19% on a breathhold gradient echo sequence [124]. Gd-BOPTA has a higher relaxivity *in vivo* than ECF CAs because of its weak HSA binding [125]. Gd-EOB-DTPA has a plasma half-life of 10 min, and an estimated relaxivity in the liver of $30 \text{ mmol}^{-1} \text{ s}^{-1}$, which is higher than that of Gd-BOPTA. The minimum dose is 12.5 or $25 \mu\text{mol kg}^{-1}$ [126], and the maximum hepatic contrast enhancement is observed at 10–20 min post-injection [120, 127].

Hepatobiliary CA-enhanced MRI is used for imaging liver lesions, malignancy, and metastases. Tumors do not have normal hepatocytes, and thus do not preferably uptake hepatocyte-targeted CAs, which leads to a greater contrast between tumors and the liver. Hepatobiliary CAs provide a longer liver contrast enhancement than ECF CAs, and an improvement in the liver-to-lesion contrast is observed in delayed-phase MRI after wash-out in the artery phase. This increases the liver-to-lesion CNR and gives a good delineation of lesions. Gd-BOPTA improves lesion characterization in dynamic and delayed MRI by 25% and 59%, respectively [128], and Gd-EOB-DTPA improves the sensitivity of lesion imaging by approximately 10% [129]. Both agents thus improve the sensitivity of liver lesion imaging.

In delayed-phase imaging, the signal increase in the liver parenchyma does not necessarily increase the conspicuity or detection of lesions because residual hepatocytes of a tumor of hepatocytic origin, such as hepatocellular carcinoma (HCC) and focal nodular hyperplasia, may influence the contrast enhancement. Gd-BOPTA is effective for use with delayed-phase MRI to detect metastases [130]. In cirrhosis, liver functioning is impaired and the number of normal hepatocytes is reduced. The entry of Gd-BOPTA into cirrhotic hepatocytes decreases, but the accumulation in the liver increases due to reduced biliary excretion [131]. As a consequence, contrast enhancement is reduced and the window of acquisition is widened. The contrast enhancement of a cirrhotic liver is therefore different from that observed in normal liver parenchyma.

Clearly, clinical CAs have their limitations in liver imaging, especially for diagnosis at the early stages of disease. As the best therapy generally occurs with an early diagnosis, a new generation of CAs that can improve the diagnosis of HCC with or without the presence of cirrhosis is needed. Such CAs would lead to better diagnosis and disease management, thus increasing the curability of liver diseases [95, 132]. An effective HCC-targeted CA for the early diagnosis of liver disease should be able to target lesions, should have a wide imaging window, should not remain in the liver, and should display a high liver-to-lesion CNR.

10.3.3 Oncology

Tumor growth is a complicated process and is regulated by numerous factors. The area surrounding tumor cells is known as the microenvironment, and consists of an extracellular matrix (ECM), blood and lymphatic vessels, infiltrating leukocytes, and stromal cells. The ECM describes physiological conditions, such as oxygen supply and pH. Angiogenesis is the formation of new blood vessels, and is regarded as a key element in the pathophysiology of cancer. As the tumor size reaches 1–2 mm, neovascularization is necessary to support tumor growth in addition to passive diffusion [133].

Unlike the imaging of morphology of vessels in MRA, the imaging of angiogenesis using MRI is conducted on a molecular basis. Molecular targets for angiogenesis include vascular endothelial growth factor (VEGF) integrins and circulating endothelial progenitor cells. The angiogenic actions of VEGF are mainly mediated by two endothelium-specific receptor tyrosine kinases [134]. The role of VEGF is to stimulate the growth of vascular endothelial cells and increase the microvessel permeability [135]. Its expression increases under hypoxia, which is a deficiency of the supply of oxygen to tissues.

Integrins are a family of cell adhesion molecules that signal across the cell membrane. $\alpha_v\beta_3$ is an integrin that is over-expressed in activated and proliferating endothelial cells, and hence

acts as a marker of malignancy. The $\alpha_v\beta_3$ binds to arginine–glycine–aspartic acid (RGD) and is significantly upregulated in the tumor vasculature [136–138].

DCE-MRI is often used in the assessment of tumor microcirculation, permeability, and perfusion, and can diagnose angiogenesis, lesions, and differentiation. The previously discussed contrast enhancement features of ECF CAs are similar in oncology, and thus HSA binding CAs, such as MS-325 and Gd-BOPTA, are capable of providing improved imaging of vascular permeability and angiogenesis [139]. The results of studies on HSA-binding CAs show good correlation with the histological findings, which indicates that they can be used to assess the therapeutic effects of anti-angiogenic drugs. For example, SU6668 targets VEGF, fibroblast growth factor (FGF), and PDGF tyrosine kinase receptors, and Gd-DTPA derivative enhanced images show good correlation with the histology after SU6668 treatment for angiogenesis [140]. DCE-MRI using Gd-DTPA-BMA has been performed to evaluate the therapeutic effect of an anti-angiogenic compound (a VEGF receptor 2 tyrosine kinase inhibitor) [141, 142]. DCE-MRI for VEGF imaging can provide information on therapy, anatomy, and functional abnormalities in malignant vessels, and can also give information on tumor biology [143, 144].

DCE-MRI is also useful in mammography [145]. Gd-DTPA and Gd-BOTPA are commonly used for MR mammography. In clinical studies, Gd-DTPA enhanced MRI has been performed to assess angiogenesis and morphological findings in breast cancer [146–149], and the results correlate well with the histological findings. Angiogenetic associated VEGF can be visualized by comparing the rim enhancement of lesions [150]. A higher ipsilateral vascularity can also be an indicator for the characterization of benign and malignant breast lesions, because malignant neoplasm has a metabolic demand and a reduced resistance to blood flow [151].

Compared with Gd-DTPA, Gd-BOPTA-enhanced MR mammography results in the better delineation of lesions and is more conspicuous [152]. This can be linked to the weak HSA binding of Gd-BOPTA, which makes it advantageous for breast lesion characterization. At 0.1 mmol kg^{-1} , Gd-BOPTA shows a superior sensitivity and specificity toward breast cancer diagnosis [153]. Contrast-enhanced images also show an association with ipsilateral breast cancer at $0.05 \text{ mmol kg}^{-1}$ [154]. These examples demonstrate that the imaging of angiogenesis via vascular mapping and the use of specific CAs are promising methods for the improvement of breast cancer diagnosis [155].

A recent example of VEGF and RGD targeting associated with Gd-based CAs is biotin–BSA–Gd-DTPA, which allows the assessment of VEGF and at the same time responds to the treatment of vasculature-targeting drugs in mice, and may be an accurate and reliable method for evaluating the mechanism of vasculature-targeting drugs [156]. RGD-targeted integrins, and therefore CAs for $\alpha_v\beta_3$ targeting are designed with an RGD peptide. A Gd-DTPA derivative with RGD mimetic characteristics has potential application in the characterization of $\alpha_v\beta_3$ related diseases, and shows an encouraging contrast enhancement in mice [157]. Such methodologies can be used to visualize the early vascular effects of treatments.

10.4 Outlook

The first generation of Gd-based CAs focused on improving the efficacy of contrast enhancement, whereas the second generation focused on the development of organ-specific CAs. Targeting disease-related proteins, receptors, or biomacromolecules are the main strategies to increase the specificity of CAs. For example, MS-325 targets HSA for MRA and Gd-BOPTA

targets hepatocytes. CAs that have a specificity toward disease-related molecular targets are currently being intensively researched.

In oncology, molecular targets are closely associated with disease status, such as angiogenic factors. The imaging of molecular targets improves the contrast enhancement and allows the correlation of signals with pathologies. CAs that have specific binding are invaluable, and especially those that respond to physiological changes. A molecular targeting CA can trace malignant tumors, but its translation into clinical application is limited by the detection sensitivity [158]. It is worth noting that a large percentage signal change and signal amplification are required for *in vivo* applications.

Cell and gene therapies are close to achieving clinical application [159], and go hand in hand with molecular, pre-symptomatic, and early disease diagnosis through the use of specific CAs with a high sensitivity. Gd-based contrast agents play an important role in this aspect of medical diagnosis, in particular when used as T_1 -agents. CAs with specific functions can exploit the inherent high resolution of MRI, and in particular can achieve a better SNR in high magnetic fields.

Future research will focus on CAs that provide not only anatomical information, but also information about the onset and progression of diseases and the functionality of transplanted cells and genes. Undeniably, molecular imaging has tremendous potential to significantly advance medicine.

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11

Electroluminescence Based on Lanthanide Complexes

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11.1 Introduction

Since the breakthrough by Kodak in 1987 [1], organic light-emitting diodes (OLEDs) have been seen as one of the most promising technologies for future display and solid state lighting applications. In the last two decades, a number of materials have been developed and improved by both academic and industrial research to fulfill the requirements of these applications [2–7]. OLEDs incorporate many advantageous properties including low driving voltage, high brightness, wide viewing angles, no back lighting requirements, rapid response, better resolution, lower power consumption, capability of multicolor emission by the selection of emitting materials, easy fabrication of thin-film devices with large-area, lighter weight, and so on. Consequently, OLEDs are being heralded as the technology for the next generation of flat panel displays. Significant improvements in device fabrication and long-term stability of OLEDs have been achieved in the past few years. As a result OLED displays have already been introduced into car stereos, digital cameras, mobile telephones, and a high resolution 3D-display visor for PC gaming and simulation.

Although the studies on OLEDs have achieved considerable success, it is still difficult to obtain pure emission colors from small organic molecules or conjugated polymers, because their emission spectra typically have a half peak width of about 100 nm. Lanthanide ions can exhibit spectrally narrow emission due to intra-atomic transitions within the 4f shell. Consequently, luminescent lanthanide complexes are good candidates as emitting materials in OLEDs.

11.1.1 Operating Principles in OLEDs

Electroluminescence (EL) is the phenomenon by which electrical energy is converted into luminous energy by the recombination of electrons and holes in the emissive material [8]. The basic structure of an OLED consists of a thin film of organic material sandwiched between two electrodes, an anode of high-work-function material such as indium tin oxide (ITO) on a glass substrate, and a cathode of a low-work-function metal such as calcium (Ca), magnesium (Mg), or aluminum (Al) or an alloy such as Mg:Ag.

To improve charge transport and injection, additional layers are often introduced into the single-layer device. In a multilayer device, the layers may consist of a hole-injection layer (HIL), hole-transporting layer (HTL), emission layer (EML), hole-blocking layer (HBL), electron-transporting layer (ETL), and electron-injection layer (EIL) (see Figure 11.1). Organic electroluminescent (OEL) materials are almost insulators, and light is produced by recombination of holes and electrons. When a voltage is applied between the electrodes, charges are injected into the organic material, the holes are from the anode and electrons from the cathode. The charges move inside the material, generally by hopping processes and then recombine to form excitons. The location of the recombination zone in the diode is a function of the charge mobility of the organic material and of the electric field distribution. After diffusion, the exciton recombines and a photon is emitted (see Figure 11.2) [9].

Organic layers are deposited mainly by thermal evaporation or spin coating from solutions for small molecule or polymeric materials, respectively. Metal layers are usually made by thermal evaporation. All layers should be chemically stable, especially under the device operating conditions, and resistant to oxidation or photo-oxidation.

There are several preferred hole-transport materials. Among them, *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) and *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1'-diphenyl-4,4'-diamine (NPB) have been studied and used extensively (Figure 11.3). The most practical and commercially used electron-transport material is tris(8-hydroxyquinolino)aluminum (AlQ) with the molecular structure shown in Figure 11.4. As the electron mobility in organic materials is generally several orders of magnitude less than the hole mobility, an electron-conducting hole-blocking layer such as 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) or 3-(4-biphenyl)-4-phenyl-5-(4-*tert*-butyl-phenyl)-1,2,4-triazole

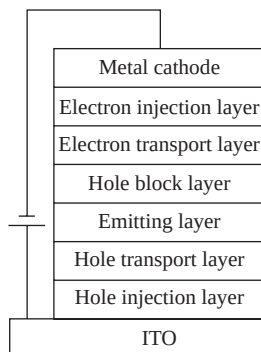


Figure 11.1 The multilayer structure in OLEDs.

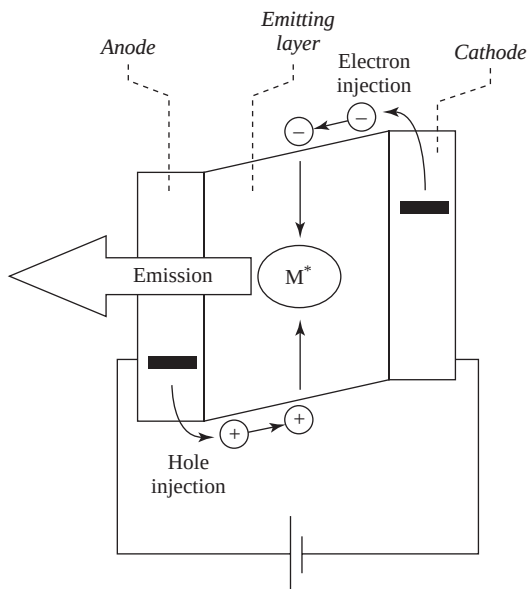


Figure 11.2 The formation of excitons [9]. (Reprinted with permission from Y. Shirota and H. Kageyama, “Charge carrier transporting molecular materials and their applications in devices,” *Chemical Reviews*, **107**, 953–1010, 2007. © 2007 American Chemical Society.)

(TAZ) shown in Figure 11.5, is often added between the layer of luminescent material and the electron-transport layer or the metallic electrode, to balance the charge injection and transport rates. Then the recombination of electrons and holes is confined to the emitting layer and consequently a high electroluminescent efficiency can be obtained. Some hole-injection materials are shown in Figure 11.6.

A number of parameters are used in the reporting of the efficiencies of OLEDs, namely quantum efficiency, current efficiency in cd A^{-1} (η_L) or luminous efficiency (η_P) in lm W^{-1} . For the quantum efficiency there are two different parameters, the external quantum efficiency (η_{ext}) and the internal quantum efficiency (η_{int}). The external quantum efficiency η_{ext} of an OLED may be expressed as:

$$\eta_{\text{ext}} = \eta_r \cdot \varphi_f \cdot \chi \cdot \eta_{\text{out}} = \eta_{\text{int}} \cdot \eta_{\text{out}}$$

where

η_r is the probability that holes and electrons recombine to form excitons

φ_f is the fluorescent quantum efficiency or the fraction of excitons that decay radiatively

χ is the probability for radiative decay to occur

η_{out} is the fraction of photons that can escape the device and is limited by waveguiding in the device layers and the substrate [8, 10].

The current efficiency (η_L), expressed in cd A^{-1} , is another way to characterize the quality of a device and represents the ratio of the luminance (L) to the current density (J) flowing into the diode. The luminous efficiency (η_P) expressed in lm W^{-1} is the ratio of the optical flux to the electrical input.

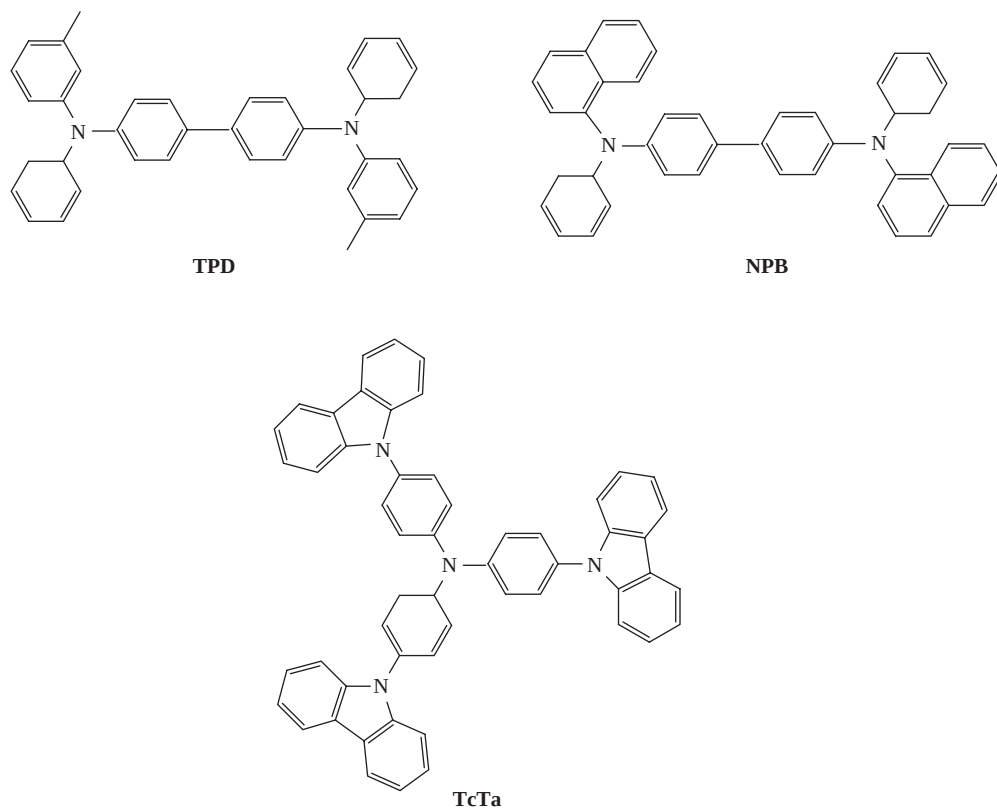


Figure 11.3 Structures of some hole-transporting materials.

11.1.2 History of OLEDs

In 1953 electroluminescence from organic compounds was first observed by Bernanose [11]. Ten years later, Pope *et al.* conducted experiments on electroluminescence in anthracene crystals, which were of the order of $10\ \mu\text{m}$ thick [12]. The devices required extremely high operating voltages ($>400\ \text{V}$), making them impractical for commercial applications. More attempts to study electroluminescence in organic crystals were made over the next two decades and these all required high driving voltages and had low power efficiency because most of the carriers move through the entire film or crystal without collisions, forming no radiative excitons in single-layer OLEDs. It was not until 1987 that electroluminescence became widely attractive. In that year, Tang and VanSlyke of the Eastman Kodak Company [1] reported results on the first multilayer organic light-emitting diode in which AlQ was used as the light-emitting layer and an aromatic diamine was used as a hole-transport layer between the indium tin oxide anode and the emissive layer. The use of multiple organic layers brought great success in developing an OLED with a luminance over $1000\ \text{cd m}^{-2}$, which is high enough for practical applications, at an operating voltage below $10\ \text{V}$. There are two merits in the multiple organic layers.

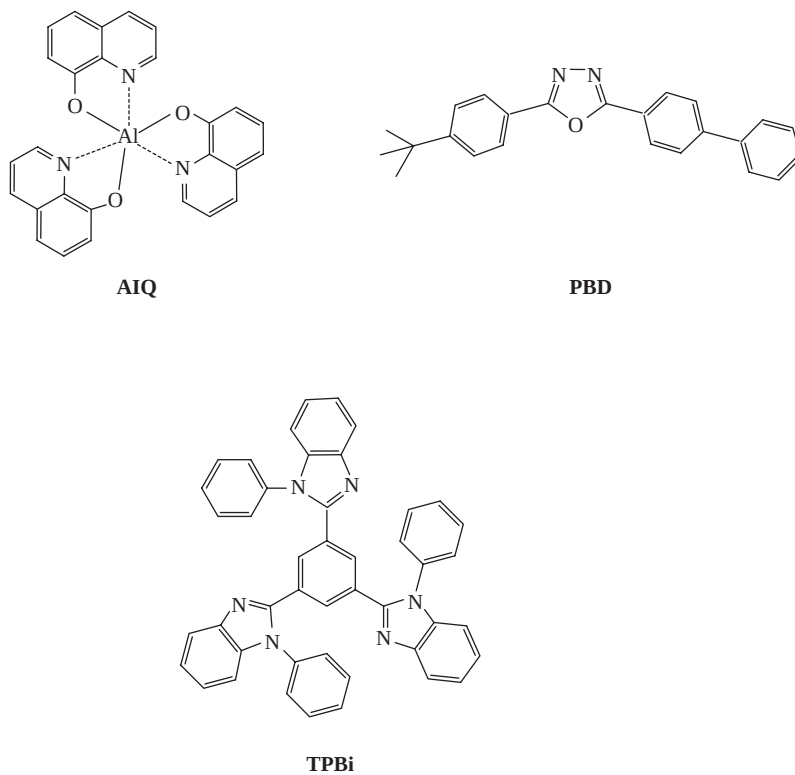


Figure 11.4 Structures of some electron-transporting materials.

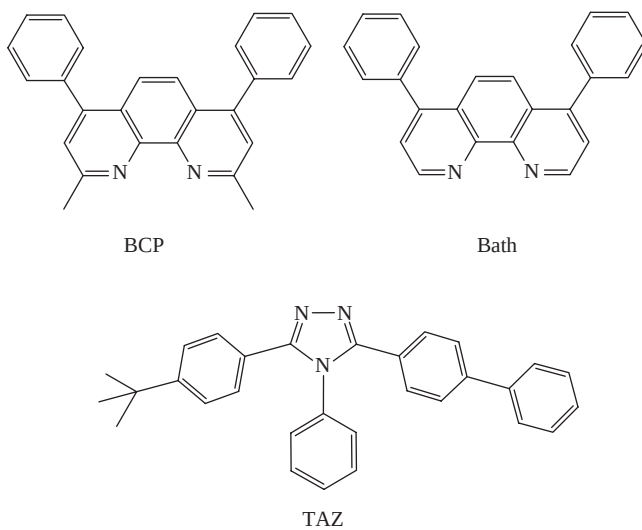


Figure 11.5 Structures of some hole-blocking materials.

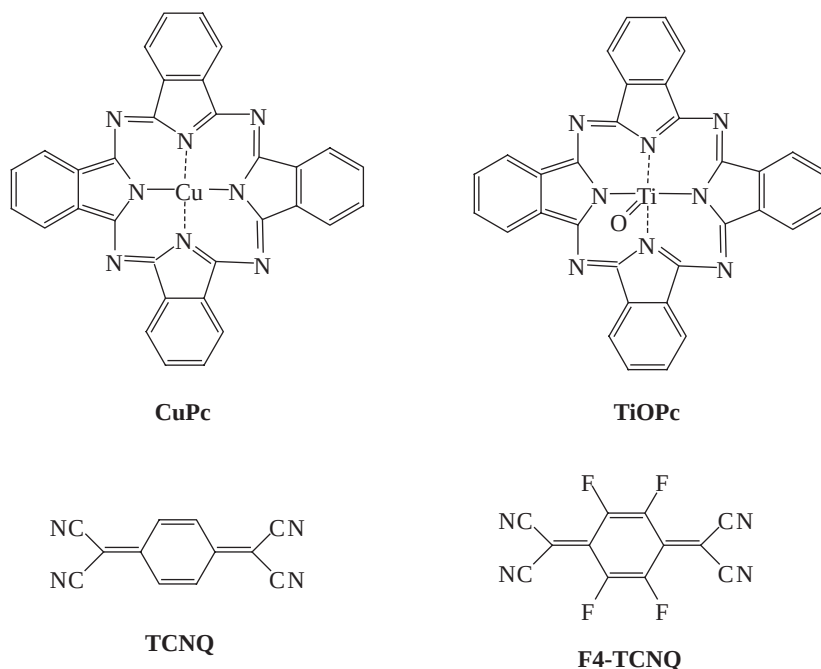


Figure 11.6 Structures of some hole-injection materials.

Firstly, matching the band levels of the organic layers to the work functions of the electrodes reduces the barrier for charge injection and reduces the operating voltage. Secondly, the organic/organic interface creates two charge-blocking barriers, which confine the injected charges to a thin interfacial region where radiative excitons are formed, and prevent recombination from occurring at the organic/electrode interfaces. Another fundamental piece of work contributing to the evolution of OLEDs was reported in 1990 by a Cambridge group [13], in which EL from devices based on the conjugated polymer poly(*p*-phenylenevinylene) (PPV) was observed. The simplicity of manufacture together with the possibility of fabricating flexible, large-area, extremely thin full-color displays generated a sudden surge of interest in this research field. Since then, thousands of papers have been published on various aspects of OLEDs ranging from the use of novel materials, structures, and processing methods to concepts such as electronic and emissive doping, and so on. Furthermore, the recent finding of triplet emitters has led to remarkable improvements in the electroluminescence quantum efficiency [14]. Now, the rapidly growing market for OLED technology is driving both academic and industrial research towards the development of new materials and advanced manufacturing technology.

11.1.3 Potential Advantages of Lanthanide Complexes Used in OLEDs

When designing light-emitting materials for OLEDs, three main issues must be addressed: emission color, emission efficiency, and lifetime. Although OLED studies have demonstrated

considerable progress, it is still difficult to optimize, simultaneously, the color, efficiency, and lifetime of the conjugated organic polymers or small molecules that are widely used for luminescent materials. It is especially difficult to obtain pure emission colors from conjugated polymers or small organic molecules because their emission spectra usually have full width at half maximum (FWHM) of 50–100 nm or more. Filtering out part of the emission can give pure color OLEDs; however these OLEDs are inefficient because only part of their emission is utilized.

In contrast to organic chromophores, luminescent lanthanide complexes are believed to be promising candidates to solve this problem. The spectroscopic properties of some lanthanide ions are ideal for use in full color displays, as is known from inorganic luminescent materials in cathode-ray and projection television tubes. Luminescent lanthanide complexes belong to a special class of emitters, exhibiting the following important advantages.

- (1) **Sharp emission band:** Lanthanide complexes are characterized by efficient intramolecular energy transfer from the excited singlet state (S_1) to the triplet state (T_1) of the ligand, and then to the excited 4f states of central lanthanide metal ion. When they relax from the excited state to the ground state of lanthanide ions, the corresponding emission will take place. The sharp spectroscopic bands, usually less than 10 nm in FWHM, originate from the f–f transitions. Compared with that of polymers or small organic molecules, the emission bands from lanthanide complexes are much narrower.
- (2) **Potentially high internal quantum efficiency:** EL efficiencies of fluorescent materials are limited to 25% excitons being formed because about 75% of the excited states formed by electron–hole recombination in the EL process populate the triplet state, which will decay non-radiatively. In contrast, in lanthanide complexes, the lanthanide ions are excited via intramolecular energy transfer from the triplet excited states of the ligands, and the relaxation from the singlet to the triplet states of the ligands also occurs through intersystem crossing. Hence the energy of both singlet and triplet excitons formed by electron–hole recombination can be utilized for emission. Although the intersystem crossing efficiency is not 100%, the lanthanide complex EL efficiency could at least exceed that of commonly used fluorescent materials, to a large extent.
- (3) **Facile ligand modification:** To improve the chemical and physical properties of the emitting materials, such as suitability for vapor phase deposition, solubility, stability or carrier transporting properties, modification of the ligands is necessary. Since the 4f shells of trivalent lanthanide ions are well shielded by the filled 5s and 5p orbitals, the 4f energy levels are only weakly perturbed by the environment outside of the lanthanide ions. Thus, the modification does not result in much shift in the emission wavelength.

For these reasons, it is believed that lanthanide complexes are good candidates as emitting materials in OLEDs.

11.2 Lanthanide Complexes Used in OLEDs

In past decades, lanthanide complexes (except Pm, Sc, and Ce complexes) and related electroluminescent devices have been studied extensively. In this section we describe recent progress in lanthanide complex-based luminophores, especially for Eu and Tb complexes, which are being developed for improving the color properties of electroluminescent displays.

11.2.1 Europium Complexes

As shown in Figure 11.7, the emissions based on europium ion peak at about 580, 592, 612, 652, and 703 nm, corresponding to the f–f electronic transitions of $^5D_0 \rightarrow ^7F_0$ (usually strongly forbidden), $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$, and $^5D_0 \rightarrow ^7F_4$, respectively [15]. Among these, the 612 nm emission from the $^5D_0 \rightarrow ^7F_2$ electronic dipole transition is dominant. The intensity ratio of $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$ transitions is defined as monochromaticity, which is determined by the symmetry environment where europium ion is located; the poorer the symmetry environment, the larger will be the monochromaticity. Usually, in the inorganic matrix, for example in $YVO_3 : \text{Eu}$ matrix, the monochromaticity is about one, while in the $\text{Eu}(\text{DBM})_3\text{L}$ complex (see Figure 11.7) it is larger than ten. Thus a pure saturated red emission can be observed when the europium complexes are used as emitters.

In 1990, Kido *et al.* [16] first reported the europium complex tris(thienyltrifluoro-acetonato) europium $[\text{Eu}(\text{TTA})_3]$, based OLED in which the complex was molecularly dispersed in hole-transporting poly(methylphenylsilane) (PMPS). Luminescence started at 12 V, and a maximum intensity of 0.3 cd m^{-2} at 18 V was achieved when the device was operated in continuous DC mode (biased ITO positive) with the configuration ITO/PMPS- $\text{Eu}(\text{TTA})_3$ /PBD/Mg/Ag [PBD = 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, the structure shown in Figure 11.4, being used as the electron-transporting layer]. Since then, many Eu(III) complexes and related electroluminescent devices have been studied extensively.

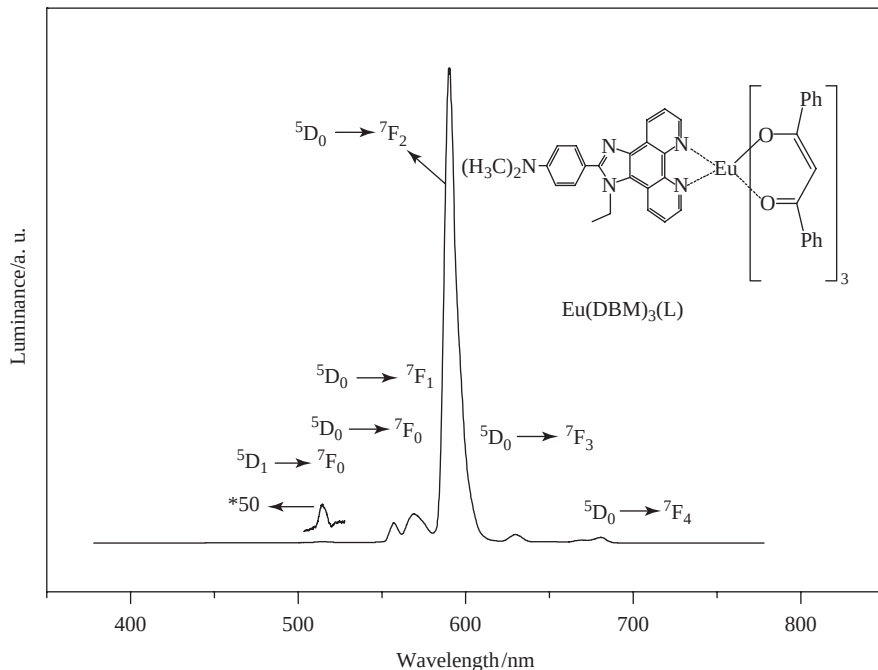


Figure 11.7 The luminescent spectrum of the europium complex $\text{Eu}(\text{DBM})_3(\text{L})$ [15].

To be a good emitting material for use in OLEDs, firstly the lanthanide complex must have high photoluminescent efficiency, which is one of the essentials for excellent electroluminescence devices. As noted above, the external quantum efficiency η_{ext} of an OLED can be expressed as $\eta_{\text{ext}} = \eta_{\text{r}} \cdot \varphi_{\text{f}} \cdot \chi \cdot \eta_{\text{out}}$. It is obvious that if the other conditions are kept unchanged, the higher the photoluminescent efficiency, the better the electroluminescence performance.

Owing to the forbidden character of the intra-4f transitions, the absorption coefficients of lanthanide ions are very low. To overcome this problem, organic chromophores that have much larger absorption coefficients are usually coordinated to lanthanide ions to form lanthanide complexes. In the case of these complexes, the sensitization process of the lanthanide ions generally consists of three steps: excitation of the singlet excited state of the ligand, the subsequent intersystem crossing to its triplet state, and energy transfer from the triplet state to the emission lanthanide ion. On the other hand, direct energy transfer from the singlet excited state of the ligand to the lanthanide ion has also been observed [17]. In most cases, the energy transfer takes the first pathway.

According to theoretical calculations and experimental data [25, 26] it is widely accepted that energy transfer is most effective if the triplet energy level of the ligand is about 2000–5000 cm^{-1} higher than the $^5\text{D}_0$ resonance level of the Eu(III) ion. Generally, the triplet energy level of the anion ligand (the first ligand) should be about 3500 cm^{-1} higher than the $^5\text{D}_0$ state, which will make energy transfer highly efficient and irreversible. Moreover, if the energy level of the neutral ligand (the second ligand) is lower than that of the $^5\text{D}_0$ state, the reverse energy transfer occurs. Thus the anion and the neutral ligands should all have suitable energy levels in a Eu(III) complex. Dibenzoylmethane (HDBM), 2-thenoyltrifluoroacetone (HTTA) and 1,10-phenanthroline (phen) and its derivatives are the most commonly used ligands for Eu(III) complexes in electroluminescence. The triplet energy levels with DBM and TTA as the anion ligands are 20 300 and 20 400 cm^{-1} [27], respectively, and that of phen used as the neutral ligand is 21 480 cm^{-1} [28], which are a little higher and agree well with the $^5\text{D}_0$ energy level of Eu(III) ion (17 250 cm^{-1}). The photoluminescent quantum efficiency of $\text{Eu}(\text{TTA})_3(\text{phen})$ (Figure 11.8, **1**) is up to 69% [29] and 36.5% [30] for solid state and solution in DMF, respectively. Indeed, the photoluminescent efficiencies of most europium complexes used in OLEDs are very high and the anion ligands used frequently are TTA (see Figure 11.8) and DBM (see Figure 11.9).

The second essential for excellent electroluminescence devices is that the lanthanide complex must have good carrier transporting properties. Much research data have shown that introducing functional groups with carrier transporting properties into ligands in europium complexes can efficiently improve their carrier transporting properties (see Figure 11.10, compounds **13–21**).

In 2000, Bazan and coworkers reported a functionalized europium complex (see Figure 11.10 compound **13**) incorporating a phenanthroline ligand for electron transport, a carbazole fragment in the diketonate ligand for hole transport, and a hexyloxy group to prevent crystallization and allow for formation of transparent clear films [41]. The photoluminescence (PL) from films of the complex is nearly monochromatic, characteristic of the europium ion, and proceeds with an efficiency of 50(3)%. Light emitting diodes (LEDs) were fabricated using the simplest possible device architecture comprising an anode (ITO), a layer of the complex, and a cathode (Ca); the light emitted from this device is identical to the PL spectrum of the complex. The turn-on voltage was observed at about 5.3 V and was similar in magnitude to that of many polymer LEDs and lower than for many multilayer organic LEDs prepared by sublimation. These characteristics demonstrate that the ligand design was successful in facilitating electron

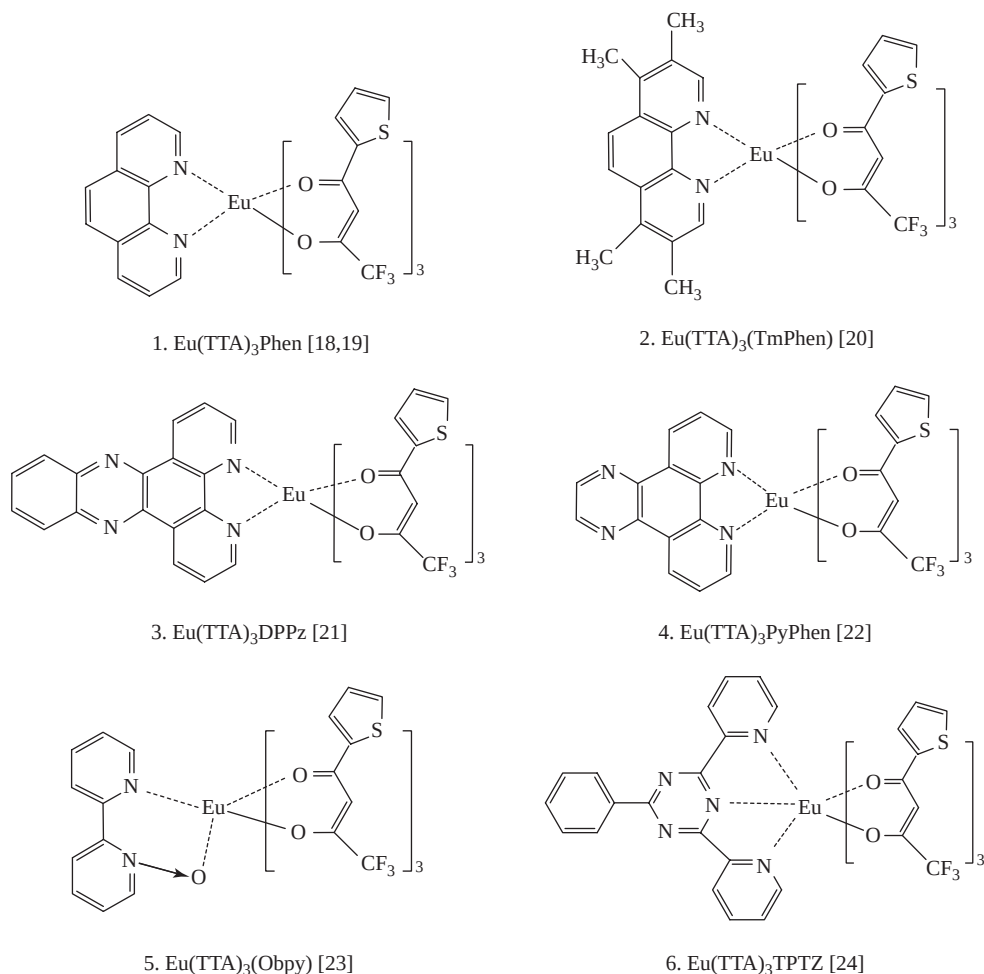


Figure 11.8 Structures of some europium complexes with TTA as the anion ligand.

and hole injection and transport into and across the europium layer. At 15 mA cm^{-2} , the light output was 9 cd m^{-2} with an external EL quantum efficiency of 0.08%.

A series of new $\text{Eu}(\text{III})$ complexes were synthesized by introducing a carbazole functional group into neutral ligands or anion ligands, β -diketones. Modification of the neutral ligand mainly focused on 1,10-phenanthroline (phen) as it was known as a good sensitizer for $\text{Eu}(\text{III})$ ion emission. The PL quantum efficiency of $\text{Eu}(\text{DBM})_3(\text{phen})$ was about 23% [41]. The device ITO/TPD (20 nm)/ $\text{Eu}(\text{DBM})_3(\text{phen})$ (40 nm)/BCP (20 nm)/AlQ (40 nm)/Mg:Ag gave a maximum brightness of 156 cd m^{-2} at 16 V and power efficiency 0.35 lm W^{-1} at 7 V, 0.20 cd m^{-2} . However, when phen was replaced by phencarz (Figure 11.10 compound **14**) in the europium complex, the highest power efficiency of 2.7 lm W^{-1} at 5 V and 0.5 cd m^{-2} , and luminance

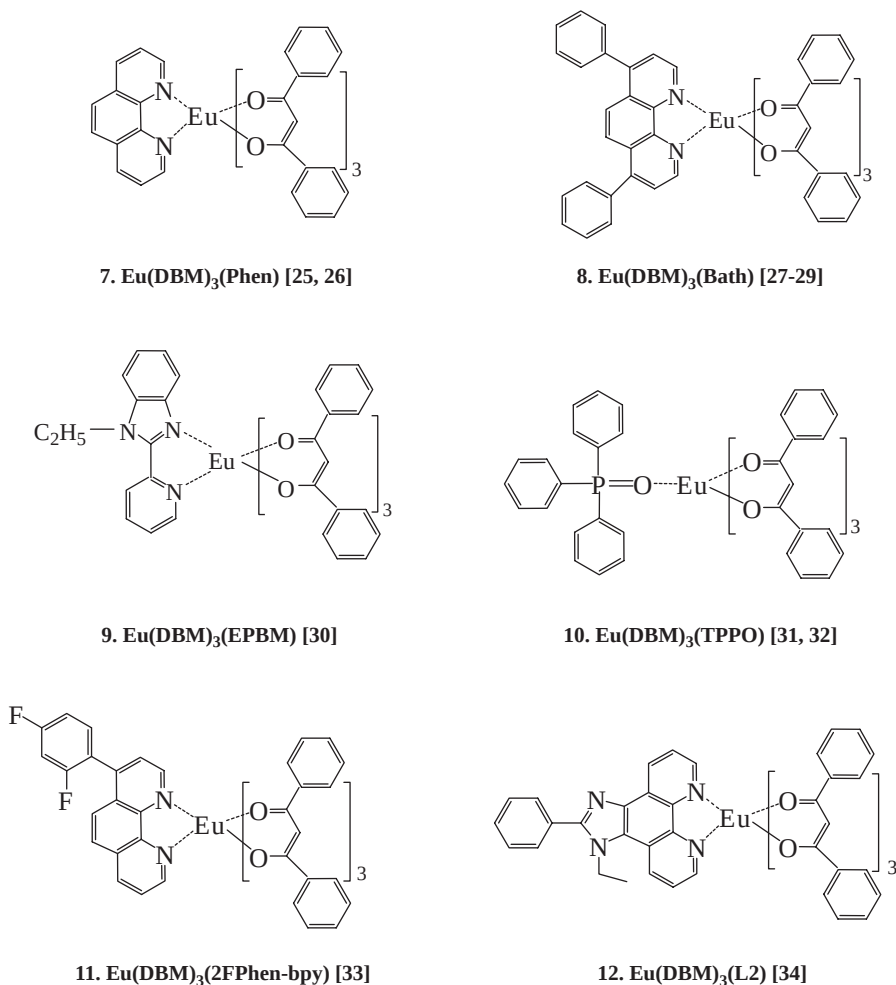


Figure 11.9 Structures of some europium complexes with DBM as the anion ligand.

exceeding 2000 cd m^{-2} at 20 V were obtained from a device with the similar configuration ITO/TPD (20 nm)/ $\text{Eu}(\text{DBM})_3(\text{phencarz})$ (40 nm)/BCP (20 nm)/AlQ (40 nm)/ $\text{Mg}_{0.9}\text{Ag}_{0.1}$ (200 nm)/Ag (80 nm) [42]. The excellent result was believed to derive from the improvement of the hole-transporting property due to the introduction of the carbazyl group.

The triphenylamine derivatives are also a well known class of hole-transporting materials. In 2003, a novel europium(III) complex, tris(dibenzoylmethanato)(2-4'-triphenylamino)imidazo[4,5-f]1,10-phenanthrolineeuropium(III), $\text{Eu}(\text{DBM})_3(\text{TPIP})$ (Figure 11.10 compound **16**), was synthesized, in which the light-emitting center, hole-transporting triphenylamine and electron-transporting phenanthroline fragments are integrated [44]. The single-layer

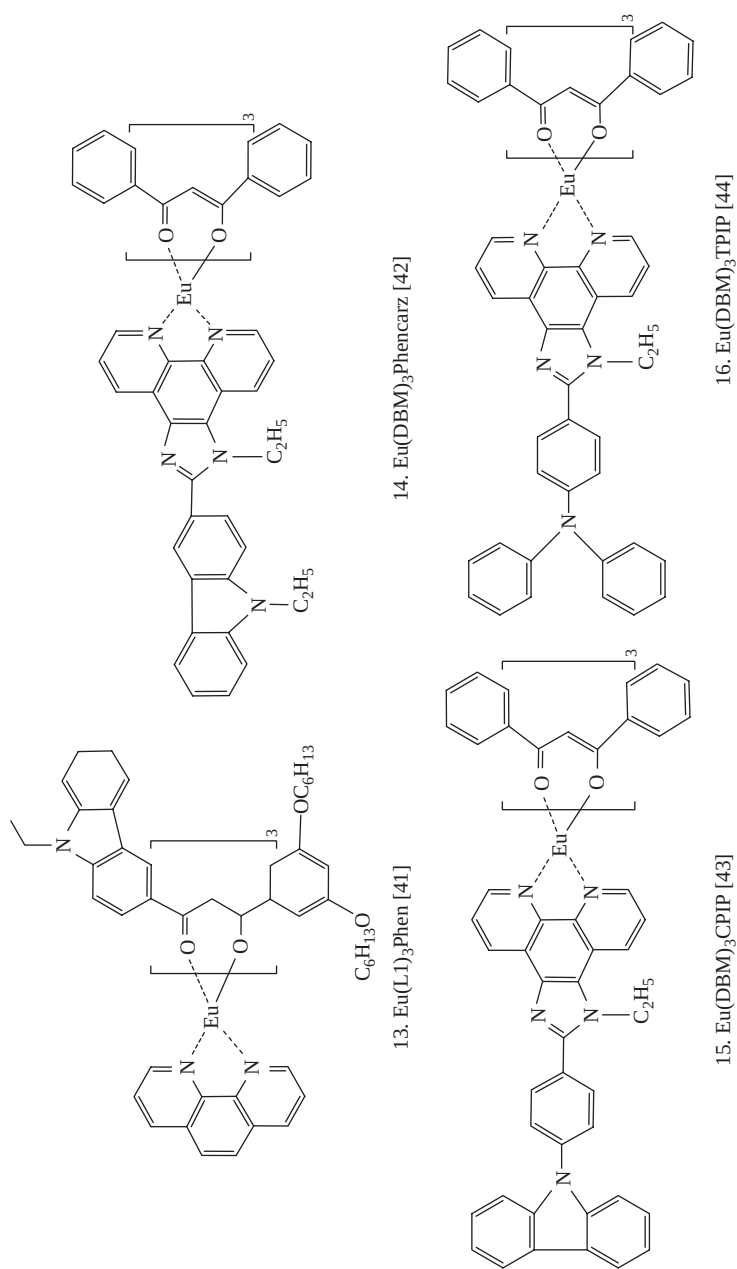
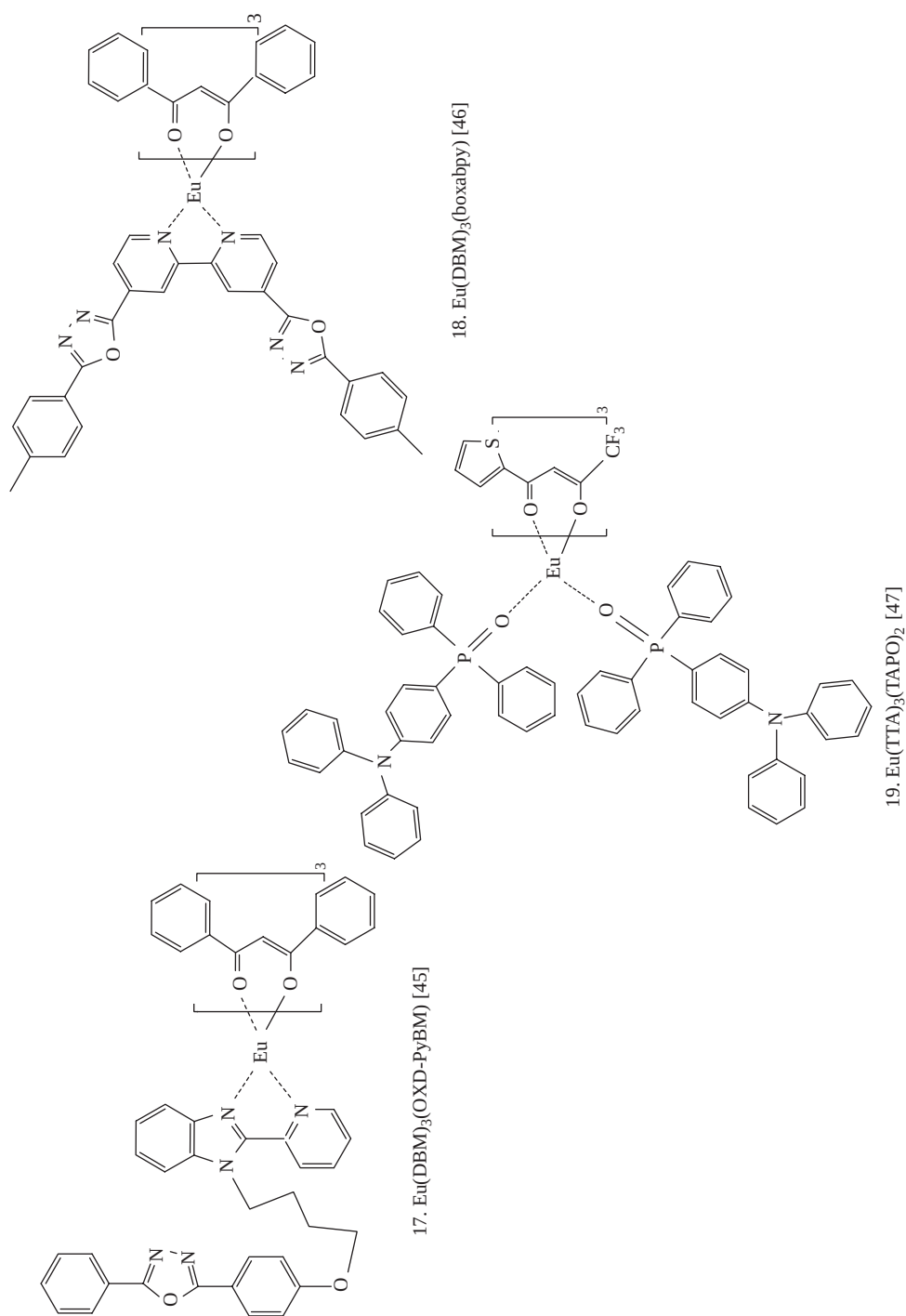


Figure 11.10 Modifications of the neutral ligands of europium complexes used in OLEDs.

**Figure 11.10** (Continued)

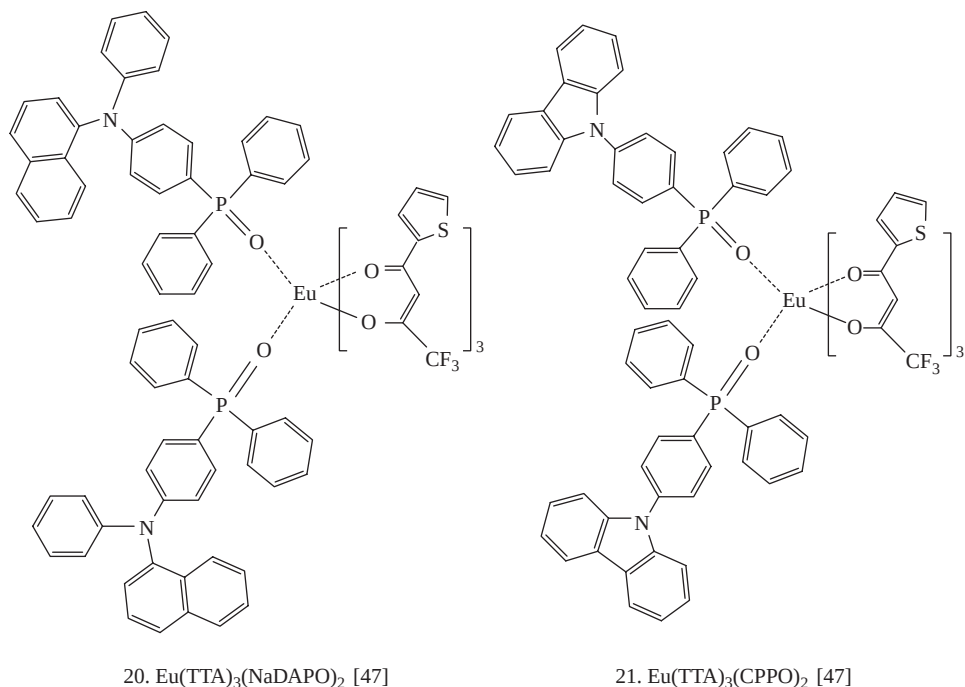


Figure 11.10 (Continued)

device ITO/ $\text{Eu}(\text{DBM})_3(\text{TPIP})$ (60 nm)/ $\text{Mg}_{0.9}\text{Ag}_{0.1}/\text{Ag}$ exhibited Eu(III) based pure red emission with maximum brightness 19 cd m^{-2} at 13.5 V and 280 mA cm^{-2} , and an onset driving voltage of 8 V. The four-layer device ITO/TPD (20 nm)/ $\text{Eu}(\text{DBM})_3(\text{TPIP})$ (40 nm)/BCP (20 nm)/AIQ (40 nm)/ $\text{Mg}_{0.9}\text{Ag}_{0.1}/\text{Ag}$ gave a maximum Eu(III) based pure red emitting luminance of 1305 cd m^{-2} at 16 V and 255 mA cm^{-2} with an onset driving voltage of 6 V; the maximum external quantum yield and luminous yield were estimated to be 0.85% and 1.44 lm W^{-1} , respectively, at 7.5 V and 0.25 mA cm^{-2} .

Oxadiazole derivatives are known as good electron-transporting and hole-blocking materials that can be introduced into ligands to improve electroluminescence properties of Eu(III) complexes. Wang and coworkers introduced an oxadiazole functional group into the benzimidazole structure and obtained a new complex $\text{Eu}(\text{DBM})_3(\text{OXD-PyBM})$ (OXD = oxadiazolyl) (Figure 11.10, compound 17) [45]. Using $\text{Eu}(\text{DBM})_3(\text{OXD-PyBM})$ as an emitting material, a double-layer device with the structure ITO/TPD (40 nm)/ $\text{Eu}(\text{DBM})_3(\text{OXD-PyBM})$ (50 nm)/LiF (1 nm)/Al (200 nm) was constructed. The maximum brightness of the double-layer EL device was about 322 cd m^{-2} at a driving voltage of 21 V. The current efficiency was estimated to be 1.9 cd A^{-1} at 57 cd m^{-2} and 13.8 V, with the external quantum efficiency as high as 1.7%. The control device utilizing $\text{Eu}(\text{DBM})_3(N\text{-alkyl-substituted PyBM})$ as an emitter exhibited poor performance with a current efficiency of 0.03 cd A^{-1} under the same conditions, which is not comparable to the oxadiazole-functionalized europium device. These results suggest that the electron-transporting ability of the resulting complex is significantly

improved by the introduction of the oxadiazolyl group into the complex. The fact that inserting an additional electron-transporting layer of AlQ between the emitting layer and the cathode did not improve the device performance, as compared with that of the double-layer device, further demonstrates that the oxadiazole segment in $\text{Eu}(\text{DBM})_3(\text{OXD-PyBM})$ indeed plays an important role in achieving a high efficiency.

In 2007, Huang Wei and coworkers designed and synthesized three functional single-coordinate phosphine oxide ligands (4-diphenylaminophenyl)diphenylphosphine oxide (TAPO), (4-naphthalen-1-yl-phenylaminophenyl)diphenylphosphine oxide (NaDAPO), and 9-[4-(diphenylphosphinoyl)phenyl]-9H-carbazole (CPPO), as direct combinations of hole-transporting moieties (amines or carbazole), and electron-transporting triphenylphosphine oxide (TPPO), together with their Eu(III) complexes: $\text{Eu}(\text{TTA})_3(\text{TAPO})_2$, Figure 11.10 compound **19**; $\text{Eu}(\text{TTA})_3(\text{NaDAPO})_2$, Figure 11.10 compound **20**; $\text{Eu}(\text{TTA})_3(\text{CPPO})_2$, Figure 11.10 compound **21** [47]. The investigation indicated that by taking advantage of the modification inertia of the phosphine oxide ligands, the direct introduction of the hole-transport groups as the chromophore made TAPO, NADAPO, and CPPO attain the most compact structure and mezzo S_1 and T_1 energy levels, which improved the intramolecular energy transfer in their Eu(III) complexes. The amorphous phase of **19–21** proved the weak intermolecular interaction, which resulted in extraordinarily low self-quenching of the complexes. The great improvement of the double-carrier transport ability of **19–21** was proven by cyclic voltammetry. Both of the four-layer devices with structure ITO/NPB (30 nm)/Eu(III) complex (40 nm)/BCP (30 nm)/AlQ (30 nm)/ $\text{Mg}_{0.9}\text{Ag}_{0.1}$ (200 nm)/Ag (80 nm) based on pure **19** and **20** had the pure characteristic emission of the Eu(III) ion at 616 nm corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_2$, which demonstrated the recombination of carriers in the emitting layers, a maximum brightness of more than 1000 cd m^{-2} , turn-on voltages lower than 5 V, maximum external quantum yields of more than 3%, and excellent spectral stability.

Reports on the modification of anion ligands are relatively scarce [41, 48]. We synthesized several modified β -diketones and their corresponding complexes (Figure 11.11, compounds **25–30**) for study in electroluminescent devices [49]. The complexes were designed with the aim of combining the electron-transporting group and the hole-transporting group in one molecule. The functional groups could be introduced to the β -diketone directly (compounds **25–27**), or through an alkoxy chain (compounds **28, 29**) or methylene (compound **30**). To adjust the recombination zone to be relatively confined in the emitting layer, β -diketone bearing different functional groups can be used to coordinate to the central ion individually (compounds **25, 26, 28, and 30**) or simultaneously (compounds **27 and 29**). For example, when $\text{Eu}(\text{c-DBM})_3(\text{Bath})$ (compound **25**) ($\text{Bath} = 4,7$ -diphenyl-1,10-phenanthroline or bathophenanthroline) was used as the emitting material to fabricate a device with the configuration ITO/TPD/ $\text{Eu}(\text{c-DBM})_3(\text{Bath})$ /BCP/AlQ/ $\text{Mg}_{0.9}\text{Ag}_{0.1}$ /Ag, green light was observed at 520 nm although BCP was used as the hole-blocking layer. This result indicates that $\text{Eu}(\text{c-DBM})_3(\text{Bath})$ acts as a hole transporter leading to recombination of excitons only in the AlQ layer. To adjust the carrier-transport properties and confine the recombination zone to the emitting layer, a new mixed ligand complex $\text{Eu}(\text{DBM})_2(\text{c-DBM})(\text{Bath})$ (compound **26**) was synthesized by replacing c-DBM partly with DBM. A device with configuration ITO/TPD(30 nm)/ $\text{Eu}(\text{DBM})_2(\text{c-DBM})(\text{Bath})$:PBD (1:1 molar ratio, 40 nm)/PBD(30 nm)/ $\text{Mg}_{0.9}\text{Ag}_{0.1}$ (200 nm)/Ag(100 nm) was fabricated, leading to better performance. The maximum Eu(III) characteristic emission was found to be 2797 cd m^{-2} (0.27 lm W^{-1} , 14 V).

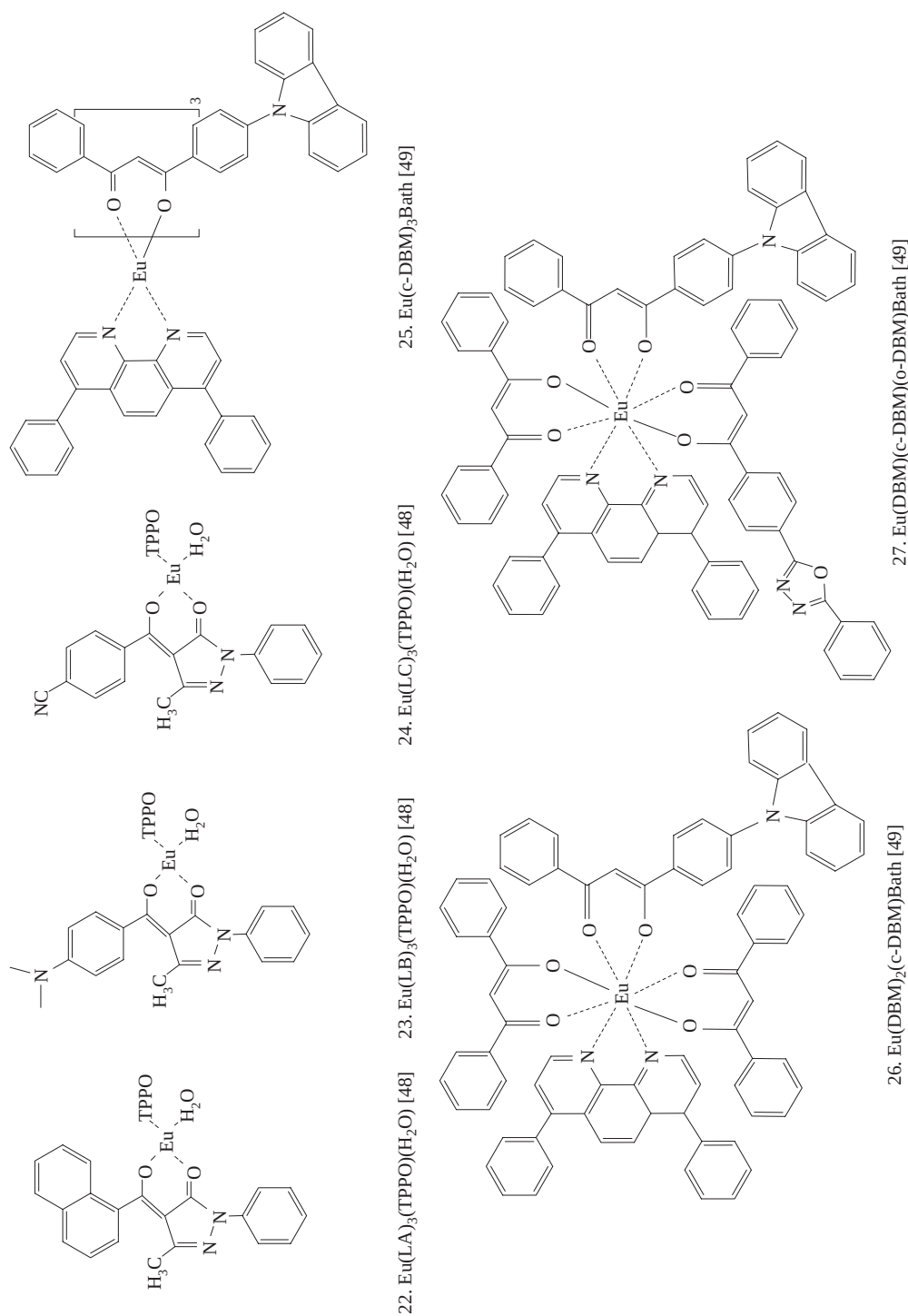


Figure 11.11 Modified diketones incorporated in the europium complexes used in OLEDs.

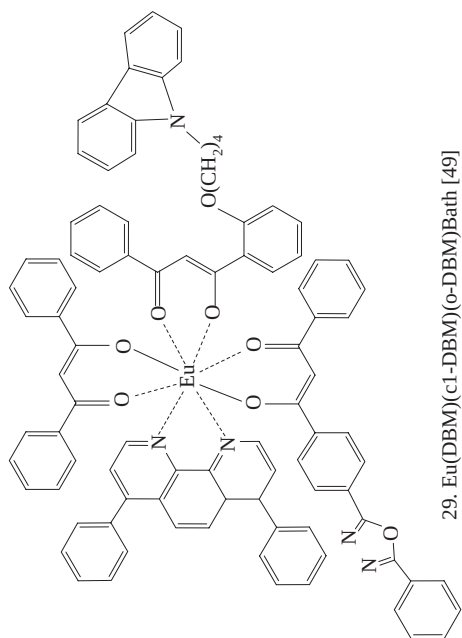
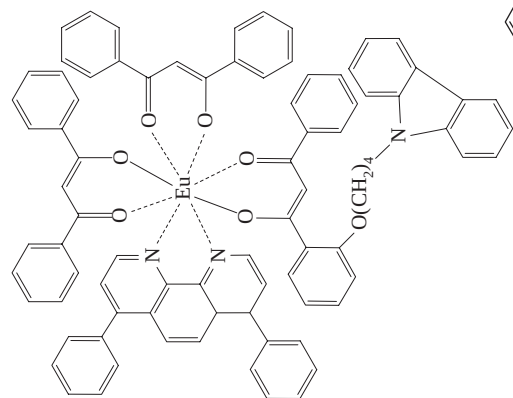
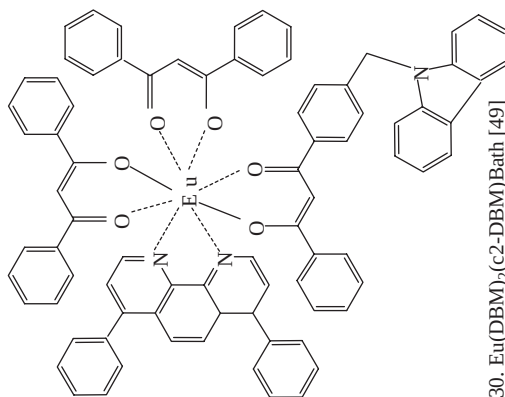
29. $\text{Eu}(\text{DBM})(\text{c1-DBM})(\text{o-DBM})\text{Bath}$ [49]28. $\text{Eu}(\text{DBM})_2(\text{c1-DBM})\text{Bath}$ [49]30. $\text{Eu}(\text{DBM})_2(\text{c2-DBM})\text{Bath}$ [49]

Figure 11.11 (Continued)

Another effective way to improve the charge transport properties of the complexes is to use doping technology. $\text{Eu}(\text{DBM})_3(\text{Bath})$ was shown to have excellent electron-transporting properties. A maximum luminance of 150 cd m^{-2} at 18 V was obtained from the device ITO/TPD (30 nm)/ $\text{Eu}(\text{DBM})_3(\text{Bath})$ (80 nm)/Mg:Ag in which $\text{Eu}(\text{DBM})_3(\text{Bath})$ was used as the electron transport emitting layer. However, when $\text{Eu}(\text{DBM})_3(\text{Bath})$ was doped to the host material TPD, the luminance from the device ITO/TPD (30 nm)/ $\text{Eu}(\text{DBM})_3(\text{Bath})$:TPD (30 nm)/ $\text{Eu}(\text{DBM})_3(\text{Bath})$ (50 nm)/Mg:Ag increased to 820 cd m^{-2} at the same voltage [34]. Similarly, using $\text{Eu}(\text{DBM})_3(\text{phen})$ as an emitter in a device with structure ITO/CuPc (5 nm)/ α -NPD (35 nm)/ $\text{Eu}(\text{DBM})_3(\text{phen})$ (20 nm)/BCP (15 nm)/AlQ (25 nm)/LiF/Al, a maximum brightness of 50 cd m^{-2} was obtained at 15 V [31]. Doping the europium complex in charge-transporting materials such as NPB or PBD is a helpful method to obtain better device performance. By doping $\text{Eu}(\text{DBM})_3(\text{phen})$ into an NPB host, a maximum brightness of 200 cd m^{-2} at 15 V was attained with the device configuration ITO/CuPc (5 nm)/ α -NPB (35 nm)/NPB: $\text{Eu}(\text{DBM})_3(\text{phen})$ (20%: 80%) (20 nm)/BCP (15 nm)/AlQ (25 nm)/LiF/Al [20]. By doping $\text{Eu}(\text{DBM})_3(\text{phen})$ into PBD host, a device with the structure ITO/TPD (40 nm)/ $\text{Eu}(\text{DBM})_3(\text{phen})$: PBD (1: 3, mol: mol) (30 nm)/AlQ (30 nm)/Mg: Ag gave a maximum brightness of 460 cd m^{-2} at 16 V [32].

An appropriate host material can efficiently transfer energy to a guest material. When the emission spectrum of the host materials has good overlap with the absorption spectrum of guest materials, and the triplet energy level is higher than that of guest materials, the energy transfer will be efficient. Heeger and coworkers chose the polymer material CN-PPP (poly[2-(6'-cyano-6'-methyl-heptyloxy)-1,4-phenylene]) as the host material due to the best spectral overlap between its emission spectrum and the absorption spectrum of $\text{Eu}(\text{DNM})_3(\text{phen})$ (Figure 11.12) [50]. As expected, energy transfer is much better for complexes whose ligands have longer conjugation lengths. $\text{Eu}(\text{acac})_3(\text{phen})$, which has almost no spectral overlap with CN-PPP, does not reduce the polymer fluorescence at all, but $\text{Eu}(\text{DNM})_3(\text{phen})$, which has good spectral overlap with CN-PPP, eliminates almost all of the polymer emission (Figure 11.13). An external quantum efficiency of 1.1% was achieved from the device ITO/PVK/ $\text{Eu}(\text{DNM})_3(\text{phen})$: CN-PPP/metal (PVK = polyvinylcarbazole).

In addition, the use of host materials with wide energy gap bipolar conducting properties can improve the efficiencies of devices. In 2000, Forrest and coworkers used a wide energy gap bipolar conducting material CBP as host material, and an external quantum efficiency of 1.4% was obtained from the device ITO/TPD/ $\text{Eu}(\text{TTA})_3(\text{phen})$ (1%): CBP/BCP/AlQ/Mg: Ag [19]. Ma and co-workers also obtained a good result using CBP as the host material [20]. The device ITO/TPD (40 nm)/ $\text{Eu}(\text{Tmphen})(\text{TTA})_3$ (Figure 11.8, compound 2): CBP (1%, 30 nm)/BCP (20 nm)/AlQ (30 nm)/LiF (1 nm)/Al (100 nm) showed good electroluminescence performance. The luminance was high (up to 800 cd m^{-2}), and an external quantum efficiency of 4.3% was obtained. Sun *et al.* reported the europium complex $\text{Eu}(\text{TTA})_3(\text{DPPz})$ (Figure 11.8, compound 3) [21] as a red emitter doped in CBP in electroluminescent devices. One such device with the configuration ITO/TPD (50 nm)/ $\text{Eu}(\text{TTA})_3(\text{DPPz})$: CBP (4.5%, 30 nm)/BCP (30 nm)/AlQ (25 nm)/ $\text{Mg}_{0.9}\text{Ag}_{0.1}/\text{Ag}$ (DPPz = dipyrido[3,2-a:2',3'-c]phenazine) exhibited external quantum efficiency 2.1%, current efficiency 4.4 cd A^{-1} , power efficiency 2.1 lm W^{-1} , and brightness 1670 cd m^{-2} . Several EL devices using $\text{Eu}(\text{TTA})_3(\text{L})$ (L denotes a substituted phenanthroline) as dopant emitters in CBP were also fabricated and tested. Some of these devices exhibited behaviors among the best reported for devices incorporating a europium complex as the red emitter [22].

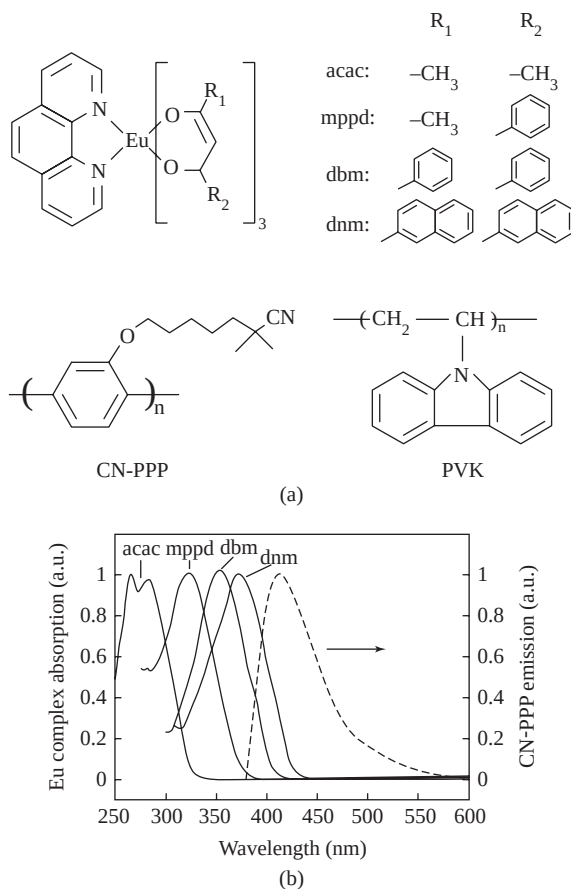


Figure 11.12 (a) The chemical structure of the Eu complexes, CN-PPP, and PVK. (b) The normalized absorption spectra of Eu complexes and the emission spectrum of CN-PPP [50]. (Reproduced with permission from M.D. McGehee *et al.*, "Narrow bandwidth luminescence from blends with energy transfer from semiconducting conjugated polymers to europium complexes," *Advanced Materials*, 1999, **11**, 1349–1354. © Wiley-VCH Verlag GmbH & Co. KGaA.)

The third essential for excellent electroluminescence devices is that the lanthanide complex must have good thermal stability. Thermal evaporation under vacuum is a very important technique in the fabrication of OLEDs. This technique is applied extensively because the film obtained is homogeneous and device structure is easily optimized to achieve high efficiency. Although the maximum brightness and the external quantum efficiency of Eu(III) complex-based devices reported has gradually increased through use of the above methods, europium complexes have been known to show partial or complete decomposition during the vacuum thermal evaporation. Typically, when carrier transporting groups are introduced, the resulting high molecular weight does not allow vacuum sublimation of the complex to occur smoothly. Uekawa *et al.* investigated systemically the thermal properties of a series of Eu(III) complexes [51]. The results from absorption spectra and NMR spectra showed that the neutral ligand phen

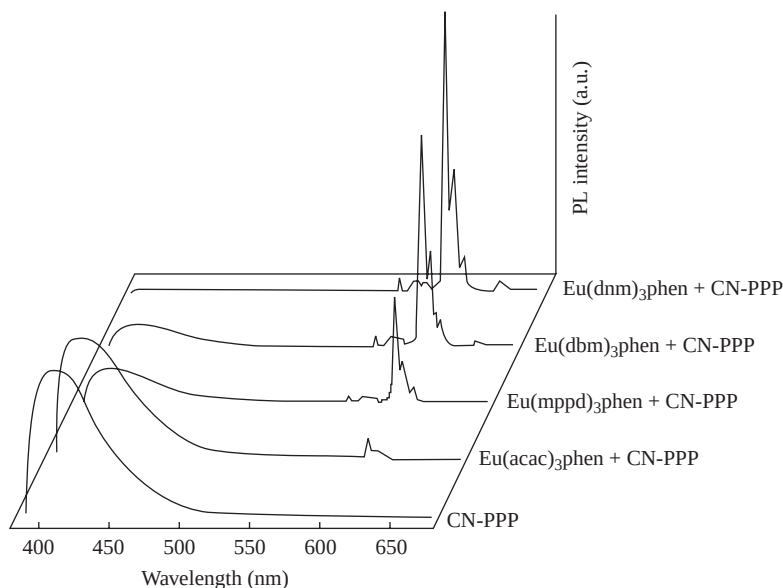


Figure 11.13 The PL spectra from CN-PPP and CN-PPP doped with 5 wt.% of the indicated Eu complexes. All of the films had the same thickness and absorbed approximately the same amount of light, so the emission spectra can be compared to each other to determine relative quantum yields [50]. (Reproduced with permission from M.D. McGehee *et al.*, “Narrow bandwidth luminescence from blends with energy transfer from semiconducting conjugated polymers to europium complexes,” *Advanced Materials*, 1999, **11**, 1349–1354. © Wiley-VCH Verlag GmbH & Co. KGaA.)

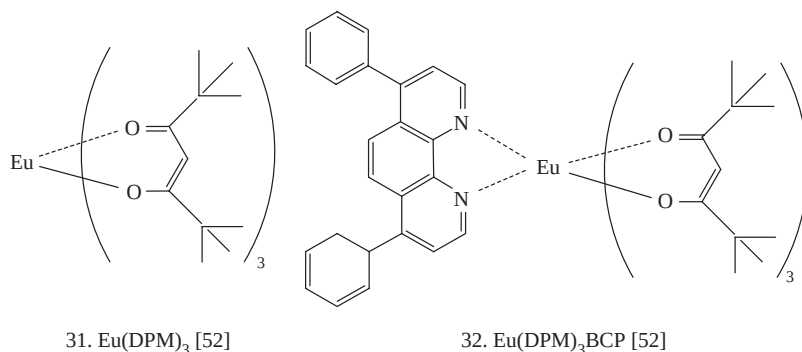
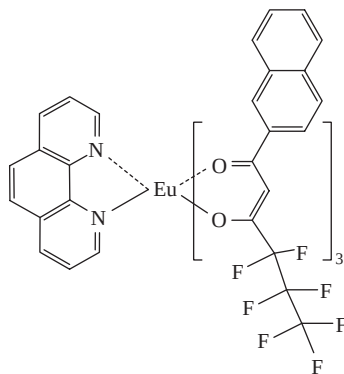


Figure 11.14 The structure of $\text{Eu}(\text{DPM})_3$ and $\text{Eu}(\text{DPM})_3(\text{BCP})$.

was slightly dissociated by vapor deposition. The dissociation of neutral ligands from $\text{Eu}(\text{III})$ complexes in vacuum evaporation generally affects the OLED performance.

To solve this problem Adachi and coworkers [52] synthesized $\text{Eu}(\text{DPM})_3:\text{BCP}$ by co-deposition of $\text{Eu}(\text{DPM})_3$ and BCP (see Figure 11.14). They introduced BCP as a neutral ligand into the complex because it can transport electrons and block holes and has satisfactory

33. $\text{Eu}(\text{HFNH})_3(\text{phen})$ [54]**Figure 11.15** The structure of $\text{Eu}(\text{HFNH})_3(\text{phen})$.

electron mobility ($\sim 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [53]. They selected HDPM as the anionic ligand due to $\text{Eu}(\text{DPM})_3$ having a relatively small molecular weight of 701.8 g mol^{-1} and three bulky non-polar *t*-butyl groups that completely surround the Eu^{3+} ion and weaken the interactions between adjacent $\text{Eu}(\text{DPM})_3$, consequently enabling $\text{Eu}(\text{DPM})_3$ to sublime easily. Data show that an external quantum efficiency of $\sim 1.0\%$ and maximum luminescence 2123 cd m^{-2} were obtained with a device configuration ITO (100 nm)/TAP (50 nm)/ $\text{Eu}(\text{DPM})_3$: BCP (molar ratio = 1 : 1) (20 nm)/BCP (10 nm)/AlQ (30 nm)/MgAg (100 nm)/Ag.

Encouraged by the results that fluorinated substituents in ligands increase the volatility of the complex, and thus facilitate thin-film fabrication, Zhang and coworkers [54] synthesized a new complex $\text{Eu}(\text{HFNH})_3(\text{phen})$ (Figure 11.15). A device based on the complex with the structure ITO/TPD (50 nm)/the complex: CBP (10%, 40 nm)/BCP (20 nm)/AlQ (30 nm)/LiF (1 nm)/Al (200 nm) exhibited maximum brightness 957 cd m^{-2} , current efficiency 4.14 cd A^{-1} , and power efficiency 2.28 lm W^{-1} with a pure red Eu^{3+} ion emission. At the high brightness of 200 cd m^{-2} , the device still had the high current efficiency 2.15 cd A^{-1} .

11.2.2 Terbium Complexes

Terbium complexes reported for electroluminescence can be separated mainly into two classes: terbium carboxylates and β -diketone complexes. Terbium carboxylates have good luminescence but they are difficult to use as efficient emission materials in OLEDs due to their multi-coordination mode and consequent formation of inorganic polymers with poor solubility or volatility. For these reasons, in this section we will focus on use of the newly developed β -diketonate terbium complexes in OLEDs.

Similar to the europium complexes, the terbium complexes used as good emitters in OLEDs also need to have high photoluminescent efficiencies, good carrier transporting properties, and sufficiently good thermal stability for small molecule materials to form a film by thermal evaporation in vacuum.

The photoluminescence emission based on the terbium ion peaks at 491, 549, 582, and 618 nm correspond to the f-f electronic transitions $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, and $^5D_4 \rightarrow ^7F_3$, respectively (Figure 11.16). Among them, $^5D_4 \rightarrow ^7F_5$ is dominant, hence a bright green emission can be observed when terbium complexes are used as emission materials.

The simplest β -diketonate used for the terbium ion is the acetylacetonate (HACAC). In 1990, Kido and coworkers [56] reported the first lanthanide complex, $[Tb(ACAC)_3(H_2O)_2]$ as an electroluminescent material in an organic light emitting double-layer device with the configuration ITO/TPD/Tb(ACAC) $_3$ (H $_2$ O) $_2$ /Al, in which TPD was used as the hole-injecting layer while Tb(acac) $_3$ (H $_2$ O) $_2$ was used as both the emitting and electron-transporting layer (Figure 11.17). The device was fabricated by vacuum deposition and exhibited the characteristic Tb $^{3+}$

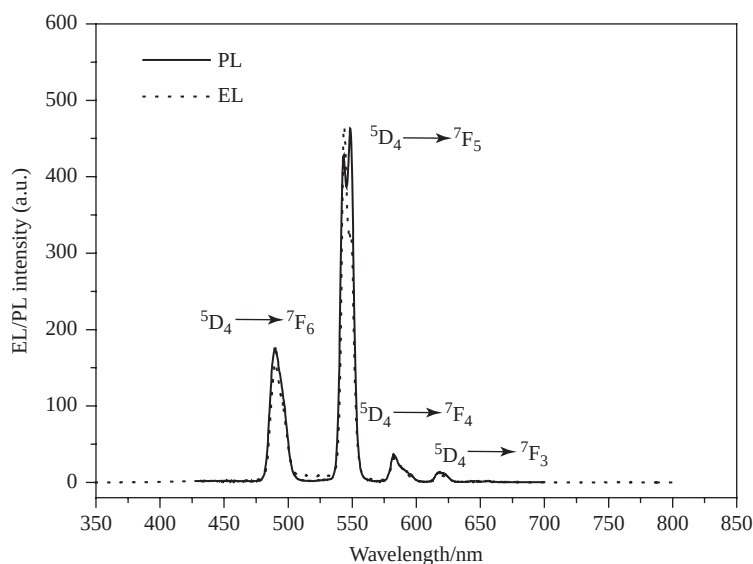


Figure 11.16 The PL spectrum of a terbium complex Tb(eb-PMP) $_3$ (TPPO) [55]. (Reprinted with permission from H. Xin *et al.*, “Efficient electroluminescence from a new terbium complex,” *Journal of the American Chemical Society*, **125**, 7166–7167, 2003. © 2003 American Chemical Society.)

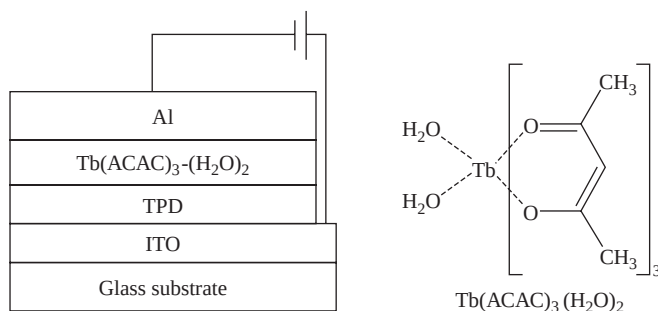
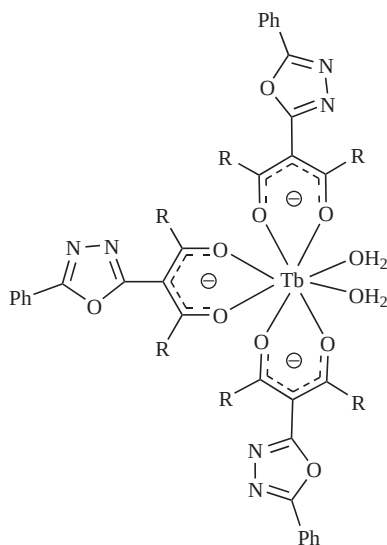


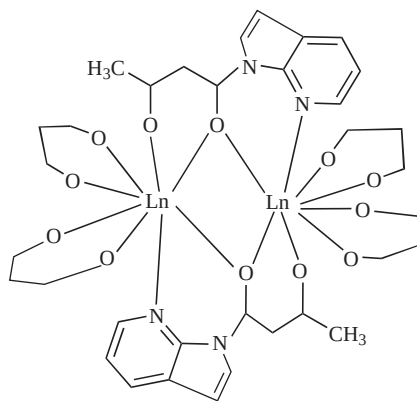
Figure 11.17 Configuration of electroluminescent device and the molecular structure of Tb(ACAC) $_3$ (H $_2$ O) $_2$ [56]. (Reproduced from J. Kido *et al.*, “Electroluminescence in a terbium complex,” *Chemistry Letters*, 657–660, 1990, with permission from the Chemical Society of Japan.)

ion green emission at around 544 nm with a luminance of 7 cd m^{-2} when operated in continuous DC mode. The current density of the device was found to be 0.4 mA cm^{-2} at the above brightness. The brightness of the device was very low, but it opened an area for green emission materials using lanthanide complexes for electroluminescence.

With the aim of realizing highly efficient OLEDs, sharp emission, and long lifetime, Zheng and coworkers sought lanthanide complexes with chelating ligands that would promote balanced injection, transport, and recombination of charge carriers. In 2001, they reported for the first time the design, synthesis, and EL application of a terbium(III) complex with oxadiazole-functionalized β -diketonate ligands (Figure 11.18, compound **34**) [57]. Using the complex to fabricate a device with the configuration ITO/PVK : PBD : the Tb complex/AIPOP/C₅F/Al, a bright green emission was observed. At 15 V, the light output reached 100 cd m^{-2} with external EL efficiency 1.1%, and 550 cd m^{-2} with efficiency 0.6% at 20 V. However, starting from 19 V a broad peak appeared at about 430 nm, which was attributable to exciplex formation between PVK and the Tb complex. Although neither the configurational nor the compositional structure of the device was optimized, it was the brightest and the most efficient EL device fabricated by spin casting a Tb(III) complex-doped polymer at that time. The results suggest that incorporating an oxadiazole moiety into the β -diketone platform is a viable strategy for modifying the physical properties and electronic structure of the corresponding lanthanide complex. This in



34. R=CH₃ [57]



35. [Ln(acac-azain)₃]₂ Ln=Tb [58]

Figure 11.18 The molecular structure of the oxadiazole-functionalized Tb(III) β -diketonate (complex **34**) and [Tb(acac-azain)₃]₂ (complex **35**) [58]. (Reprinted with permission from R.Y. Wang *et al.*, "Syntheses, structures, and electroluminescence of Ln₂(acac-azain)₄(μ -acac-azain)₂ [acac-azain = 1-(*N*-7-azaindoly)-1,3-butanedionato, Ln = Tb(III) and Y(III)]," *Inorganic Chemistry*, **41**, 5187–5192, 2002. © 2002 American Chemical Society.)

turn may lead to more stable devices with brighter and more efficient emission due to more balanced injection, transport, and recombination of charge carriers in an appropriately configured device.

In 2002 Wang *et al.* reported a dinuclear luminescent terbium complex with formula $[\text{Tb}(\text{acac-azain})_3]_2$ [acac-azain = 1-(*N*-7-azaindoly)-1,3-butanedionato] as shown in Figure 11.18 (compound **35**) [58]. Owing to the high molecular weight of the compound it cannot be sublimed in vacuum and so cannot be used as an emitter in OLEDs by vacuum deposition. Using PVK as the host/hole-transport layer and PBD as the electron transport layer, a double-layer device with configuration ITO/PVK: $[\text{Tb}(\text{acac-azain})_3]_2$ (20%, 50 nm)/PBD (30 nm)/LiF (1.5 nm)/Al (150 nm) was fabricated. Characteristic Tb (III) emission bands were observed which matched the PL of the compound (Figure 11.19). A weak emission band at 400 nm generated from PVK was also observed. The turn-on voltage was 11 V and the highest efficiency (0.65 cd A^{-1}) for the double-layered device was achieved at 13 V and 1.72 mA cm^{-2} . Under the same conditions, the efficiency of the $\text{Tb}(\text{acac})_3$ devices with PVK as the host is at least ten times less, demonstrating that the 7-azaindoly group in the complex plays an important role in promoting energy transfer from the ligand to the metal center. The reason is that there is no solvent quenching and the molecule is locked in a rigid crystal lattice in the solid state.

Pyrazolone and its derivative are the most common ligands used for Tb(III) complexes in electroluminescence. In 1998 the first example of an electroluminescent device using a terbium pyrazolonate complex, tris(1-phenyl-3-methyl-4-isobutyl-5-pyrazolone)-bis-(triphenyl phosphine oxide) terbium $[\text{Tb}(\text{ip-PMP})_3(\text{TPPO})_2]$ (Figure 11.20, compound **36**),

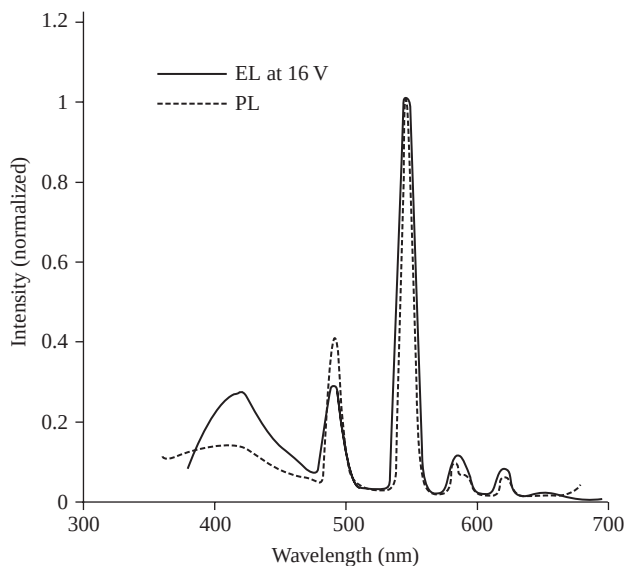


Figure 11.19 PL of $[\text{Tb}(\text{acac-azain})_3]_2$ in PVK and EL of the double-layer device [58]. (Reprinted with permission from R.Y. Wang *et al.*, "Syntheses, structures, and electroluminescence of $\text{Ln}_2(\text{acac-azain})_4(\mu\text{-acac-azain})_2$ [acac-azain = 1-(*N*-7-azaindoly)-1,3-butanedionato, Ln = Tb(III) and Y(III)]," *Inorganic Chemistry*, **41**, 5187–5192, 2002. © 2002 American Chemical Society.)

as emitter was reported by our group [59]. With the configuration ITO/TPD/Tb(ip-PMP)₃(TPPO)₂/AlQ/Al, the device gave maximum brightness 920 cd m⁻² at a drive voltage of 18 V, and luminous efficiency 0.51 lm W⁻¹ at current density 0.70 mA cm⁻². Two years later, Christou and coworkers [60] prepared OLEDs based on modifying the above system with the device configuration ITO/MTDATA/TPD/Tb(tb-PMP)₃(TPPO)/TAZ/Al [MTDATA = 4,4',4''-tris-[N-(3-methylphenyl)-N-phenylamino]triphenylamine]. A maximum brightness of 2000 cd m⁻² with luminescence efficiency 2.63 lm W⁻¹ was observed. They thought that the device current was apparently hole limited for Tb(tb-PMP)₃(TPPO) (Figure 11.20 compound **39**). However, when appropriate transport layers MTDATA and TAZ were used, charge recombination was moved away from the electrode/phosphor interface to the transport/phosphor interface, which was rationalized in terms of an energy level diagram (see Figure 11.21) in which the HOMO (highest occupied molecular orbital) of the phosphor was placed at 6.4 eV.

Early in 1999, the properties of a series of terbium complexes based on 1-phenyl-3-methyl-4-R-5-pyrazolone were analyzed to determine how both the central ligand and the neutral ligand significantly affect the PL and EL quantum efficiency [63]. Of the materials listed in Figure 11.22, PMIP-Tb-TPPO shows the highest EL efficiency and luminance, corresponding to its high PL efficiency.

Our recent results further proved that the neutral ligands used in terbium complexes strongly affected their photoluminescence and electroluminescence performances. For the complexes Tb(tba-PMP)₃(TPPO), Tb(tba-PMP)₃(H₂O), and Tb(tba-PMP)₃(phen) (compounds **40–42**), the integral emission intensities are very different and in the ratio 2.1:1.3:1 for **40**, **41**, and **42**, respectively (Figure 11.23). Obviously, this difference originated from the different

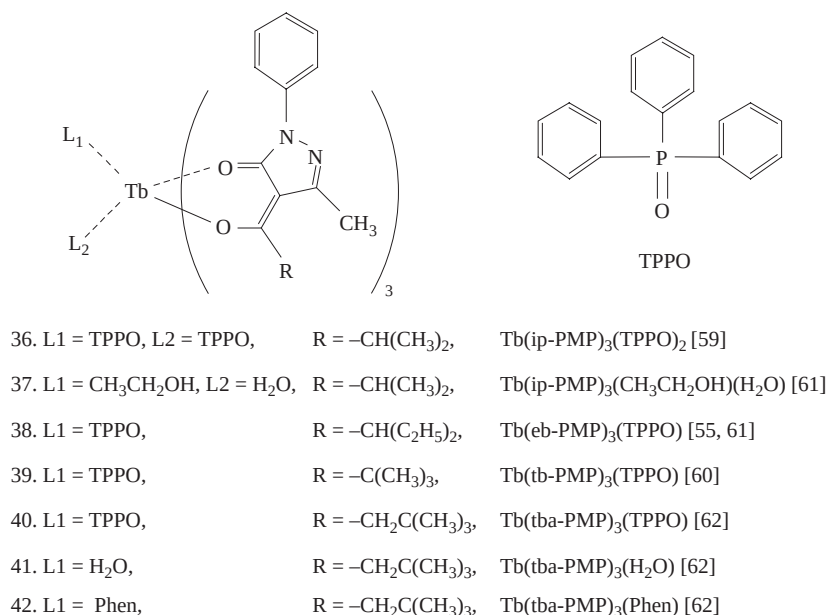


Figure 11.20 Structures of some terbium pyrazolonate complexes.

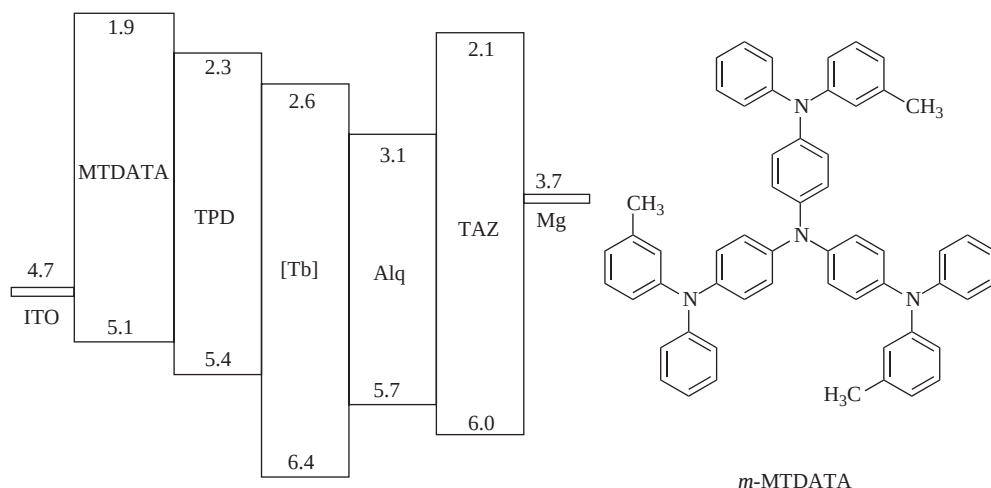
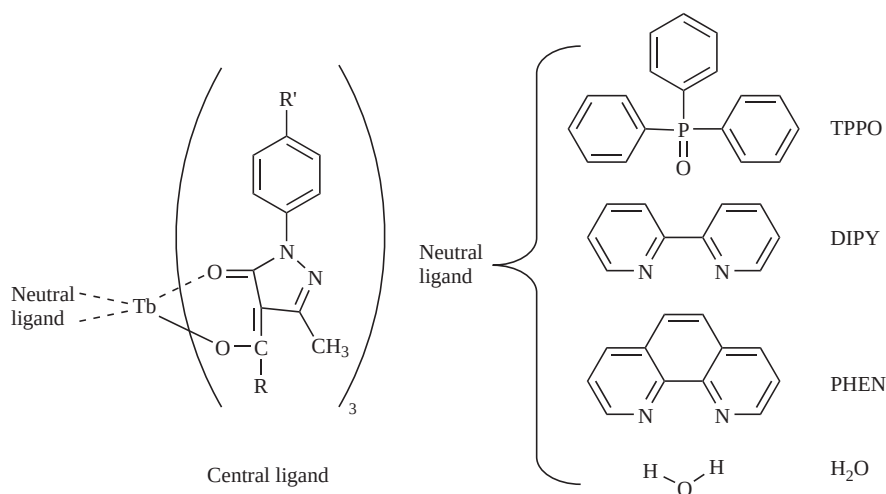


Figure 11.21 Proposed energy level diagram of the HOMO and LUMO energies of the materials used to prepare OLEDs based on Tb(tb-PMP)₃(TPPO) [60]. (Reproduced with permission from S. Capecchi *et al.*, “High-efficiency organic electroluminescent devices using an organoterbium emitter,” *Advanced Materials*, 2000, **12**, 1591–1594. © Wiley-VCH Verlag GmbH & Co. KGaA.)

coordination environments caused by the varying neutral ligand. Compared with the complex Tb(tba-PMP)₃(H₂O) without a neutral ligand (H₂O was lost during the vacuum deposition), TPPO strengthened the PL intensity of the complex Tb(tba-PMP)₃(TPPO). On the other hand, phen decreased the PL intensity of the complex Tb(tba-PMP)₃(phen). The results are caused by the different excited energy levels between tba-PMP, TPPO, and phen. The energy levels were obtained from their phosphorescence spectra measured with their corresponding gadolinium complexes Gd(tba-PMP)₃(H₂O)(EtOH), Gd(TPPO)₂(NO₃)₃, and Gd(phen)₂(NO₃)₃, as shown in Table 11.1.

The excitation energy absorbed by TPPO can be efficiently transferred either to tba-PMP and then to the central ion Tb³⁺, or transferred directly to Tb³⁺ ion since TPPO's excited singlet and triplet energy levels match the excited states of tba-PMP and the ⁵D₄ energy level of Tb³⁺, and consequently enhance the PL intensity of the complex Tb(tba-PMP)₃(TPPO). On the contrary, back energy transfer occurred between phen and tba-PMP or Tb³⁺, as the triplet energy level of phen is lower than that of tba-PMP and also the ⁵D₄ energy level of Tb³⁺. The terbium complex electroluminescence also greatly depended on its PL intensity. The performances achieved for the complexes Tb(tba-PMP)₃(TPPO), Tb(tba-PMP)₃(H₂O), and Tb(tba-PMP)₃(phen) were 7.2, 1.17, and 0.13 lm W⁻¹, respectively, with the power efficiency ratio of 55 : 9 : 1, which was greatly increased compared with their PL intensity ratio of 2.1 : 1.3 : 1.

After a systematic study of the terbium pyrazolonate complexes, we demonstrated that Tb(ip-PMP)₃(TPPO)₂ (compound **36**) had very good electron transport properties and the recombination zone was confined mainly to the TPD layer, while Tb(ip-PMP)₃(H₂O)(EtOH) (compound **37**) showed only a hole-transport property and the recombination zone was confined mainly to the AlQ layer (Figure 11.24). To adjust the carrier-transport properties and make the recombination zone easily confined to the terbium complex layer, we synthesized



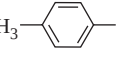
Central ligand		
R	R'	Name
CH ₃ -	H	PMAP
CH ₃ CH ₂ -	H	PMPP
CH ₃ CH ₂ CH ₂ -	H	PMBP
(CH ₃) ₂ CH-	H	PMIP
CH ₃ CH ₂ O-	H	PMOP
(CH ₃) ₂ N-	H	PMNmP
Ph ₂ N-	H	PMNpP
CH ₃ - 	H	PMmBP
	H	PMaNp
F ₇ C ₃ -	-CH ₃	PMFP

Figure 11.22 Structures of the terbium complexes researched in Reference [63]. (Reproduced from *Synthetic Metals*, **99**, X.C. Gao *et al.*, "Photoluminescence and electroluminescence of a series of terbium complexes," 127–132, 1999, with permission from Elsevier.)

a new terbium complex tris-[1-phenyl-3-methyl-4-(2-ethylbutyryl)-5-pyrazolone] (triphenyl phosphine oxide) terbium, [Tb(eb-PMP)₃(TPPO), compound **38**] by modifying the ligand [55, 61]. As the coordination number of lanthanide complexes is changeable, the goal of the modification was to increase the steric hindrance of the β -diketonate and to fashion an environment which has no space available for two TPPO to coordinate to the central Tb³⁺ ion.

The results revealed that holes and electrons were more easily confined to this complex by constructing a proper device configuration. To prevent the hole from entering the AlQ layer, a 20 nm layer of hole blocking material, BCP, was inserted between complex **38** and AlQ in the device with configuration ITO/TPD (20 nm)/complex **38** (50 nm)/BCP (20 nm)/AlQ

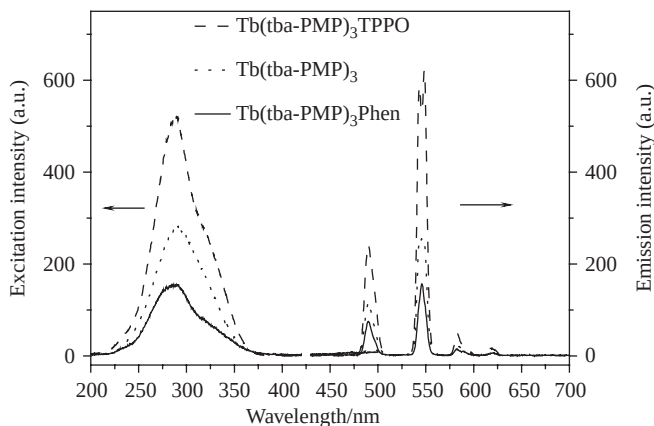


Figure 11.23 Photoluminescence spectra ($\lambda_{\text{ex}} = 285 \text{ nm}$; $\lambda_{\text{em}} = 545 \text{ nm}$) of $\text{Tb}(\text{tba-PMP})_3(\text{TPPO})$, $\text{Tb}(\text{tba-PMP})_3(\text{H}_2\text{O})$, and $\text{Tb}(\text{tba-PMP})_3(\text{phen})$ measured from their 80 nm vacuum evaporated films on quartz substrates [62]. (Reprinted with permission from H. Xin *et al.*, “The effect of different neutral ligands on photoluminescence and electroluminescence properties of ternary terbium complexes,” *The Journal of Physical Chemistry B*, **108**, 10796–10800, 2004. © 2004 American Chemical Society.)

Table 11.1 The singlet and triplet state energy levels of the ligands [62].

Complex	Singlet energy level/eV	Triplet energy level/eV
$\text{Gd}(\text{tba-PMP})_3(\text{H}_2\text{O})(\text{EtOH})$	3.81	2.51
$\text{Gd}(\text{TPPO})_2(\text{NO}_3)_3$	4.51	2.35
$\text{Gd}(\text{phen})_2(\text{NO}_3)_3$	3.87	2.09

(Reprinted with permission from H. Xin *et al.*, “The effect of different neutral ligands on photoluminescence and electroluminescence properties of ternary terbium complexes,” *The Journal of Physical Chemistry B*, **108**, 10796–10800, 2004. © 2004 American Chemical Society.)

(30 nm)/ $\text{Mg}_{0.9}\text{Ag}_{0.1}$ (200 nm)/Ag (80 nm). Peak current efficiency and power efficiencies of 21 cd A^{-1} and 9.4 lm W^{-1} were achieved at 7 V, 87 cd m^{-2} . Moreover, peak power efficiency of 11.3 lm W^{-1} at 7 V was achieved from a device with configuration ITO/NPB (10 nm)/ $\text{Tb}(\text{eb-PMP})_3(\text{TPPO})$ (50 nm)/BCP (20 nm)/AlQ (40 nm)/ $\text{Mg}_{0.9}\text{Ag}_{0.1}$ (200 nm)/Ag (800 nm).

Encouraged by the fact that modification of the ligand improves the electroluminescence performance, a neutral ligand 9-(4-*tert*-butylphenyl)-3,6-bis(diphenylphosphineoxide)-carbazole (DPPOC) and its complex $\text{Tb}(\text{PMIP})_3\text{DPPOC}$ (Figure 11.25) were synthesized [64]. DPPOC has a suitable lowest triplet energy level (24691 cm^{-1}) for the sensitization of $\text{Tb}(\text{III})$ ($^5\text{D}_4$: 20400 cm^{-1}), and significantly greater thermal stability (glass transition temperature 137°C) compared with the familiar ligand TPPO. Experiments revealed that the emission layer of the $\text{Tb}(\text{PMIP})_3\text{DPPOC}$ film could be prepared by vacuum co-deposition of the complexes $\text{Tb}(\text{PMIP})_3(\text{H}_2\text{O})_2$ and DPPOC (molar ratio = 1 : 1). The electroluminescent device ITO/NPB (10 nm)/ $\text{Tb}(\text{PMIP})_3$ (20 nm)/co-deposited $\text{Tb}(\text{PMIP})_3\text{DPPOC}$ (30 nm)/BCP (10 nm)/AlQ (20 nm)/ $\text{Mg}_{0.9}\text{Ag}_{0.1}$ (200 nm)/Ag (80 nm) exhibited pure emission from terbium ions, even at the highest current density. The highest efficiency obtained was 16.1 lm W^{-1} , 36.0 cd A^{-1} at 6 V. At a practical brightness of 119 cd m^{-2} (11 V) the efficiency remained above 4.5 lm W^{-1} , 15.7 cd A^{-1} .

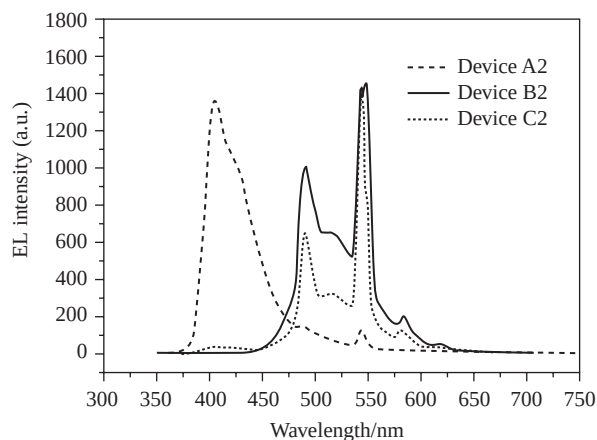


Figure 11.24 EL spectra of devices with the same configuration ITO/TPD (20 nm)/Tb-complex (50 nm)/AlQ (30 nm)/Mg_{0.9}Ag_{0.1} (200 nm)/Ag (80 nm) using complexes **36** (A2), **37** (B2), and **38** (C2) as emitters with applied voltage 10 V [61]. (Reprinted with permission from H. Xin *et al.*, “Carrier-transport, photoluminescence, and electroluminescence properties comparison of a series of terbium complexes with different structures,” *Chemistry of Materials*, **15**, 3728–3733, 2003. © 2003 American Chemical Society.)

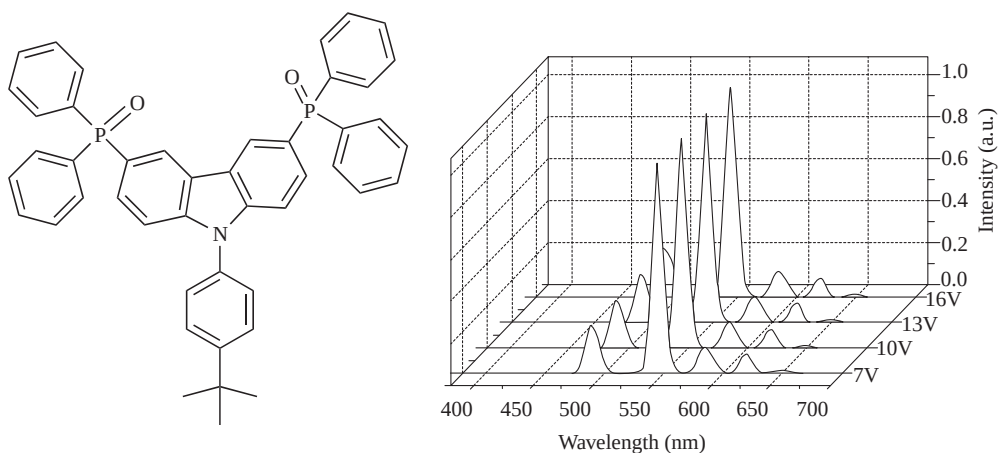


Figure 11.25 Structure of CTPPO and EL spectra of the device ITO/NPB (10 nm)/Tb(PMIP)₃ (20 nm)/co-deposited Tb(PMIP)₃DPPOC (30 nm)/BCP (10 nm)/AlQ (20 nm)/Mg_{0.9}Ag_{0.1} (200 nm)/Ag (80 nm) at different applied voltages [64]. (Reproduced from *Organic Electronics*, **10**, Z.Q. Chen *et al.*, “A highly efficient OLED based on terbium complexes,” 939–947, 2009, with permission from Elsevier.)

The EML with a multilayer structure for the lanthanide ions is very different from that of other phosphor materials such as iridium complexes. Multilayer structures with EMLs usually emit hybrid light which is used in white light emitting OLEDs [33]. For lanthanide complexes extremely pure light is achievable, because their emission is due to electronic transitions of

the central ions and this emission is different to the MLCT emission of iridium complexes. Multilayer EMLs of lanthanide complexes are thus advantageous as their sharp emission bands are maintained, while ligands are modified to improve PL efficiencies and balance carrier transport abilities for better EL.

11.2.3 Other Lanthanide Complexes

Although trivalent europium and terbium complexes are of great interest for the development of OEL emitting materials, other lanthanide complexes with abundant luminescent characteristic have rarely been studied for OEL purposes due to their poor fluorescent quantum yields. However, it has been reported recently that other lanthanide complexes can be used as promising light-emitting materials. For example, blue emitting devices based on Tm complexes [65], reddish–orange emitting devices based on Sm complexes [54, 66], white emitting devices based on Dy complexes [67], and near-infrared emitting devices based on Er [68], Nd [69], and Yb [70] complexes have been fabricated.

As shown in Figure 11.26, the EL emissions based on the samarium ion peaks at about 564, 598, 645, and 710 nm, corresponding to the $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$, $^4G_{5/2} \rightarrow ^6H_{9/2}$, and $^4G_{5/2} \rightarrow ^6H_{11/2}$ transitions, respectively, of the Sm^{3+} ion.

So far, a few samarium complexes have been reported for OLEDs, such as $Sm(HFNH)_3(phen)$ (HFNH = 4,4,5,5,6,6,6-heptafluoro-1-(2-naphthyl)hexane-1,3-dionate) [54], $[Sm(hfa)_3(phen)_2]$ (hfa = hexafluoroacetylacetonato) [66], $Sm(TTA)_3(TPPO)_2$ [71], $Sm(bfa)_3(phen)$ (bfa = 4,4,4-trifluoro-1-phenyl-1,3-butanedionate) [72], $Sm(DBM)_3(Bath)$ [73], and $Sm(TTA)_3(phen)$ [74], and so on. Among them, the best result was obtained from the complex $Sm(DBM)_3(Bath)$. Using the complex as an emitter, the device ITO/TPD (30 nm)/TPD: $Sm(DBM)_3(Bath)$ (30 nm)/ $Sm(DBM)_3(Bath)$ (30 nm)/Mg:Ag was fabricated by depositing three layers of organic films successively, from which a pure emission of the Sm^{3+} ion was clearly observed. It was found that the EL emission threshold bias was lowered

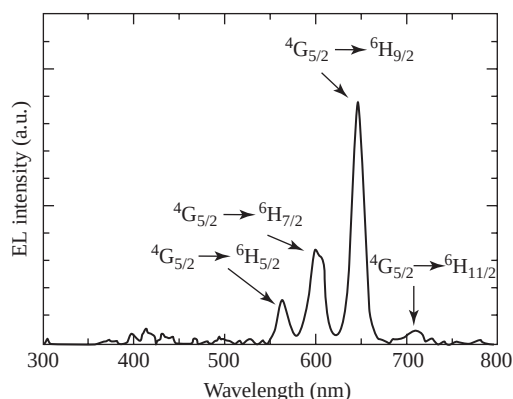


Figure 11.26 The EL spectrum based on samarium ion [66]. (Reproduced from *Thin Solid Films*, **516**, Z. Kin *et al.*, “Optical and electroluminescent properties of samarium complex-based organic light-emitting diodes,” 2735–2738, 2008, with permission from Elsevier.)

to 3 V, a maximum luminance of 490 cd m^{-2} at 15 V was obtained, and external quantum efficiency of 0.6% was obtained at current density 0.17 mA cm^{-2} in the visible region.

The Sm^{3+} ion with $4f^5$ -orbital configuration has numerous energy levels, even covering the NIR spectral range (Figure 11.27), which may be the reason that the PL quantum yields of most Sm complexes are very low.

Dysprosium(III) complexes exhibit characteristic $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ transitions leading to blue (about 480 nm) and yellow (about 572 nm) emissions (Figure 11.28, d), respectively. The Commission Internationale de L'Eclairage (CIE) coordinates of the photoluminescence of the Dy complex are calculated as $x = 0.35$ and $y = 0.40$, which are located in the white region.

In 2007, the new dysprosium complex $\text{Dy}(\text{PM})_3(\text{TP})_2$ [PM = 1-phenyl-3-methyl-4-isobutyryl-5-pyrazolone and TP = triphenyl phosphine oxide] was reported. A series of devices with various structures were fabricated to investigate the EL performance of $\text{Dy}(\text{PM})_3(\text{TP})_2$. The best device with the structure ITO/CuPc (15 nm)/Dy complex (70 nm)/BCP (20 nm)/AlQ (30 nm)/LiF (1 nm)/Al (100 nm) exhibited maximum brightness 524 cd m^{-2} , current efficiency 0.73 cd A^{-1} , and power efficiency 0.16 lm W^{-1} . The low PL quantum yield (3.5%) of the complex caused poor EL performance [75].

The thulium (III) ion exhibits spectrally narrow light emission at about 480 nm. Li and coworkers were the first to use the Tm^{3+} ion in OLEDs [65]. They prepared a Tm complex $\text{Tm}(\text{acac})_3(\text{phen})$ and constructed double-layer cells with structure ITO/PVK/Tm complex/Al. The electroluminescence spectrum of the OLED with drive voltage 10 V and the photoluminescence spectrum with excitation wavelength at 350 nm are shown in Figure 11.29. The emitting intensity of 6.0 cd m^{-2} was achieved when a 16 V forward bias voltage was applied.

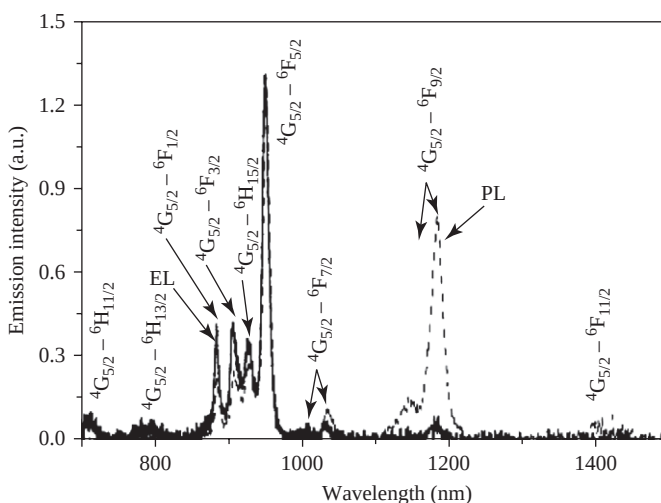


Figure 11.27 PL spectrum (--) for $\text{Sm}(\text{DBM})_3(\text{Bath})$ film by excitation at 448 nm and EL spectrum (–) for the device driven by 4.5 V in the NIR region [73]. (Reproduced from B. Chu *et al.*, “Observation of near infrared and enhanced visible emissions from electroluminescent devices with organo samarium(III) complex,” *Journal of Physics D: Applied Physics*, **39**, 4549–4552, 2006, with permission from Institute of Physics and IOP Publishing Limited.)

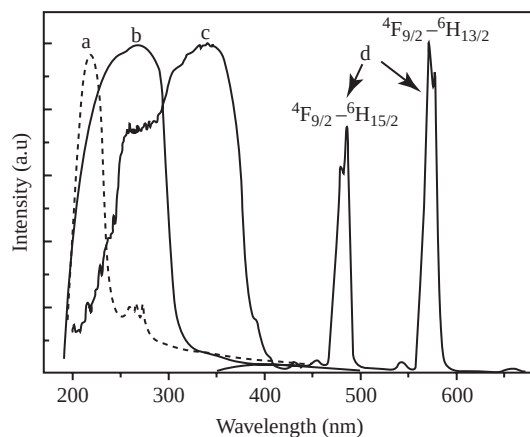


Figure 11.28 (a and b) UV-vis absorption spectra of ligand TP and PM. (c) Photoluminescence spectra include excitation and (d) emission of the complex $\text{Dy}(\text{PM})_3(\text{TP})_2$ [75]. (Reprinted with permission from Z.F. Li *et al.*, "Synthesis, structure, photoluminescence, and electroluminescence properties of a new dysprosium complex," *The Journal of Physical Chemistry C*, **111**, 2295–2300, 2007. © 2007 American Chemical Society.)

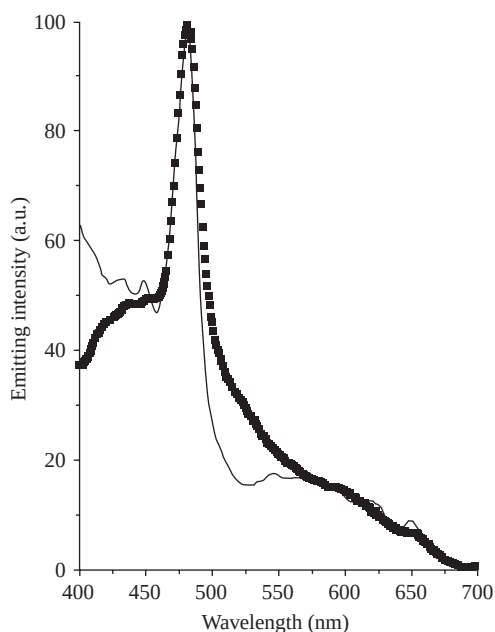


Figure 11.29 Square symbols – the EL spectrum of the device ITO/PVK/Tm complex/Al at drive voltage 10 V; solid line – the PL spectrum of the $\text{Tm}(\text{ACAC})_3(\text{phen})$ powder (excitation wavelength 350 nm) [65]. (Reproduced from *Synthetic Metals*, **104**, Z.R. Hong *et al.*, "Spectrally-narrow blue light-emitting organic electroluminescent devices utilizing thulium complexes," 165–168, 1999, with permission from Elsevier.)

Compared with the lanthanide elements that have strong emission in the visible region, the elements which have emission in the near-infrared region, such as Nd, Yb, and Er, have much lower ($\varphi_{\text{PL}} \sim 10^{-4}$ – 10^{-6}) emission quantum efficiencies due to the fact that the deactivation process often occurs through non-radiative relaxation. In principle, research efforts are often directed toward: (i) design of ligands with large steric hindrance or other effects to avoid relaxation of energy via resonance vibration [76]; (ii) adjustment of the triplet energy level of the ligand to match the lowest unoccupied orbital of the central ion [77–79]; (iii) improvement of energy transfer by using heterobimetallic compounds or introduction of functional groups into the emitting molecule or blending the electronic conductive material directly with the emitting material, such as conductive polymers, and so on, promoting the transport of the electrons and holes [80, 81].

Curry and Gillin [82] fabricated an Er-containing OLED in which the Er-tris(8-hydroxyquinoline) complex was used as the emitting material. All of the organic layers and the cathode were fabricated by vacuum deposition. Characteristic Er emission at $1.53 \mu\text{m}$ due to the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ intra-atomic electron transition was obtained from the device ITO/TPD/ErQ/Al. By incorporating Nd^{3+} into the same chelate emissions at $0.900 \mu\text{m}$ ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$), $1.06 \mu\text{m}$ ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$), and $1.32 \mu\text{m}$ ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$) have been demonstrated, and similarly emission at $0.98 \mu\text{m}$ from $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ of the Yb(III) ion in Yb-tris(8-hydroxyquinoline) has been obtained, as shown in Figure 11.30. There are also other Nd, Er, or Yb complexes [83–85] used in OLEDs, but the performance reported so far is not satisfactory.

The 4f electronic configurations of Sc^{3+} ($4f^0$), Y^{3+} ($4f^0$), La^{3+} ($4f^0$), Gd^{3+} ($4f^7$), and Lu^{3+} ($4f^{14}$) ions belong to “empty,” “half filled” or “all filled” configurations. Consequently, f–f

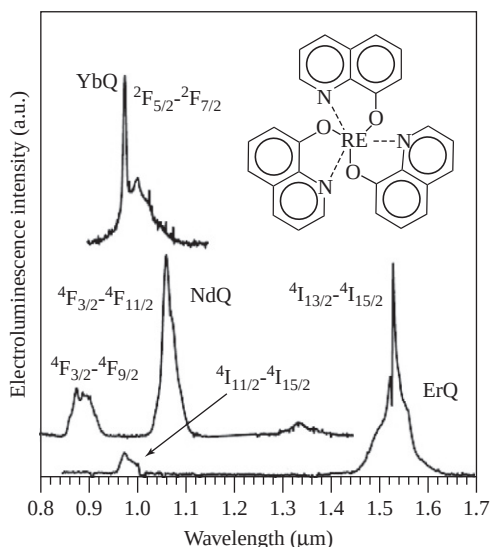


Figure 11.30 The electroluminescence spectra obtained from RE tris(8-hydroxyquinoline) (REQ, RE = Nd, Er, or Yb) based OLEDs [82]. (Reproduced from *Current Opinion in Solid State & Materials Science*, 5, no. 6, R.J. Curry and W.P. Gillin, “Electroluminescence of organolanthanide based organic light emitting diodes,” 481–486, 2001, with permission from Elsevier.)

transition emission cannot occur with the exception of gadolinium complexes which emit in the ultraviolet region. This class of ions cannot give emission in the visible region, however, some complexes do have emission in the visible region when suitable ligands are coordinated to these lanthanide ions, which are classified as ligand emission complexes [86–89] similar to AIQ.

11.3 Outlook

Even though considerable progress has been achieved with OLEDs based on lanthanide complexes as emitting materials, the performance of either materials or devices are still unsatisfactory for practical utilization. Before they can be used commercially, greater effort should be devoted to obtaining lower cost, more easily fabricated, and better chemically and thermally stabilized lanthanide complexes. Of course, complexes with higher quantum yield and good carrier transporting ability are very important as well.

Acknowledgments

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12

Near-Infrared (NIR) Luminescence from Lanthanide(III) Complexes

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12.1 Introduction

Recent studies on near-infrared (NIR) luminescence from lanthanide ions have been highly influenced by two significant applications, including the development of optical fibers for telecommunications and imaging for biomedical assays [1–10]. NIR emission is around 1.32–1.55 μm and lies in the telecommunication windows, in which silica is especially transparent. NIR emission from lanthanides is readily achieved by visible light instead of UV light, which may damage biological molecules. Biological tissues in particular are optically transparent in the spectral range of 0.7–1.1 μm , in which light transmission is maximized and can penetrate the biological tissue more effectively, thus improving significantly the detection limit and efficiency in bioassays.

More than half of the trivalent lanthanide, Ln(III), ions display NIR luminescence with transition wavelengths longer than 700 nm. The most investigated NIR-emitting lanthanide(III) ions include Nd(III), Yb(III), and Er(III) ions, whereas NIR-emitting Pr(III), Sm(III), Dy(III), Ho(III), and Tm(III) ions have been much less explored. Several of the lanthanide(III) ions are characterized by both visible and NIR emission, including Pr(III), Sm(III), Dy(III), Ho(III), and Er(III). The NIR emission from most of the Ln(III) ions is fluorescent except for that from Pr(III) or Sm(III) ion. Typical NIR emission spectra of Nd(III), Pr(III), Ho(III), Er(III), Tm(III), Yb(III), Dy(III), and Sm(III) are depicted in Figure 12.1.

The NIR emission from the Nd(III) ion occurs in three separate spectral regions, including 0.87–0.92, 1.06–1.09, and 1.32–1.39 μm due to $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$, $^4\text{I}_{11/2}$, and $^4\text{I}_{13/2}$ transitions, respectively. The first and second emission lines are in the spectral region that is suitable for imaging in bioassays. The longest wavelength emission at 1.32–1.39 μm is situated in the region of the first telecommunication window and is useful for amplification of the signals at 1.32 μm .

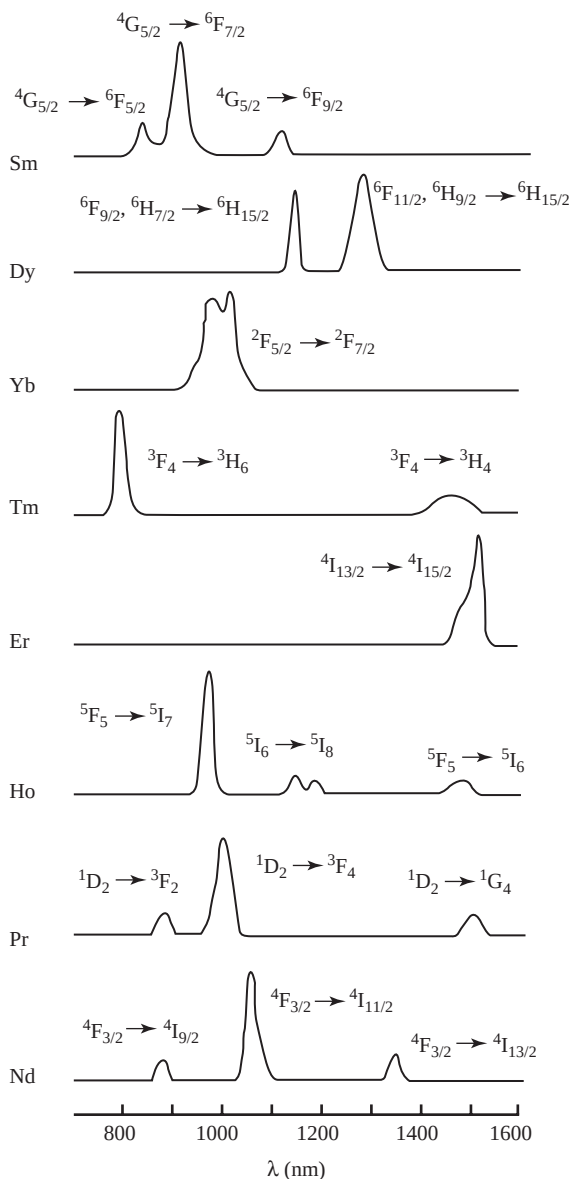


Figure 12.1 Typical NIR emission spectra of Nd(III), Pr(III), Ho(III), Er(III), Tm(III), Yb(III), Dy(III), and Sm(III).

The Yb(III) ion has a single emission line at 0.96–1.03 μm due to the only $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition. In view of the relatively long-lived NIR emission together with the highest quantum efficiency for the Yb(III) ion in comparison with that for other NIR emitting Ln(III) ions, the emission from the Yb(III) ion has the most extensive applications in biomedical imaging. The Er(III) ion affords both visible and NIR luminescence, where the NIR emitting bands

at 1.54–1.60, about 1.7, and about 2.7 μm result from $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{9/2}$, and $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ transitions, respectively. The emitting band around 1.55 μm is undoubtedly useful for signal amplification in fiber optic telecommunication amplifiers. The Pr(III) ion displays two main NIR emitting bands at 1.01–1.04 and 1.30–1.33 μm due to $^1\text{D}_2 \rightarrow ^3\text{F}_4$ and $^1\text{G}_4 \rightarrow ^3\text{H}_5$ transitions, respectively, where the longer wavelength band can be used in telecommunication for amplification of the signals at 1.32 μm .

As for other less studied NIR emitting Ln(III) ions, Sm(III) ion has three spin-forbidden NIR emission bands at 0.88, 1.02–1.04, and 1.16–1.17 μm due to $^4\text{G}_{5/2} \rightarrow ^6\text{F}_{5/2}$, $^6\text{F}_{7/2}$, and $^6\text{F}_{9/2}$, respectively. Apart from yellow emission due to transitions from $^4\text{F}_{9/2}$ to the ground multiplet, Dy(III) ion displays three NIR emission bands at 1.28–1.34, 1.7–1.8, and 2.89–3.02 μm ascribed to $^6\text{H}_{9/2}$, $^6\text{F}_{11/2} \rightarrow ^6\text{H}_{15/2}$, $^6\text{H}_{11/2} \rightarrow ^6\text{H}_{15/2}$, and $^6\text{H}_{13/2} \rightarrow ^6\text{H}_{15/2}$ transitions, respectively, where the emitting band at 1.28–1.34 μm is another candidate for amplification of the 1.32 μm signals in telecommunication. The Ho(III) ion affords the richest NIR emitting properties among all lanthanide(III) ions, where four main NIR emitting bands usually occur at 0.98–0.99 μm ($^5\text{F}_5 \rightarrow ^5\text{I}_7$), 1.16–1.19 μm ($^5\text{I}_6 \rightarrow ^5\text{I}_8$), 1.48–1.51 μm ($^5\text{F}_5 \rightarrow ^5\text{I}_6$), and 1.63–1.68 μm ($^5\text{I}_5 \rightarrow ^5\text{I}_7$) separate from two other low-energy NIR bands at 1.98–2.10 μm ($^5\text{I}_7 \rightarrow ^5\text{I}_8$) and 2.39–2.45 μm ($^5\text{F}_5 \rightarrow ^5\text{I}_5$). For the Tm(III) ion, three main NIR emitting bands occur at 1.40–1.51, 1.75–1.90 and about 2.33 μm due to $^3\text{H}_4 \rightarrow ^3\text{F}_4$, $^3\text{F}_4 \rightarrow ^3\text{H}_6$ and $^3\text{H}_4 \rightarrow ^3\text{H}_5$ transitions, respectively.

NIR luminescence from f–f transitions of Ln^{III} complexes is usually weak so that achieving long-lived NIR emission is a tremendous challenge for both synthetic and material chemists. The lifetimes of NIR emission from Ln(III) complexes are typically in the range 10^{-7} – 10^{-5} s, about three orders of magnitude lower than those in visible emitting Eu^{3+} and Tb^{3+} complexes. To achieve long-lived NIR emission with high efficiency from lanthanide complexes, one key point is to increase the amount of energy that can be pumped into the excited states, and the other important point is to minimize radiationless deactivation processes. Because of the narrow energy gap between the emitting level and the ground state on the lanthanide centers, it is well established that NIR-emitting Ln(III) ions are particularly prone to vibrational deactivation. NIR luminescence from Ln(III) ions is readily quenched by O–H or N–H oscillators directly bound to the metal centers and by unbound C–H oscillators nearby, leading to reduced luminescence intensities and shorter excited-state lifetimes. Suppression of vibrational deactivation including that induced by solvents such as water and alcohol is always accessible by fluorination or deuteration of the ligands in deuterated solvents. Elimination of energy migration between luminescent centers or so-called concentration quenching is another feasible approach to reducing nonradiative decay by making large complexes with long fluorinated or deuterated alkyl chains or by dispersing them into polymer matrices.

12.2 Organic Antenna Chromophores as Sensitizers

To overcome the problem of weak f–f oscillator strengths due to the forbidden transitions when exciting the lanthanide ions directly, luminescence from lanthanide complexes is usually sensitized by excitation of an adjacent strongly absorbing antenna chromophore [1–8]. Energy transfer is often operating from the surrounding organic ligand to the lanthanide ion. Sensitization of lanthanide luminescence always involves a three-step process, including absorption of light by the surrounding ligands, followed by energy transfer onto the lanthanide ion, and then sensitizing the lanthanide emission. The overall process is fairly complex and involves

several mechanisms and energy levels. In most of the lanthanide complexes, aromatic ligands are bound directly to the lanthanide centers and strongly absorb the UV–vis light, thus serving as antennae to stimulate emission from the lanthanide ions.

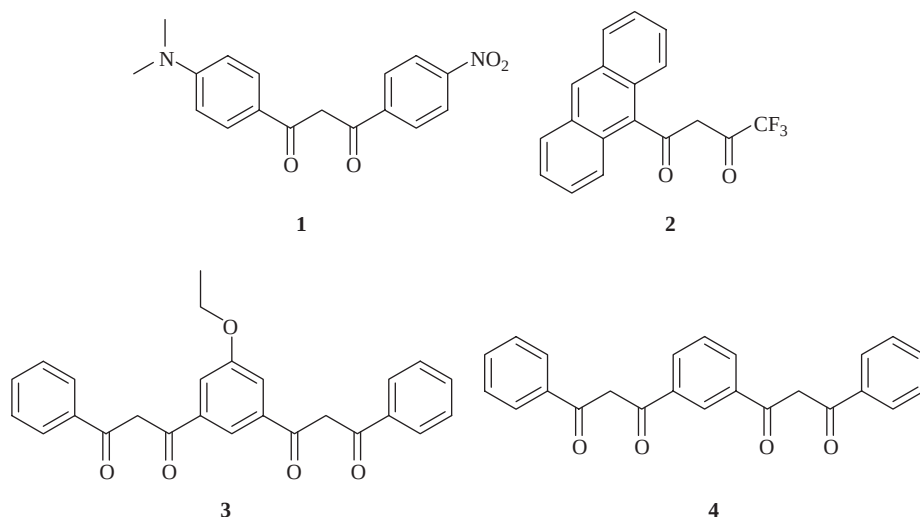
In order to favor the sensitization process and to prevent a nonradiative deactivation process for NIR luminescence from lanthanide complexes, synthetic chemists have developed several synthetic strategies for the design of a variety of the organic ligands, including: (i) acyclic polydentate and multifunctional ligands such as β -diketonates, polyaminocarboxylates, quinoline derivatives, and derivatized dendrimers, and so on and (ii) macrocyclic receptors, among which porphyrins, derivatized calixarene, pendant-arm fitted cyclens, cryptands, and coronands are the most investigated.

12.2.1 Acyclic Ligands as Antenna Chromophores

12.2.1.1 1,3-Diketone Ligands and the Analogs

Complexation of β -diketonates with lanthanide(III) ions forms stable complexes that exhibit intense absorptions in UV–vis region. It has been well demonstrated that β -diketonates are ideal candidates as the light-harvesting organic ligands for sensitization of visible and NIR luminescence from lanthanide(III) ions. A large number of tris(β -diketonate) and tetrakis(β -diketonate) lanthanide(III) complexes have been synthesized by controlling the reactant ratios between deprotonated ligands and lanthanide(III) salts [1–3]. Introducing bulky and fluorinated substituents in β -diketonates can significantly improve lanthanide luminescence, especially for NIR emission, by suppressing radiationless processes through O–H, N–H, and C–H vibrations in close proximity to the lanthanide centers. Hasegawa *et al.* demonstrated that replacement of C–H bonds in β -diketones with lower-energy C–F oscillators clearly induced longer lanthanide luminescence lifetimes in solutions [11]. For tris(β -diketonate) lanthanide(III) complexes, introducing a bi- or polydentate chelating ligand [12], such as 2,2'-bipyridine, 1,10-phenanthroline, 2,2':6',2''-terpyridine, and so on, usually gives rise to remarkably enhanced lanthanide luminescence by displacing the coordinated solvent molecules because of the elimination of nonradiative deactivation from O–H, N–H, or C–H vibrations in close proximity to the lanthanide ions.

Most of the β -diketonates absorb light in the UV region with wavelengths less than 400 nm, at which sensitized NIR luminescence from lanthanide(III) centers can be achieved by energy transfer from UV absorbing antenna chromophores. To improve the energy transfer efficiency from the β -diketonate antenna chromophores to the NIR emitting lanthanide(III) centers, and to decrease the energy gap between the UV excitation and NIR emission, one feasible approach is to incorporate a condensed aromatic group [13], ferrocene [14], or a conjugated polyene chain [15] into the β -diketone ligands. Another possible strategy to achieve red-shift of the absorption spectrum and its triplet-state energy is to introduce an electron-donor and an electron-acceptor group into the β -diketonato ligand. A low-energy absorption band due to an intraligand charge-transfer character thus occurs in the visible spectral region. Several Nd(III), Er(III), and Yb(III) complexes of β -diketone **1** containing both an electron-donor [4-(dimethylamino)benzene] and an electron-acceptor (4-nitrobenzene) group were recently reported by Bünzli and coworkers [16]. These complexes display an intense absorption at 400–550 nm due to intraligand charge-transfer absorption, which allows visible-light excitation of NIR-emitting Nd(III), Er(III), and Yb(III) ions with excitation wavelengths up to 550 nm.

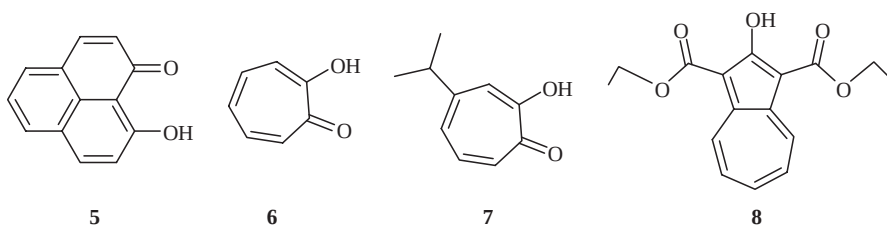


NIR luminescence of β -diketonate lanthanide(III) complexes is sensitized in most instances by energy transfer from triplet excited states of the organic antenna chromophore to the lanthanide center. In a few cases, however, sensitized NIR emission from lanthanide ions is achieved by direct energy transfer from singlet excited states of the β -diketone ligands. Recent literature [17] described Nd(III) and Er(III) complexes with 1-(9-anthryl)-4,4,4-trifluoro-1,3-butanedione **2**, where tetrakis(β -diketonate) lanthanide(III) complexes afford sensitized NIR luminescence via the excitation of anthracene. As the phosphorescence of anthracene is generally forbidden, this suggests that intramolecular energy transfer could occur from the singlet excited state of anthracene to the resonance levels of the lanthanide(III) ions. Moreover, the energy transfer in $[\text{Nd}(\mathbf{2})_4]^-$ is more efficient than that in $[\text{Er}(\mathbf{2})_4]^-$ due to the larger energy gap between the singlet excited state of the anthracene and the emission level of the Er(III) ion.

Pikramenou and coworkers [18] reported bis(β -diketone) ligands including 1,3-bis(3-phenyl-3-oxopropanoyl)benzene (**3**) and 1,3-bis(3-phenyl-3-oxopropanoyl) 5-ethoxybenzene (**4**) with two conjugated diketonate binding sites linked by a 1,3-phenylene spacer. Reaction of **3** or **4** with lanthanide(III) chloride in the presence of triethylamine induced formation of dimetallic triple- or quadruple-stranded complexes $[\text{Ln}_2(\mathbf{3})_3]$ ($\text{Ln} = \text{Eu}, \text{Nd}, \text{Sm}, \text{Y}, \text{Gd}$) and $[\text{Ln}_2(\mathbf{4})_3]$, ($\text{Ln} = \text{Eu}, \text{Nd}$) or anionic quadruple-stranded dinuclear lanthanide units $[\text{Eu}_2(\mathbf{3})_4]^{2-}$. Upon excitation at about 350 nm, sensitized luminescence from lanthanide(III) ions was achieved with the quantum yields and lifetimes being 5% and 220 μs for $[\text{Eu}_2(\mathbf{3})_3]$, 0.16% and 13 μs for $[\text{Sm}_2(\mathbf{3})_3]$, and 0.6% and 1.5 μs for $[\text{Nd}_2(\mathbf{3})_3]$, respectively. It was demonstrated that the dinuclear complexes of the bis(1,3-diketone) ligand exhibited much stronger (about 11 times) luminescence intensity compared with that of the mononuclear analogs. In addition, quadruple-stranded dinuclear Eu(III) complexes with a tetrakis(1,3-diketone) structure display more intense luminescent signals than the corresponding tris complexes. It appears that binucleating bis(1,3-diketone) ligands afford diverse arrays of dinuclear lanthanide(III) complexes to give strong emission in the visible and NIR regions.

9-Hydroxyphenalen-1-one (**5**) is a "polycyclic" β -diketone. A large π -delocalization in **5** causes a remarkable red shift of the absorption bands, which can be exploited to achieve NIR lanthanide luminescence by visible light excitation with wavelengths up to 475 nm.

The lack of an α -H atom in **5** is favorable for NIR luminescence because C–H bonds in close proximity to the lanthanide(III) ion would deactivate the excited states in a nonradiative process. Tris(phenalenonate) lanthanide(III) complexes $\text{Ln}(\mathbf{5})_3$ [19] were prepared by reaction of lanthanide(III) salts with 3 equiv of **5** using ammonia as the base, whereas tetrakis(phenalenonate) lanthanide(III) complexes $[\text{Ln}(\mathbf{5})_4]^-$ were isolated as a pure product when 4 equiv of the ligand were used with NaOH or NEt_4OH as the base. Both the tris- and tetrakis(phenalenonate) $\text{Ln}(\text{III})$ ($\text{Ln} = \text{Nd}, \text{Er}, \text{Yb}$) complexes displayed characteristic NIR luminescence with microsecond scale emissive lifetimes in both solid state and solution upon excitation with visible light up to 475 nm. As revealed by X-ray crystallography, solvent coordination to the lanthanide(III) is present in the tris complexes $\text{Ln}(\mathbf{5})_3$, whereas the four ligands in the tetrakis complexes $[\text{Ln}(\mathbf{5})_4]^-$ form a protective shielding around the central lanthanide(III) ion. The anionic tetrakis complexes $[\text{Ln}(\mathbf{5})_4]^-$ indeed show better luminescence properties than those of their tris counterparts $\text{Ln}(\mathbf{5})_3$ with a 25–60% increase in emissive lifetimes from the tris to tetrakis species. NIR emitting $\text{Nd}(\mathbf{5})_3$ complexes doped organic light emitting diode (OLED) devices [19c] have been fabricated using simple polymer spin-casting techniques with an efficiency comparable to small molecule vacuum deposited devices, showing its potential towards applications.

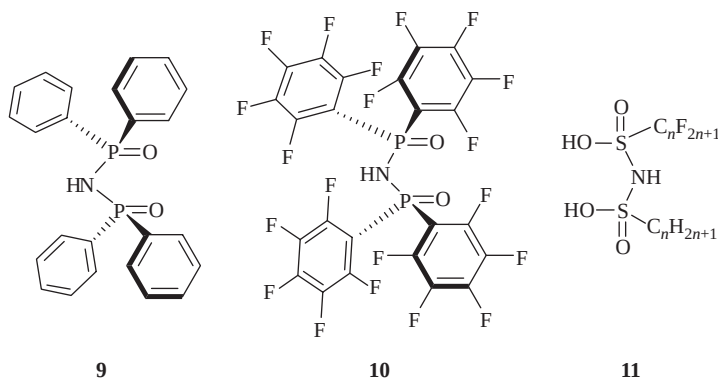


Tropolone (**6**) is a “cyclic” 1,3-diketone with a seven-membered ring. The hard Lewis base character of tropolone is suitable for forming strong bonds with $\text{Ln}(\text{III})$ ions, making it behave as a bidentate oxygen-donor chelator upon deprotonation. A series of tris(tropolonate) and tetrakis(tropolonate) lanthanide(III) complexes, $\text{Ln}(\mathbf{6})_3$, and $[\text{Ln}(\mathbf{6})_4]^-$, were isolated by controlling molar ratios between the lanthanide(III) salt and the ligand at 1 : 3 and 1 : 4, respectively [20]. With K^+ as the counterion, the complexes of $\text{K}[\text{Ln}(\mathbf{6})_4]$ (dmf) (dmf = *N,N'*-dimethylformamide) were fully characterized by X-ray crystallography, where the coordination geometry around the lanthanide ion is a distorted dodecahedron. The K^+ ion seems to play a significant role in the crystal packing. The tropolonato ligands are able to sensitize several lanthanide cations including NIR emitting $\text{Nd}(\text{III})$, $\text{Ho}(\text{III})$, $\text{Er}(\text{III})$, $\text{Tm}(\text{III})$, and $\text{Yb}(\text{III})$ ions in both aqueous and organic solutions. In particular, it is unprecedented that four emission bands from the holmium complex $[\text{Ho}(\mathbf{6})_4]^-$ are detected. The emission bands at 975 and 1479 nm are due to $^5\text{F}_5 \rightarrow ^5\text{I}_7$ and $^5\text{F}_5 \rightarrow ^5\text{I}_6$ transitions, respectively, whereas those at 1148 and 1187 nm originate from the same $^5\text{I}_6 \rightarrow ^5\text{I}_8$ transition split into two components. Quantum yields of $\text{Yb}(\text{III})$ luminescence in $[\text{Yb}(\mathbf{6})_4]^-$ ($\Phi_{\text{em}} = 1.9\%$ in DMSO (dimethyl sulfoxide) and 2.2% in DMSO-d_6) are comparable to the highest reported quantum yields of other NIR emitting lanthanide complexes in organic solvents. The presence of nonradiative effects explains the low quantum yields observed for $\text{Yb}(\text{III})$ complexes ($\Phi_{\text{em}} = 2.4 \times 10^{-4}$ in H_2O and 7.4×10^{-3} in D_2O) in water, in which water exerts a significant deactivation on the luminescence of lanthanide ions due to the coordination of water molecules to $\text{Ln}(\text{III})$, which were not present in the solid states. To probe the NIR emission by varying the chemical surroundings at the

lanthanide(III) ions, two ternary tris(tropolonato) erbium(III) complexes $[\text{Er}(\mathbf{7})_3(\text{phen})]$ and $[\{\text{Er}(\mathbf{7})_3\}_2(\text{pdon})]$ were prepared by reaction of $[\text{Er}(\mathbf{7})_3]_n$ with the appropriate bidentate N chelating ligand [21]. The two Er(III) complexes show NIR emissions at about 1550 nm upon excitation at 355 nm, which could possibly be used as the active material for the realization of plastic amplifiers in telecommunications.

Recently, Zhang and Petoud [22] reported a series of tetrakis(azulene) lanthanide(III) complexes $[\text{Ln}(\mathbf{8})_4]^-$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{and Lu}$) with the bidentate azulene-based ligand diethyl 2-hydroxyazulene-1,3-dicarboxylate (**8**), a derivative of tropolone. The azulene ligand **8** possesses a state located at significantly lower energy ($13\,600\text{ cm}^{-1}$) compared with that of the tropolonate ligand **6** ($17\,200\text{ cm}^{-1}$). Therefore, ligand **8** acts as a more efficient sensitizer for several NIR emitting lanthanide ions including Yb(III), Nd(III), Er(III), and Tm(III) because its triplet is located at a lower energy and closer to the energy of the accepting levels of these NIR emitting lanthanide cations. As there are no solvent molecules bound to the lanthanide(III) ion in the $[\text{Ln}(\mathbf{8})_4]^-$ complexes, this protects the lanthanide(III) ion efficiently against nonradiative deactivation. In fact, both the quantum yields and the emissive lifetimes for $[\text{Nd}(\mathbf{8})_4]^-$ ($\Phi_{\text{em}} = 0.53\%$, $\tau = 2.68\text{ }\mu\text{s}$ in CD_3CN) and $[\text{Yb}(\mathbf{8})_4]^-$ ($\Phi_{\text{em}} = 3.6\%$, $\tau = 32.8\text{ }\mu\text{s}$ in CD_3CN) complexes are among the highest values reported for NIR emitting lanthanide complexes in solutions, due most likely to a combination of efficient ligand to lanthanide energy transfer and good shielding of the lanthanide ions.

Tetraphenyl imidodiphosphinate (**9**) is analogous with β -diketonates, but without any O–H, C–H or N–H bonds in the binding site that can induce quenching of the lanthanide emission. There exists a “hydrophobic shell” around the lanthanide ion formed by three ligands in the neutral tris(imidodiphosphinate) lanthanide(III) complexes $\text{Ln}(\mathbf{9})_3$. X-ray crystallography [23] revealed that the Ln(III) centers are located in a distorted octahedral or trigonal prismatic environment composed of six oxygen donors. Intramolecular CH– π interactions are probably operating between the phenyl rings of the same ligand with C(–H) to centroid distances of about $3.8\text{ }\text{\AA}$. The absence of any N–H or O–H and the presence of few C–H vibrations in close proximity to the lanthanide centers and the effective shielding of the 12 phenyl groups from solvent molecules make ligand **9** act as an efficient sensitizer for NIR lanthanide luminescence. The $\text{Ln}(\mathbf{9})_3$ ($\text{Ln} = \text{Nd}, \text{Er}, \text{Yb}$) complexes displayed strong NIR luminescence in acetonitrile with lifetimes being $52.8\text{ }\mu\text{s}$ for Yb(III), $2.7\text{ }\mu\text{s}$ for Nd(III), and $6.5\text{ }\mu\text{s}$ for Er(III) species, much longer than the corresponding ones containing fully fluorinated β -diketonate ligands. This result indicates that deactivation pathways from the high-energy vibrations of framework structure in ligand **9** are minimized.



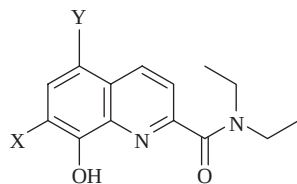
To further eliminate the C–H oscillators from phenyls in tetraphenyl imidodiphosphinate (**9**), fluorinated imidodiphosphinate ligand, *N*-{*P,P*-di(pentafluorophinoyl)}-*P,P*-dipentafluorophenyl-phosphinimidic acid (**10**) was prepared and was demonstrated to be a better sensitizer to NIR luminescence from lanthanide(III) ions [24]. Fluorination of aromatic C–H leads to dramatic improvements in the lanthanide luminescence efficiency with as high as 30-fold increase in emissive lifetimes. The NIR-emitting complexes [Ln(**10**)₃] (Ln = Nd, Er, Yb) show unprecedented long lifetimes with $\tau = 44\ \mu\text{s}$ for Nd(III), $741\ \mu\text{s}$ for Er(III), and $1111\ \mu\text{s}$ for Yb(III) species in deuterated acetonitrile, where the [Yb(**10**)₃] complex shows a luminescence lifetime of more than half the value of the radiative ion lifetime (2 ms). This demonstrates unambiguously that the elimination of high-energy C–H vibrations by fluorination is a key step for achieving long-lived NIR lanthanide luminescence with high efficiency.

Using bis(perfluoroalkylsulfonyl)amine (**11**), an inorganic 1,3-diketone analog, as bulky ligands with low vibrational frequencies, Hasegawa and Yanagida *et al.* [25] prepared a series of NIR emitting Nd(III) complexes containing three bis(perfluoroalkylsulfonyl)iminate ligands. Systematic luminescence studies indicated that introduction of long-chain perfluoroalkyl groups is always favorable for achieving enhanced emissions. Later studies [26] also demonstrated that an obvious increase of the Er(III)- or Yb(III)-centered NIR luminescence intensity could be achieved by using 1,10-phenanthroline as the light-harvesting moiety in tris(bis-perfluoromethanesulfonyliminate)(1,10-phenanthroline)lanthanide(III) complexes. The phenanthroline moiety has a good energetic match with the bis(perfluoroalkylsulfonyl)imide erbium(III) system and the energy absorbed by the phenanthroline could be efficiently transferred to the lanthanide(III) center.

12.2.1.2 Quinoline Ligands

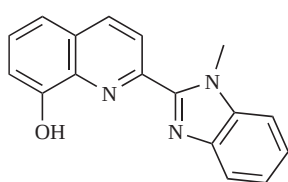
Although lanthanide(III) complexes of 8-hydroxyquinoline ligands have been investigated for several decades, the puzzle concerning their compositions and structures has been revealed through structural and spectroscopic characterization in recent years. Three basic types of 8-hydroxyquinolate lanthanide(III) complexes with different compositions and structural features have been isolated and identified by X-ray crystallography, depending on the reaction conditions such as solvents, reactant ratios, and substituents in 8-hydroxyquinoline ligands. These include tris complexes with a 1 : 3 metal-to-ligand ratio, tetrakis complexes with a 1 : 4 metal-to-ligand ratio, and trimeric complexes with a 3 : 8 or 3 : 9 metal-to-ligand ratio [27, 28]. Most synthetic approaches to obtain lanthanide(III) quinolates actually produced a mixture of hydrated tris, tetrakis, and trimeric complexes. Synthetic methods can be adapted to give a higher percentage of one or the other species, or even to obtain pure species. In any cases, the lanthanide(III) ions are usually surrounded with eight O and N donors from the organic ligands, which prevent solvent and water molecules from entering the lanthanide coordination sphere. Both structural and spectroscopic studies suggest that the NIR luminescence quenching in the 8-hydroxyquinolate lanthanide(III) complexes is due uniquely to the deactivation excitation from aromatic C–H vibration in the ligands. As a result, more efficient NIR emission is most probably accessible by halogenation of 8-hydroxyquinoline. As anticipated, substitution of the C–H bonds with C–X (X = F, Cl, Br, I) ones indeed gives remarkably enhanced NIR luminescence using 5,7-dihalo-8-hydroxyquinoline (halo = chloro, bromo, or iodo) as ligands [29, 30]. For instance, substitution of the hydrogen atoms in the 5- and 7-positions of the quinoline moiety by halogen atoms (Cl and Br) induces about 30% increase in the

NIR luminescence intensity for the Nd(III) or Yb(III) species. The most intense NIR emitting 8-hydroxyquinolate lanthanide(III) complexes are the tetrakis complexes with 5,7-dihalo-8-hydroxyquinoline ligands.

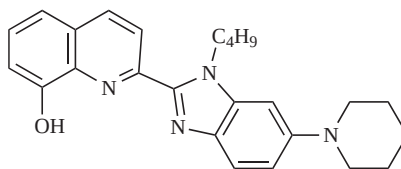


12 X, Y = H; **12-Br** X = H, Y = Br; **12-Br₂** X, Y = Br

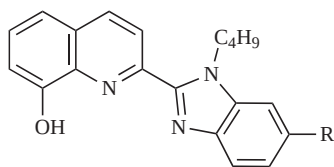
In order to obtain neutral tris complexes with the lanthanide(III) ion surrounded by three tridentate ligands to form a nine-coordinated geometry, an amide is introduced to the 2-position of 8-hydroxyquinoline, affording the tridentate derivatives **12**, **12-Br**, and **12-Br₂** [31]. In these tris complexes, the lanthanide(III) ion is shielded against intrusion by the solvent molecules into the first coordination sphere. As revealed by X-ray crystallography, the three stranded ligands coordinate to the lanthanide(III) ion in a helical fashion, leading to a coordination



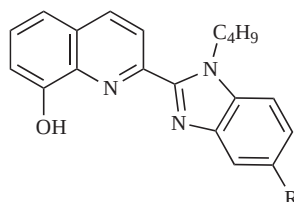
13a



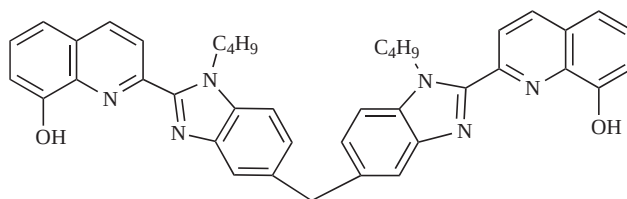
13b



13-Me R = Me
13-OMe R = OMe
13-Cl R = Cl



14-OMe R = OMe
14-Cl R = Cl

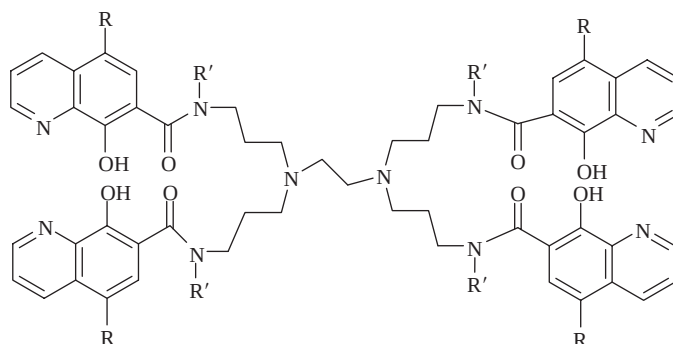


15

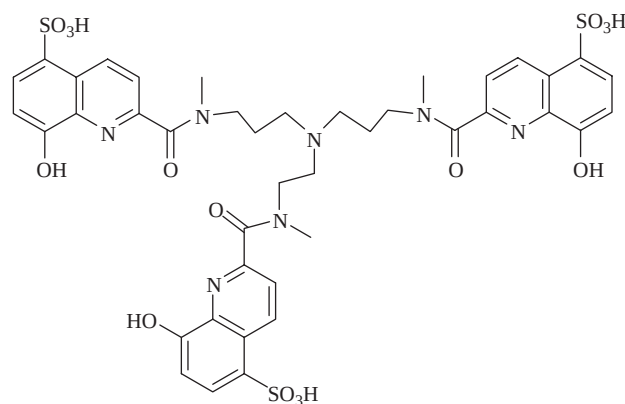
number of nine at the Er(III) or Yb(III) ion. Upon excitation at 277, 370, or 522 nm, which correspond to absorption bands of the ligands, the lanthanide(III) complexes display similar spectra with a broad emission band centered at 650 nm at 298 K. On the one hand, Eu-centered emission was not observed, probably due to the low-lying excited states of the quinoline derivatives, which prevent transfer of energy to the Eu(III) center from the light harvesting chromophores. On the other hand, the electronic features of **12**, **12-Br**, and **12-Br₂** are better suited for populating the NIR emitting excited states from Nd(III), Er(III), and Yb(III) ions. The quantum yields of the lanthanide NIR luminescence upon ligand excitation is enhanced in the series $\text{Ln}(\mathbf{12})_3 < \text{Ln}(\mathbf{12-Br})_3 < \text{Ln}(\mathbf{12-Br}_2)_3$. The presence of two bromine atoms causes a total 2.5–3 fold improvement in quantum yields and 2–4 fold increase in lifetimes, due to the “heavy atom effect” of the bromine substituents, which reduces the nonradiative deactivation process.

Fairly recently, Bünzli and coworkers [32] reported a series of neutral tris(tridentate ligand) lanthanide complexes using a new class of benzimidazole-substituted 8-hydroxyquinoline ligands with monoanionic tridentate N,N,O donors (**13–15**). Crystallographic characterization of 11 complexes with six different ligands indicated that the lanthanide ion is nine-coordinated by three ligands arranged in an “up-up-down” fashion. The geometry around the lanthanide ion can be described as a tricapped trigonal prism with the capping positions occupied by quinoline N-donors. The low-energy absorption band centered at 466–483 nm with $\epsilon = 7200\text{--}18\,000\text{ M}^{-1}\text{ cm}^{-1}$ is tentatively assigned to an intraligand phenolate-to-pyridyl charge transfer transition centered on the 8-hydroxyquinolate chromophore. Upon irradiation in the ligand absorption region, these Nd(III) complexes display characteristic metal-centered NIR luminescence with quantum yields and lifetimes as high as 0.34% and 1.2 μs in solid states at room temperature. Introducing a substituent to different positions in benzimidazole conducted the absolute quantum yields of Nd(III) complexes to decrease in the order **14-OMe** > **13-OMe** > **14-Cl** > **13-Cl** > **15** = **13b** > **13-CH₃** > **13a**. It is worth noting that substitution of C–H group by the C–OCH₃ group is more efficient than that of a C–Cl or C–CH₃ group in improving the luminescence efficiency of the Nd(III) complexes. Although both C–OCH₃ and C–CH₃ groups have three C–H bonds, the C–H oscillators in the C–OCH₃ group are further apart from the Nd(III) centers in the Nd(III) complexes and are more decoupled from the benzimidazole ring by virtue of the “insulator” C–O bond and thus would be less likely to deactivate the Nd(III) excited state. This suggests that substituting C–H groups in the vicinity of Nd(III) centers with halogen or alkoxy groups is a feasible approach to improving the luminescence efficiency of Nd(III) complexes with benzimidazole substituted 8-hydroxyquinoline ligands.

With the aim of obtaining water solvable NIR emitting lanthanide(III) complexes, Imbert *et al.* designed novel polydentate ligands **16**, **17**, and **17-CH₃** with bidentate 8-hydroxyquinolate subunits connected to an *N,N,N',N'*-tetraaminopropyl-1,2-ethylenediamine framework [33]. Water soluble and stable lanthanide(III) chelates are formed using these novel hydroxyquinoline-containing tetrapodal ligands, which are good sensitizers for NIR luminescence from Nd(III) and Yb(III) complexes. The 1 : 1 chelating mononuclear complexes of **16**, **17**, and **17-CH₃** exist as the major species in aqueous solutions at physiological pH. From lifetime determinations of the Nd(⁴F_{3/2}) and Yb(²F_{5/2}) excited levels in both H₂O and D₂O, the absence of water molecules bound in the inner coordination sphere of the Ln(III) ions and the complete coordination of the four pendant arms of the podand, which acts as an octadentate ligand, was suggested. The absolute quantum yield of lanthanide(III) complexes with **17** is 0.02% for Nd(III) and 0.18% for Yb(III) species in aqueous solutions.



16 R = H, R' = H
17 R = SO₃⁻, R' = H
17-Me R = SO₃⁻, R' = Me

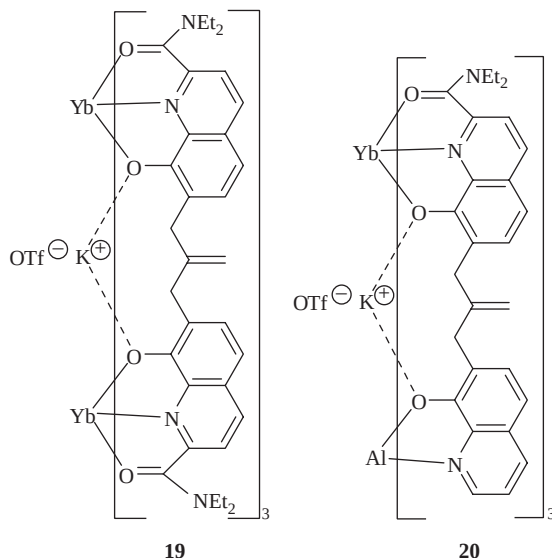


18

It appears that tetrapodal ligand **17** is an excellent sensitizer for the Yb(III) luminescence in water and a reasonable one for the Nd(III) emission. Methylation of the amide group eliminates the deactivation processes from the proximate N-H vibrations and increases both the lifetimes and quantum yields of the **17-CH₃** complexes with the NIR emitting quantum yield being 0.04% for Nd(III), and 0.37% for Yb(III) species. Thus these molecular designs meet all the requirements for the development of NIR probes for bioanalyses.

A tris(tridentate) tripodal ligand **18** [34] has recently been synthesized to take advantage of the chelating effect of tridentate 8-hydroxyquinolate subunits. This podand acts as a non-adentate ligand to wrap around the Ln(III) ions, yielding hydrolysis-resistant, stable podates at physiological pH, as demonstrated by the equivalence of the three arms in the NMR spectra and by the absence of water molecules in the inner coordination sphere. The low energy of the triplet state allows efficient energy transfer from the ligand to the lanthanide(III) ions. The sensitization efficiency of the NIR luminescence is 75% for Nd(III) and 100% for Yb(III) with overall quantum yields and lifetimes being 0.027% and 0.15 μ s for Nd(III), and 0.13% and 2.47 μ s for Yb(III) in aqueous solutions at physiological pH. The Er(III) luminescence is also detected at pH = 7.4. The NIR emitting properties are comparable to those obtained for the

tetrapodal ligand **17**, but still better than most of the reported complexes [1]. Although the Yb(III) podate complexes at concentrations of up to 250 mM do not display sizeable cytotoxicity for Jurkat cells after 24 h of incubation, it was shown to couple to human serum albumin (HSA), leading to an increase of 50% in the NIR luminescence intensity.

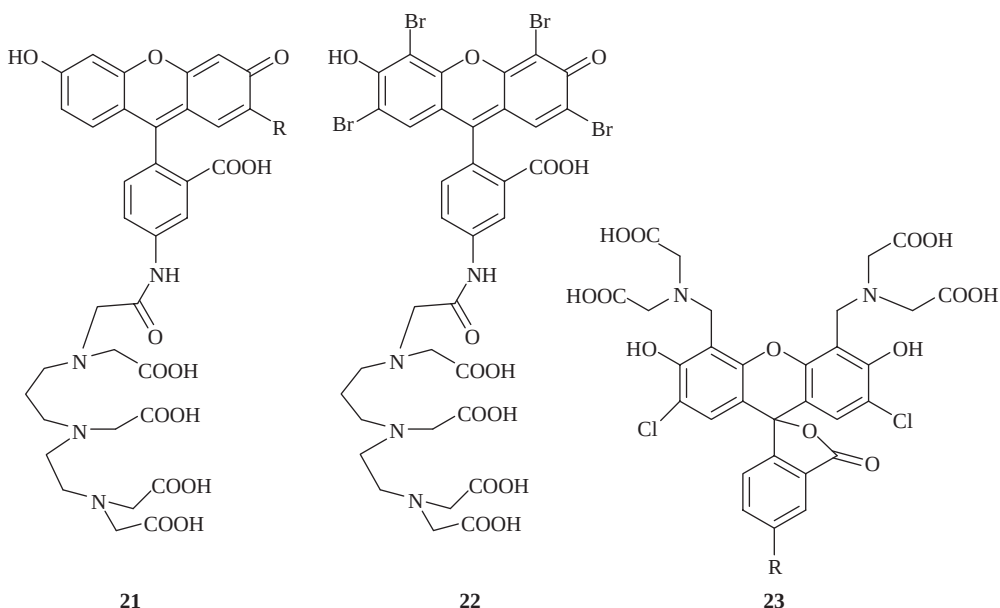


Two highly efficient NIR emitting Yb–Yb (**19**) and Yb–Al (**20**) helicates were recently reported by Albrecht *et al.* [35], where Yb(III) is surrounded by three tridentate syn-arranged 2-amidoquinolinate and Al(III) is coordinated by two bidentate hydroxyquinolinate. The Yb–Yb complex **19** was prepared from the ligand and ytterbium(III) triflates in a 2 : 3 ratio, whereas the heterodinuclear Yb–Al complex **20** was obtained from ytterbium(III) triflates, aluminum(III) chloride, and the ligand in a 1 : 1 : 3 ratio using potassium carbonate as a base and as a template. Potassium is incorporated in an unusual $K^+ - \pi$ interaction of $C=C$ η^2 -bond type in the cavity of the complexes. With excitation at 350 nm, Yb–Yb (**19**) and Yb–Al (**20**) complexes display efficient NIR emission arising from the $Yb(^2F_{5/2} \rightarrow ^2F_{7/2})$ transition with $\Phi_{em} = 1.04 \pm 0.07\%$ and $\tau_{em} = 18.8 \pm 0.1 \mu s$ for **19**, and $\Phi_{em} = 1.17 \pm 0.07\%$ and $\tau_{em} = 22.6 \pm 0.2 \mu s$ for **20**. The longer luminescence lifetime and larger quantum yield of the heterodinuclear Yb–Al complex is probably due to less competitive nonradiative decay of the Yb(III) ion as well as effective $Al \rightarrow Yb$ energy transfer from the aluminum quinolate chromophore to the ytterbium(III) amidoquinolate moiety.

12.2.1.3 Polyaminocarboxylate Ligands

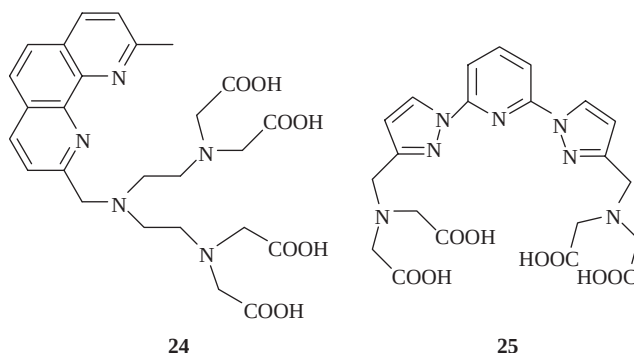
Functionalized organic dyes with polyaminocarboxylate have been widely utilized as feasible sensitizers to afford visible region excitation for sensitization of NIR lanthanide luminescence [36–45]. Verhoeven and coworkers [36, 37] first prepared a series of neodymium(III), erbium(III), and ytterbium(III) complexes with polyaminocarboxylate-functionalized fluorescein (**21**) and eosin (**22**) as sensitizing chromophores. These complexes show sensitized NIR

luminescence from all three lanthanide ions upon excitation of the chromophore with visible light [38]. However, the energy transfer from the chromophores to the lanthanide(III) ions is considerably slow and not very efficient in these complexes because the phenyl ring, as a spacer between the chromophore and the lanthanide ion, would reduce their interactions, which are crucial to the efficiency of sensitization. Molecular oxygen can also compete with the lanthanide ion as an alternative acceptor of the triplet energy of the chromophore so as to quench significantly the NIR lanthanide luminescence. Using 4',5'-bis[*N,N*-bis(carboxymethyl)aminomethyl]-fluorescein (**23**) or fluorexon as the ligand [39, 40], the corresponding neodymium(III), erbium(III), and ytterbium(III) complexes display enhanced sensitization of Yb^{3+} (980 nm), Nd^{3+} (main transition at 1060 nm), and Er^{3+} (1530 nm) compared with the complexes with **21** and **22**. Because of the shortened distance in the fluorexon–lanthanide ion system, the intersystem crossing and the transfer of triplet energy to the lanthanide ion is much faster and more efficient, so that oxygen cannot compete as an alternative acceptor.



The preparation of an interesting ligand (**24**) featuring a combination of a single phenanthroline chromophore and a diethylenetriamine tetracarboxylic (DTTA) unit as a lanthanide (Ln) coordination site has been reported [41]. A series of water soluble complexes of lanthanide(III) with ligand **24** were thus synthesized to display a 1 : 1 stoichiometric ratio with an association constant $>10^7 \text{ s}^{-1}$. These lanthanide complexes of **24** afforded high efficiencies of the sensitized emission in both water and deuterated water, consistent with cooperation of the phen and DTTA moieties to occupy all coordination sites of the Ln(III) centers. The visible-light emitting quantum yield is 0.24 for Eu and 0.15 for Tb in air-equilibrated water with lifetimes of 1.25 ms for Eu and 0.78 ms for Tb. For NIR emitting lanthanide complexes, the quantum yields are 2.5×10^{-3} (lifetime 13 μs) for Sm(III), 3×10^{-5} for Pr(III), 2×10^{-5} for Ho(III),

2×10^{-4} for Yb(III) (lifetime 2.5 μ s), and 4×10^{-5} for Nd(III) species in aerated aqueous solutions.

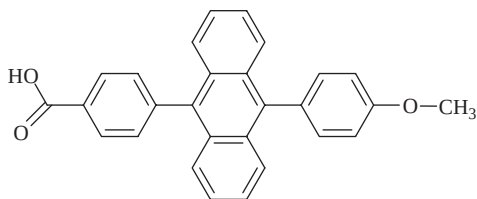
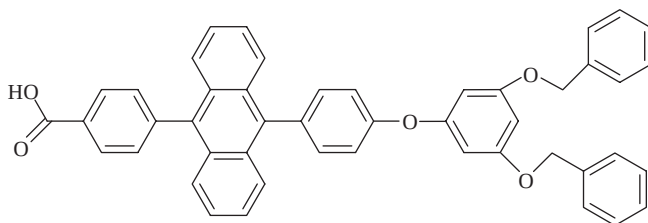


The complexation behavior, stability, solution structure, and NIR emitting properties of lanthanide complexes with the ligand 2,6-bis[3-[*N,N*-bis(carboxymethyl)aminomethyl]pyrazol-1-yl]pyridine (**25**) were recently described [45]. The stability constants for the formation of the $[\text{Ln}(\mathbf{25})]^-$ complexes (Ln = La, Nd, Eu, Ho, and Lu) were determined in water with log *K* increasing from 14.56(9) (La) to 16.68(2) (Ho) and decreasing to 15.42(2) (Lu). These complexes present stabilities in aqueous solution comparable to those of EDTA for the large Ln(III) ions. Owing to the conformational variation in these $[\text{LnL}]^-$ complexes, this ligand adopts a chiral Δ or Λ enantiomeric form. The $\Delta \rightleftharpoons \Lambda$ interconversion process is fast on the NMR time scale for La(III) but slow at room temperature in the case of the Yb(III) and Lu(III) complexes. Sensitized NIR luminescence from the corresponding lanthanide(III) centers occurred in these $[\text{Ln}(\mathbf{25})]^-$ complexes for Pr(III), Nd(III), Er(III), or Yb(III) in air-equilibrated water. The $[\text{Yb}(\mathbf{25})]^-$ complex displays a relatively long lifetime in water (3.0 μ s).

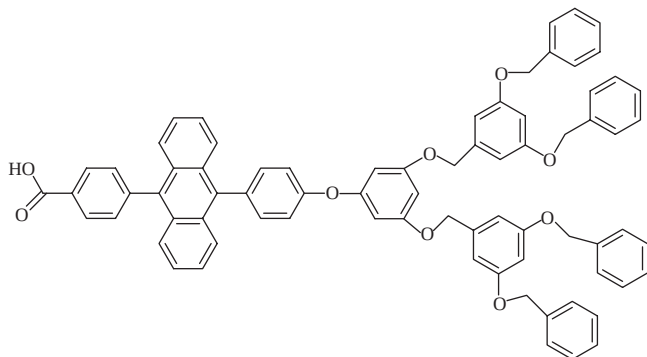
12.2.1.4 Dendrimeric Ligands

One of the feasible approaches for achieving efficient lanthanide luminescence is the use of dendrimers as the light-harvesting systems. Dendrimer ligands provide high functionalization of lanthanide complexes. Vogtle and coworkers prepared Nd(III)-dendrimer complexes to give intense NIR luminescence [46, 47] and Petoud and coworkers developed the highly ordered Eu(III) complexes on the dendrimer periphery as effective emitters [48]. The encapsulated lanthanide(III) ions by dendrimeric ligands can be shielded from a nonradiative environment so that excited energy can be efficiently transferred from the peripheral chromophores to the lanthanide center of the dendrimer. It has been demonstrated that the site-isolation and antenna effects exert significant influences on the luminescent properties of spherical lanthanide(III)-cored dendrimer complexes with Eu(III), Tb(III), or Er(III) ions [49–52]. To achieve the site isolation for enhanced lanthanide luminescence, the Ln(III) ion is usually surrounded by a dendritic shell of aryl-ether-type dendrons. The enhanced luminescent intensity is highly dependent on the morphology of the dendrimer, which affords efficient energy transfer from the photonic antenna to the lanthanide center.

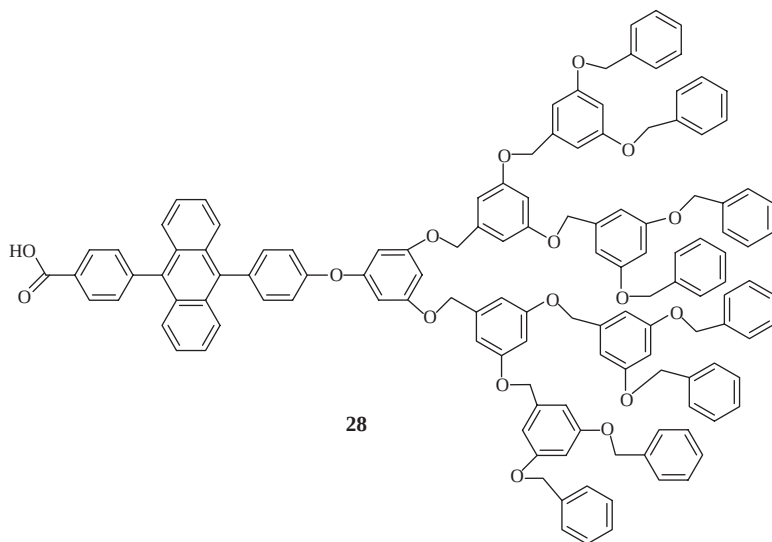
Kim and coworkers developed a series of stable and inert encapsulated Ln(III) complexes with artificial light-harvesting systems that use dendritic luminescent ligands based on naphthalene units [53] or metalloporphyrins [54, 55] bearing aryl-ether dendrons. Taking advantage of dendritic 9,10-diphenylanthracene ligands **26–28** [53], a series of inert and photostable encapsulated lanthanide(III) ternary complexes were prepared that contain three dendritic ligands and one 2,2' : 6',2''-terpyridine to satisfy nine coordination sites. These complexes display intense NIR luminescence via highly efficient energy transfer from the excited states of the peripheral antennae to Er(III), Nd(III), and Yb(III) ions. The NIR lanthanide emission in the encapsulated Ln³⁺–dendrimer complexes are dramatically enhanced on increasing the generation number of dendrons, due to site-isolation and light-harvesting effects. The energy-transfer efficiency from the excited singlet state of the dendritic anthracene ligands to the lanthanide center is estimated to be 90–97%. The NIR lanthanide emitting lifetimes are 2 μ s for the Er(III) species, 11 μ s for the Yb(III) species, and 0.7 μ s for the Nd(III) species of **28** in thin films. The calculated intrinsic quantum yields of the Ln(III) ions are 0.025% for the Er(III) species, 0.28% for the Nd(III) species, and 0.55% for the Yb(III) species.

**26a****26b**

Ternary Er(III) complexes with three dendritic Pt(II)-porphyrin ligands (**29–31**) and one 2,2' : 6',2''-terpyridine (tpy) has been recently described by Kim and coworkers [54, 55]. The functionalized Pt(II)-porphyrin ligands have been designed to provide enough coordination sites for the formation of inert and stable nine-coordinated Er(III)-cored complexes, where Er(III) ions are encapsulated by the three Pt(II)-porphyrin ligands. These Er(III) complexes exhibit strong NIR emission bands via highly efficient energy transfer from the excited triplet state of the Pt(II)-porphyrin to the Er(III) center. The NIR luminescence from Er(III) ion at 1530 nm ($^4I_{13/2} \rightarrow ^4I_{15/2}$) is dramatically enhanced upon increasing the generation number of the aryl ether dendrons due to site-isolation and light-harvesting (LH) effects. The NIR emission of Er(III) complex with **31** is 30-fold stronger than that of Er(III) species with **29**. The energy transfer efficiency from the dendritic Pt(II)-porphyrin to the Ln(III) center is increased on increasing the generation number of the dendrons from 12% to 43%. The lifetimes of NIR



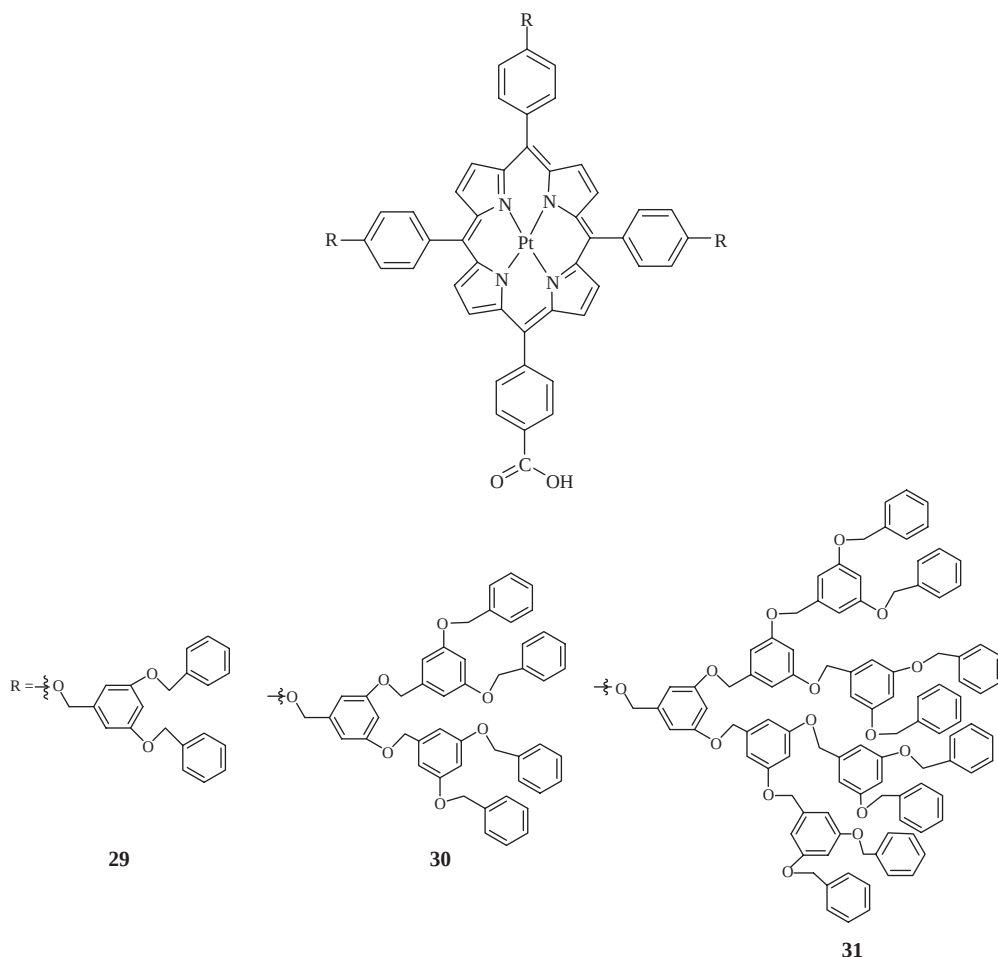
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luminescence are 0.98, 1.64, and 6.85 μs for Er(III) complexes containing the ligands **29–31** in thin films, respectively.

Dendrimer-type ligand (**32**) serves as a lanthanide container to exhibit “on–off” switchable luminescence upon lanthanide complexation in response to external anions [56]. Because of the presence of two classes of coordination sites for the lanthanide cations at the inner and outer spheres, the dendrimer **32** exhibits two different binding modes to afford “on–off” lanthanide luminescence, in which “outer” complexation at the tetradentate tripod site offers the “on” luminescence state upon quinoline excitation; whereas, “inner” complexation at the multidentate core site corresponds to the “off” luminescence state. Upon complexation of **32** with $\text{Yb}(\text{CF}_3\text{SO}_3)_3$, the quite weak NIR luminescence from the Yb(III) center suggests that the Yb(III) ion is most probably located at the inner coordination sites and apart from the excited quinoline moieties. Nevertheless, addition of SCN^- anion to the **32**– $\text{Yb}(\text{CF}_3\text{SO}_3)_3$ system induced remarkable spectral changes around the quinoline absorption band and about ninefold enhancement in luminescence intensity at around 980 nm. As the intense Yb luminescence appeared upon quinoline excitation, the employed SCN^- anion promoted the tripod– Yb^{3+}

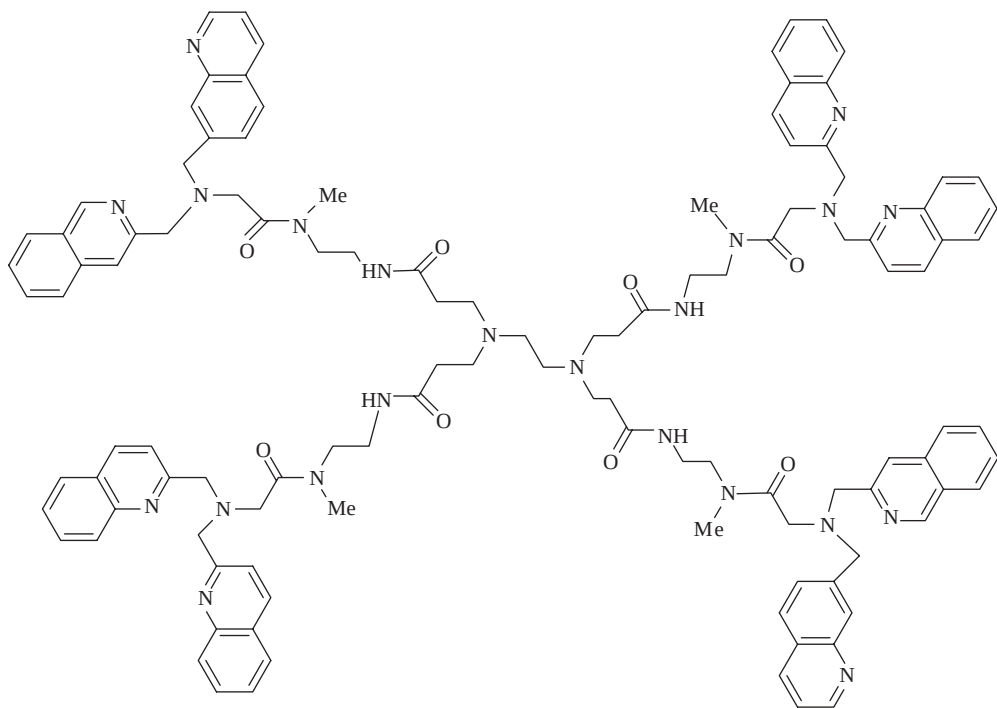


complexation at the outer coordination sites. Such dynamic structural changes of the dendrimer 32-Yb^{3+} complex switched the NIR luminescence on.

12.2.1.5 Other Chelating Ligands

Apart from several typical classes of acyclic ligands mentioned above, some other types of chelating ligands can be also offered as feasible light-harvesting antenna for effective sensitization of NIR lanthanide luminescence [57–68]. A boradiazaindacene dye appending terpyridine (**33**) was utilized by Ziessel and Bunzli and coworkers as antenna chromophore for achieving sensitized NIR lanthanide luminescence. Mononuclear lanthanide complexes [$\text{Ln}(\mathbf{33})(\text{NO}_3)_3$] are formed [57], where the lanthanide ion is bound to the terdentate terpyridine and the nine-coordinated geometry is further completed by three bidentate nitrate anions to afford a distorted tri-capped antiprism. The lanthanide(III) complexes exhibit intense absorption in the visible spectral region with molar extinction coefficients being about $65\,000\text{ M}^{-1}\text{ cm}^{-1}$ at 529 nm.

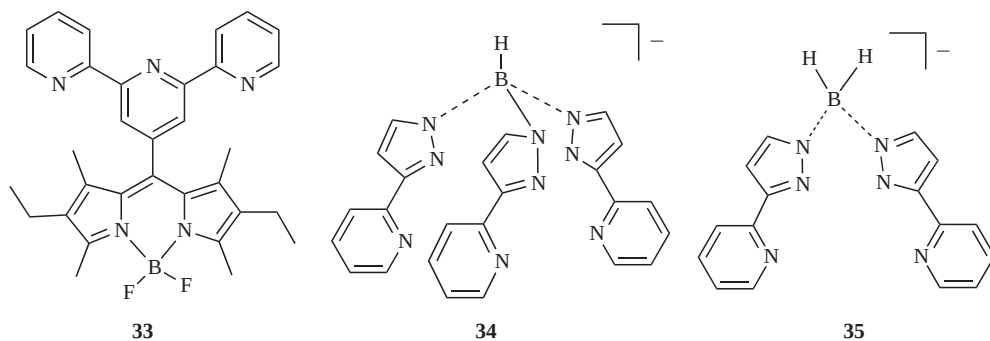
NIR luminescence (900 to 1600 nm for Ln = Yb, Nd, and Er) was detected in both the solid state and solution upon excitation of the electronic state of the indacene moiety at 514 nm. The quantum yield of the Yb(III) complex in dichloromethane is 0.31%, corresponding to about 63% sensitization efficiency from the ligand.



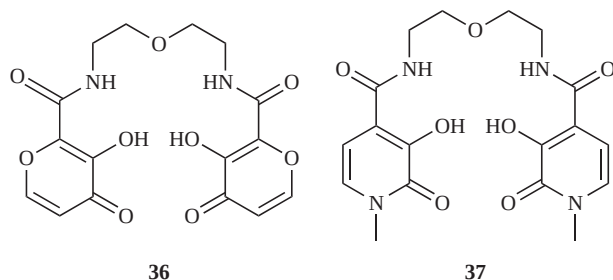
32

Using hexadentate tris[3-(2-pyridyl)pyrazol-1-yl]hydroborate (**34**) or tetradentate bis[3-(2-pyridyl)pyrazol-1-yl]dihydroborate (**35**) as a ligand, Ward and coworkers reported the preparation, characterization, and photophysical properties of a series of binary or ternary complexes of lanthanide(III) complexes with dibenzoylmethane anions (dbm) or nitrate anion as a co-ligand [58–60]. Sizeable NIR emission was detected for these pyrazolylborate-derived complexes of Nd(III), Pr(III), Er(III), and Yb(III) ions. They gave longer lifetimes of lanthanide luminescence than those of aminocarboxylate complexes due to the lack of C–H oscillators in close proximity to the lanthanide(III) ions in the pyrazolylborate complexes compared with that in the aminocarboxylate species.

The preparation, characterization, aqueous stability, and photophysical properties of NIR emitting lanthanide complexes with tetradentate chelating ligands **36** and **37** were described by Raymond and coworkers [61, 62]. In aqueous solution, the chelating ligand **36** or **37** forms stable complexes with Ln(III) ions, and sensitized NIR lanthanide luminescence was detected for the complexes with Pr(III), Nd(III), Ho(III), or Yb(III) ions. For [Ln(**36**)₂][−] complexes, the luminescence decay curves were biexponential due to partial hydrolysis of the complexes or alternately the presence of a slowly exchanging equilibrium mixture with a hydrated form of the complexes. For [Ho(**37**)₂][−], the NIR band due to ⁵F₅ → ⁵I₇ transition of the Ho(III)

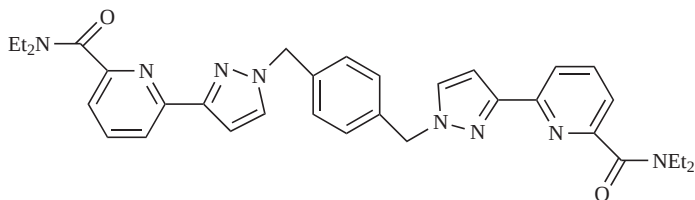


ion is detected at 908 nm with a weaker shoulder at 1018 nm and the luminescence lifetime in the NIR region was monoexponential, with $\tau_{\text{em}} = 6.5 \pm 0.3$ ns in aqueous solution. The NIR emission of the $[\text{Pr}(\mathbf{37})_2]^-$ complex occurs at 1030 nm due to $^1\text{D}_2 \rightarrow ^3\text{F}_4$ transition, and the lifetime obtained was monoexponential with a τ_{em} value of 8.0 ± 0.4 ns.

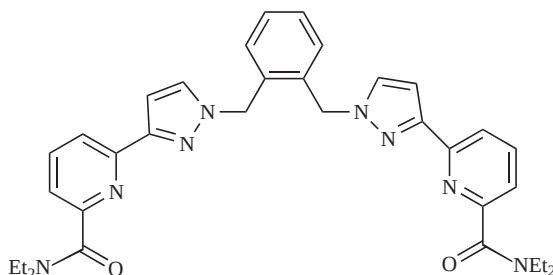


Three bis-tridentate bridging ligands **38–40** have been prepared with *N,N',O*-tridentate amide substituted pyrazolyl–pyridine units linked via methylene units to a central *o*, *m*, or *p*-phenylene spacer [63]. The *p*-phenylene spaced ligand **38** affords lanthanide(III) complexes with a 2:3 or 1:1 metal : ligand ratio. The 2:3 complexes displays triple stranded “mesocates” with a cylindrical structure with all three bridging ligands spanning both lanthanide(III) ions. Depending on the lanthanide ion and crystallization conditions, the 1:1 lanthanide complexes show various architectures including a dinuclear double-stranded mesocate, a tetranuclear cyclic helicate, and a one-dimensional coordination polymer. The *o*-phenylene spaced ligand **39** and *m*-phenylene spaced ligand **40** form dinuclear 1:1 lanthanide(III) complexes, in which the two ligands can be arranged in a helical or non-helical architecture about the two metal ions. Upon excitation of the ligand-based $\pi-\pi^*$ absorption in the UV region, sensitized NIR luminescence was observed at 1060 nm for the Nd(III) species. For the cylindrical complex $[\text{Nd}_2(\mathbf{38})_3][\text{ClO}_4]_6$ with saturated coordination in the Nd(III) centers, the luminescence lifetime is 0.9 μs .

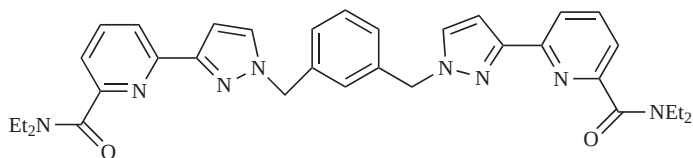
The photophysical properties of the triple-stranded dimetallic helicates $[\text{Ln}_2(\mathbf{41})_3]$ ($\text{Ln} = \text{Nd}$, Sm, Dy, Yb) were investigated in water and D_2O solutions by Bünzli and coworkers [64]. Lanthanide-centered luminescence is well sensitized in the triple stranded homodimetallic helicate complexes. The absolute quantum yield of the ligand-centered luminescence decreases dramatically upon formation of the lanthanide helicates because of a significant enhancement



38



39



40

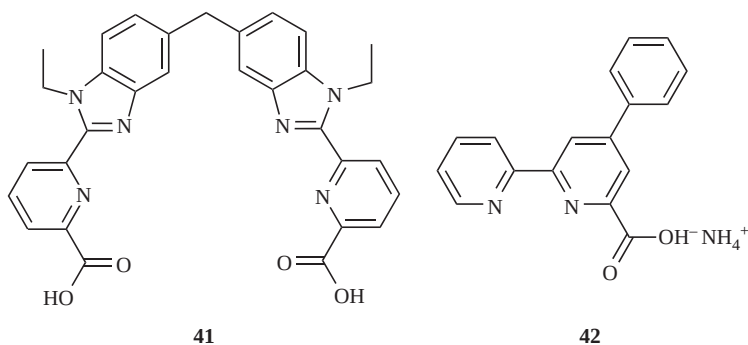
in the intersystem crossing rate constant and subsequent energy transfer to the lanthanide ions. The quantum yields of Yb(III) and Sm(III) helicates are 1.8 and 1.1% in deuterated water, respectively.

Using 4-phenyl-2,2'-bipyridine-6-carboxylate (**42**) as a terdentate chelating ligand, neutral, nine-coordinated lanthanide complexes were prepared [65], giving the typical narrow emission spectra, large Stokes shifts, and long luminescence lifetimes typical of Ln(III) ions. The tris-terdentate chelating coordination favors light-harvesting from the chelating chromophore for energy transfer to the Ln(III) ion with high efficient NIR emission ($\Phi_{\text{em}} = 0.7\%$ for Yb species in acetonitrile), which is probably due to the exclusion of vibronically deactivating solvent molecules from the inner coordination sphere of the complexes.

12.2.2 Macrocyclic Ligands as Antenna Chromophores

12.2.2.1 Cyclen Ligands

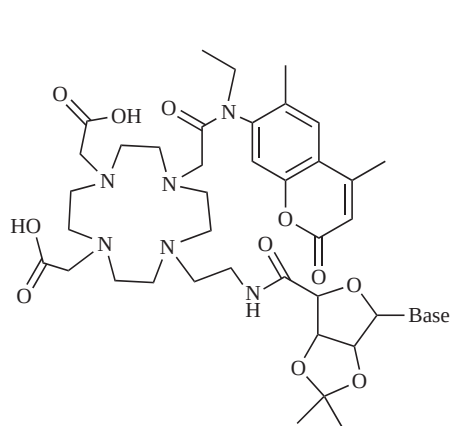
Derivatized 1,4,7,10-tetraaza-dodecane ligands with a 12-membered ring bearing four amino functions are one of the most investigated classes of macrocyclic ligands [1, 5]. Their tri- or tetra-carboxylic derivatives have been extensively utilized as light-harvesting chromophores for sensitization of lanthanide luminescence as well as contrast agents in magnetic resonance



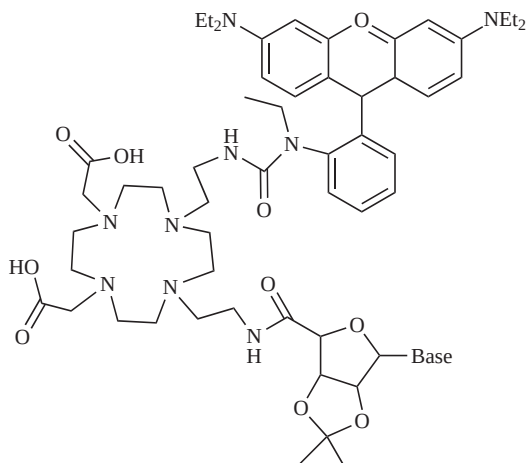
imaging upon complexation with Gd(III) ions. Several synthetic strategies to prepare asymmetrically substituted cyclen derivatives have been established and applied in the preparation of ligands for the NIR emitting lanthanides complexes [69–82]. These ligands are able to regulate to some degree the energy transfer process between the antenna chromophore and the lanthanides and therefore it is possible to modulate the extent of energy transfer between the antenna and the lanthanides by an external chemical stimulus.

A series of NIR-emitting Yb(III) and Nd(III) complexes with unsymmetrical cyclen-based ligands (**43** and **44**) incorporating an antenna and photoactive donor–acceptor quencher triads were described by Borbas and Bruce [69, 70], where a nucleoside quencher is used to regulate the extent of energy transfer between the donor and the acceptor. The interaction between the quencher and the antenna can be regulated by the addition of the complementary base or DNA to the complexes, resulting in enhancement in the intensity and lifetimes from lanthanide luminescence. This highly efficient and flexible synthetic approach enables the straightforward introduction of other antenna–quencher pairs to fine-tune the photophysical and recognition behavior of similar lanthanide complexes.

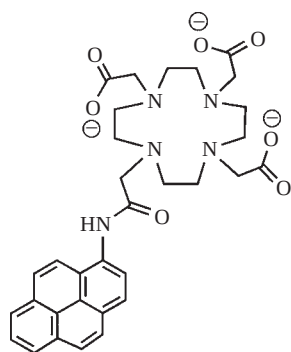
In order to probe the energy transfer processes for the systems with the same chromophores but with different spacers between the chromophore and lanthanide(III) centers, two azamacrocyclic derivatives (**45** and **46**) bearing pendent pyrene groups and their NIR emitting Nd and Yb complexes were prepared by incorporating a covalently bound pyrene chromophore to the cyclen [71]. Ligands **45** and **46** differ in that **46** has a methylene spacer to isolate the chromophore from the amide donor, while the chromophore and the donor group are directly linked together in **45**. The emission quantum yield for the Yb complexes of **45** with the pyrene chromophore linked directly to the ligand is 1.6-fold higher than that for **46** with a methylene spacer group. This is consistent with a falling off in the efficiency of the energy transfer process with increasing separation of the ligand and the chromophore. Likewise, the lifetimes in the Yb and Nd complexes of **45** are much longer compared with those in the corresponding complexes of **46**, suggesting that the complexes with **45** exhibit more efficient energy transfer than that in the complexes with **46**. Complexation of triazolophthalazine appended macrocyclic ligand **47** with lanthanide ions gives a series of the corresponding lanthanide complexes (Ln = Nd, Eu, Yb, Er) [72]. They are all luminescent and exhibit sensitized lanthanide luminescence upon excitation of the triazolophthalazene chromophore with emissive lifetimes being 0.02, 0.09, and 1.87 μ s for Nd, Er, and Yb species in aqueous solutions, respectively.



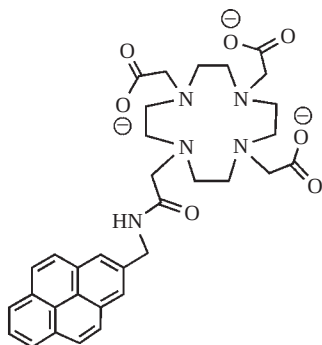
43a Base = urdine
43b adenosine



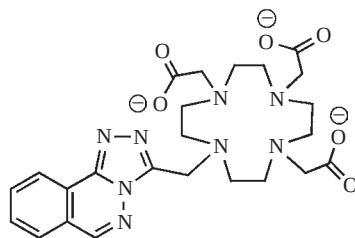
44a Base = urdine
44b adenosine



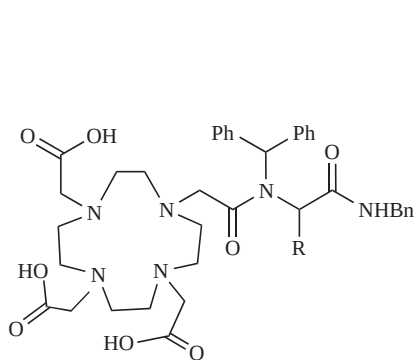
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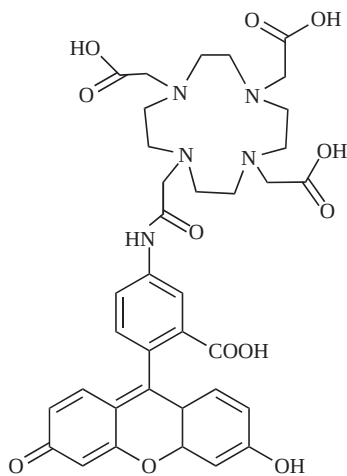
46



47



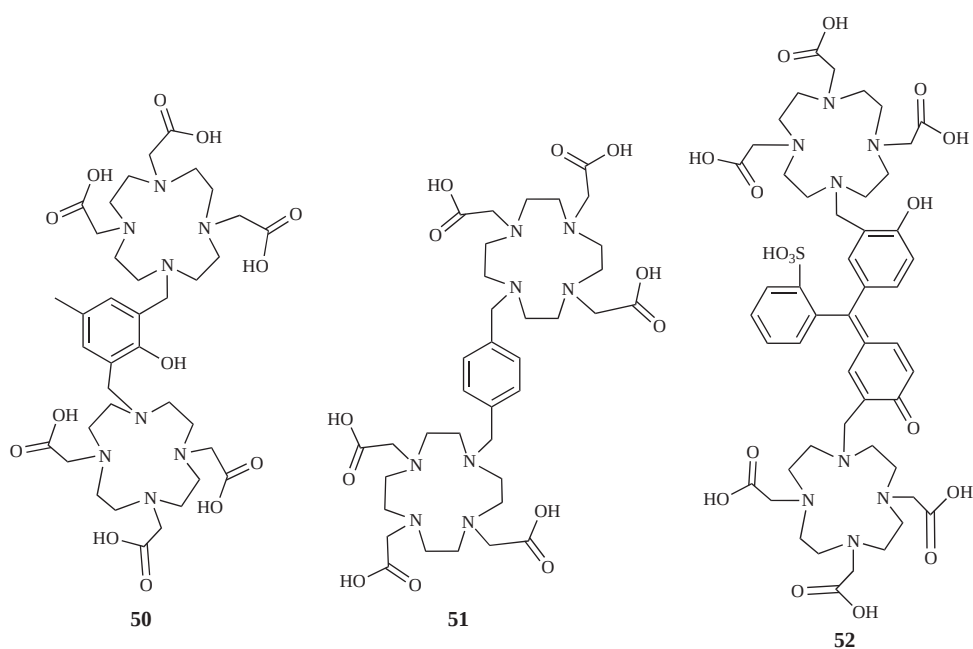
48a R = Ph
48b Np
48c 2-pyrenyl
48d 3-indolyl



49

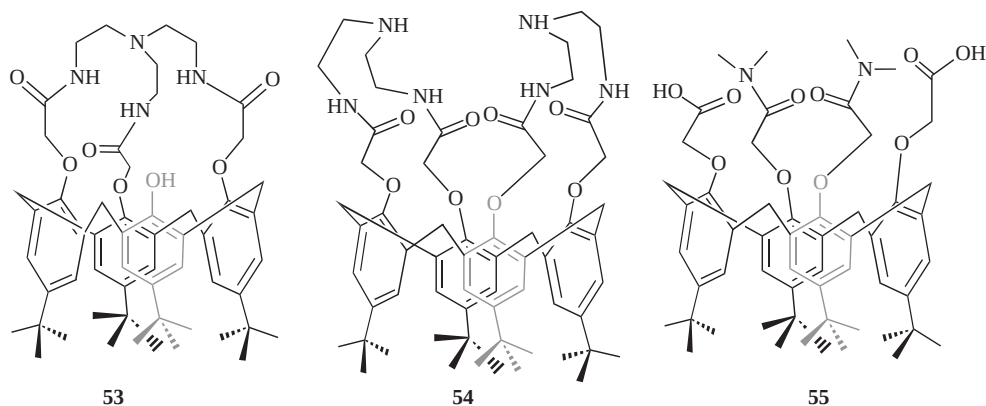
Very recently, an effective synthetic approach was introduced for preparation of a series of novel DOTA monoamide derivatives and their lanthanide complexes using the Ugi multicomponent reaction as a key step [73]. This approach gave rapid access to a variety of DOTA labeled compounds **48a–48d**, where the incorporated chromophores can be modified with different aromatic groups for efficient sensitized luminescence from lanthanide(III) ions. Attaching a fluorescein moiety to DOTA, ligand **49** was synthesized by the reaction of 4-aminofluorescein with 1,4,7,10-tetraazacyclododecane in three-step reactions [74]. Upon excitation of the fluorescein moiety at 488 nm the Nd(III) complex of **49** emits long-lived NIR luminescence with a lifetime of 2.3 μ s.

Two DO3A units can be linked by an aromatic spacer, such as a phenol and xylyl, to give the ligands **50** and **51** [80, 81]. A series of well defined, kinetically stable homobinuclear lanthanide complexes have been thus prepared from DO3A derived systems containing one seven- and one eight-coordinated or two seven-coordinated domains. Luminescence studies demonstrated that the lanthanide ions behave as isolated centers on the luminescence time scale. Two derivatized 1,4,7,10-tetraaza-dodecan units can also be linked together by organic dyes of the sulfophenylphthalexones group to give **52** [82]. Upon excitation at 532 nm, the Nd(III) and Yb(III) complexes of **52** display intense NIR luminescence with lifetimes of 1.45 μ s for the Nd(III) species and 12.60 μ s for the Yb(III) complex in aqueous solutions because of efficient energy transfer from the dye moiety to the lanthanide(III) ion.



12.2.2.2 Calixarene Ligands

Calixarenes are particularly useful as molecular scaffolds for the design of luminescent lanthanide complexes because they can be conveniently functionalized with various chromophores [83]. The introduction of an antenna chromophore can be accomplished by either use of the



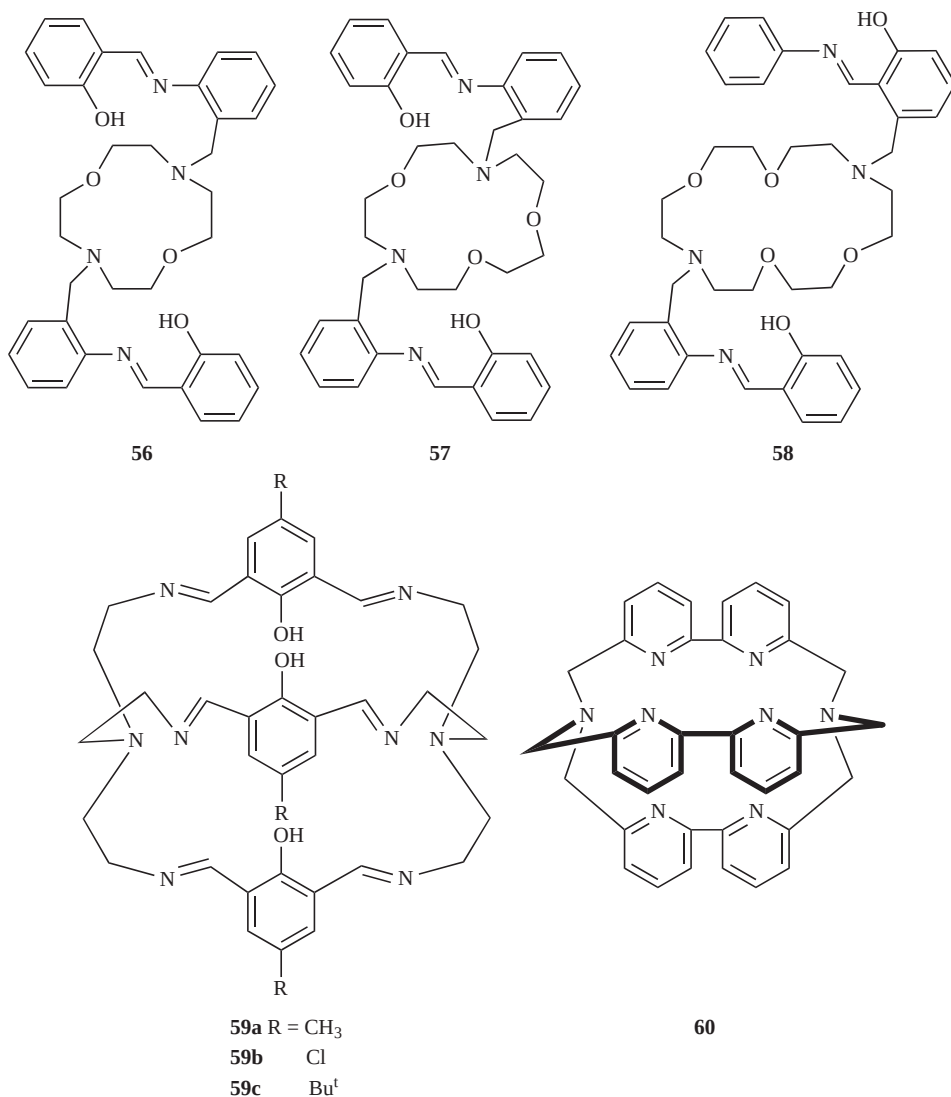
aromatic moieties of the calixarene itself or attachment of a chromophore to the upper or lower rim of the calixarene. A large number of visible-light emitting Eu(III) and Tb(III) complexes with various functionalized calixarenes have been described [84–88], which generally display a millisecond range of lifetimes with high quantum efficiency in aqueous solutions. In contrast, NIR emitting lanthanide complexes with functionalized calixarenes have been much less investigated [89, 90].

Oueslati and Pischel and coworkers reported two calix[4]azacrowns, **53** and **54**, capped with two aminopolyamide bridges [89]. They contain amide and amine functionalities and both are known for their capability to bind lanthanide ions via interaction with C=O oxygen atoms and amine nitrogen atoms. Upon complexation of **53** and **54** with lanthanide ions including Eu(III), Tb(III), Nd(III), Er(III), and La(III), the formation of 1:2 and 1:1 complexes was observed. The stability constants were determined by UV absorption and fluorescence spectroscopy with $\log \beta_{11} = 5\text{--}6$ and $\log \beta_{12} = 10$. The NMR studies suggested that the complexation occurred outside the ionophoric cavity for **53**, whereas the lanthanide ion was encapsulated inside the cavity for **54**. Fluorescence enhancement was detected for **53** due to blocking of photoinduced electron transfer from amine groups upon complexation with the lanthanide ion. The complexes of **54**, however, showed fluorescence quenching relative to that of the free ligand, resulting most likely from heavy-atom induced intersystem crossing. Both **53** and **54** served as effective organic antenna chromophores for the energy-transfer sensitization of long-lived lanthanide luminescence by excitation at the $\pi \rightarrow \pi^*$ band of the aromatic moieties. For the Nd(III) complexes, a strong emission band at 1058 together with a weaker one at 1328 nm was detected due to $^4F_{3/2} \rightarrow ^4F_{11/2}$ and $^4F_{3/2} \rightarrow ^4F_{13/2}$ transitions, respectively. The NIR luminescence of the Er(III) complexes with **53** or **54**, however, was not detected.

In ternary lanthanide complexes [Ln(**55**)(dbm)] with a calix[4]arene unit and dbm as a co-ligand [90], the antenna is brought in close contact with the lanthanide center, causing NIR emission from the Yb(III), Nd(III), and Er(III) ions. The lanthanide ion in the [Ln(**55**)(dbm)] complex is encapsulated by ten oxygen donor atoms, including four ether oxygen atoms, two negatively charged carboxylate oxygen, two amide oxygen donors together with two oxygen donors from dbm. These NIR emitting complexes exhibit the typical line-like lanthanide emission upon excitation of the dbm antenna chromophore at 360 nm. The luminescence lifetimes of these lanthanide(III) complexes are 12.5, 1.3, and 0.9 μs for Yb(III), Nd(III), and Er(III) species in deuterated dichloromethane solutions, respectively.

12.2.2.3 Cryptand and Coronand Ligands

The cyclic framework of crown ethers with multidentate O and N donors affords a feasible platform for complexation with the lanthanide(III) ions. The crown ethers can be readily functionalized with organic chromophores so as to enhance the binding ability and the selectivity of the parent crown ethers. In particular, the hard acid character of the crown moiety makes crown ethers serve as feasible chelating ligands for complexation with the lanthanide ions, which are frequently encapsulated within its cavity, thus effectively preventing nonradiative deactivation processes and inducing highly efficient lanthanide luminescence. Crown ether ligands such as cryptand and coronand receptors are good candidates for sensitization of lanthanide luminescence because the electronic delocalization in these ligands induces a relatively low-lying triplet state, thus providing an efficient conversion of the visible light absorbed into NIR emitting from the Nd(III), Pr(III), Er(III) or Yb(III) ions.



Three Schiff base ethers containing salicylaldimino-benzyl pendant arms and derived from 4,10-diaza-12-crown-4 (**56**), 1,10-diaza-15-crown-5 (**57**) or 4,13-diaza-18-crown-6 (**58**) were described by Rodríguez-Blas and coworkers [91–93]. Depending on the ring size of the crown moiety, they behave as a highly selective receptor towards lanthanide(III) ions. The ligand **58** forms only stable complexes with the three lightest lanthanides including La(III), Ce(III), and Pr(III) ions as a consequence of the combination of the relatively large ring size of the crown moiety and the presence of a relatively rigid pendant. The smaller ring size of **57** produces stable complexes with the Ln(III) ions from La(III) to Ho(III), whereas **56** exhibits a certain degree of selectivity toward the heaviest Ln(III) ions from Ho(III) to Lu(III). Upon excitation of the low energy $^3\pi\pi^*$ state of **56–58**, sensitized NIR emission was detected in the corresponding Nd(III), Er(III) or Yb(III) complexes. Time-resolved studies of lanthanide(III) complexes confirmed that the solvent was excluded from the inner coordination sphere in solution. The luminescence properties of these complexes make them ideally suitable for use as luminescent tags in protic media.

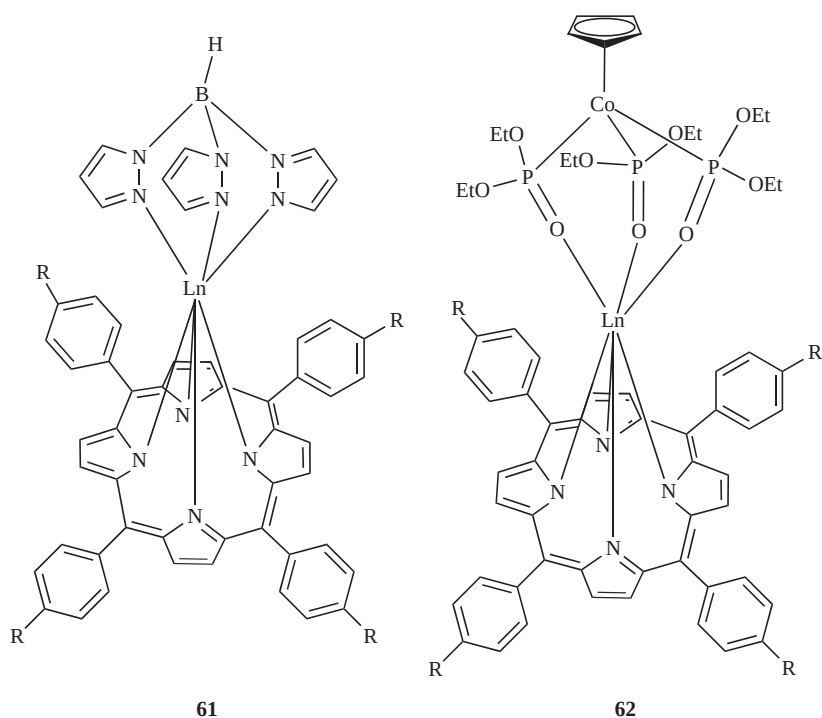
The Schiff base macrobicyclic phenolic cryptands **59a–59c** are versatile ligands that allow the formation of both monometallic and bimetallic lanthanide cryptates [94–97]. X-ray structural determination of several Ln–Ln and Ln–Zn structures revealed that the ligands are helically wrapped around the two lanthanide ions, which are held into the cavity of the cryptand at a very short distance from each other. The emission from the Eu(III) ion is most effectively sensitized by the ligand triplet state, whereas the Tb(III) sensitization occurs via the singlet state. The quantum yield of the Eu-centered luminescence in the Eu–Zn cryptate is 1.05% upon ligand excitation. The low energy of the ligand $^3\pi\pi^*$ state also allows efficient sensitization of NIR emission from the Nd(III) and Yb(III) cryptates. The emission spectrum of the binuclear Yb–Yb complex is consistent with the presence of two Yb ions in different coordination environments. Complexation of macrobicyclic cryptand **60** with lanthanide ions results in the formation of the corresponding lanthanide cryptates [98]. The cryptand with N₈ donors serves as an excellent light harvesting antenna chromophore for sensitization of NIR luminescence from Nd(III) and Yb(III) ions. Upon excitation of the 2,2'-bipyridyl chromophore at 355 nm, NIR emission was detected at 980 nm for the Yb(III) species and at 880, 1055, and 1340 nm for the Nd(III) complex. The Nd(III) complex exhibits longer-lived NIR emission ($\tau_{\text{em}} = 0.10 \mu\text{s}$) in aqueous media compared with that with aminocarboxylate ligands, ascribed to the relatively small number of C–H oscillators in this cryptate.

12.2.2.4 Porphyrin Ligands

Porphyrin is one of the most widely studied macrocyclic systems suitable for complexation with lanthanide(III) ions. Porphyrins can absorb strongly in the UV–vis region so as to serve as efficient photo-sensitizers, making lanthanide(III) porphyrinate complexes ideal candidates for luminescence imaging agents. Indirect excitation of porphyrin antenna chromophores in close proximity to lanthanide ions can make the energy in the triplet state of the porphyrin ligand transfer efficiently to the excited state of the lanthanide ion so as to sensitize the lanthanide luminescence, particularly NIR emission.

Synthetic routes for the preparation of lanthanide monoporphyrinate complexes with non-diketonate anionic axial ligands have been developed in recent years. Wong and coworkers developed a convenient synthetic route for the preparation of cationic lanthanide(III) monoporphyrinate complexes $[\text{Ln}(\text{porphyrin})(\text{H}_2\text{O})_3]\text{Cl}$ via the protonolysis of lanthanide(III) amide

with porphyrin free bases [99–107]. The aqua $[\text{Ln}(\text{porphyrin})(\text{H}_2\text{O})_3]\text{Cl}$ complexes are very labile and can be utilized as excellent precursors for construction of lanthanide porphyrin arrays with desired properties. They tend to form bridging dinuclear complexes and can be easily displaced by anions or donor solvents. They formed hydroxyl-bridged dimers when reacted with base, and chloro-bridged dimers with aqueous HCl. When $[\text{Ln}(\text{porphyrin})(\text{H}_2\text{O})_3]\text{Cl}$ reacted with anionic tripodal ligands including hydridotris(pyrazol-1-yl)borate and (cyclopentadienyl)tris(diethylphosphito)cobaltate, stable neutral ternary lanthanide(III) monoporphyrinate complexes (**61** and **62**) were isolated in high yields. Photophysical studies showed that the porphyrinate antenna could transfer its absorbed visible energy of the Q-band to the excited state of the lanthanide(III) ion, resulting in sensitization of NIR luminescence from Nd(III), Er(III), and Yb(III) ions.



The NIR emission intensity of the lanthanide porphyrinate complexes follows the trend $\text{Yb} > \text{Nd} > \text{Er}$. This agrees with observations on other luminescent lanthanide complexes and reflects the fact that the efficiency of nonradiative decay increases as the energy of the luminescent state decreases. The emission yields of the ternary lanthanide(III) monoporphyrinate complexes with hydridotris(pyrazol-1-yl)borate or (cyclopentadienyl)tris(diethylphosphito)cobaltate as a co-ligand are generally higher than those of other Yb(III), Nd(III), and Er(III) complexes because the coordination environment provided by the porphyrinate in combination with the tripodal anion effectively shields the Ln^{3+} ion from interacting with solvent (C–H) vibrational modes that enhance the rate of nonradiative decay.

12.3 Metal–Organic Chromophores as Sensitizers

12.3.1 *d*-Block Chromophores

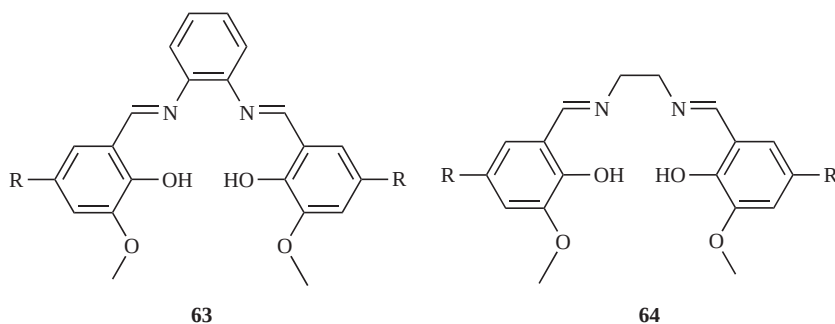
Using transition metal complexes as energy donors to sensitize NIR lanthanide luminescence is a recently developed approach [1, 108–110]. Compared with purely organic chromophores, the *d*-block metallorganic sensitizers afford several advantages, including: (i) low-energy absorption in the visible region arising from red-shifted ILCT or MLCT transitions, causing better energy match between organometallic donors and Ln(III) acceptors and thus less waste in energy; (ii) relatively high triplet quantum yields due to the rapid intersystem crossing arising from the heavy metal effect; (iii) relatively long-lived triplet excited states that facilitate energy transfer to the adjacent Ln(III) centers; and (iv) facile detection of both quenching of the organometallic chromophores and the sensitized emission from the lanthanide(III) centers.

A key step for fabrication of *d*-block metal and lanthanide heteronuclear (*d*–*f*) arrays is to design suitable bridging connectors that can promote the energy transfer from the *d*-block antenna chromophores to the lanthanide centers [110]. Apparently, a π -conjugated pathway between energy donor and acceptor is favorable for energy-transfer via a double electron exchange (Dexter) process, and hence promotes energy-transfer rates. Judicious selection of bifunctional bridging ligands with high π -conjugation is vital to effective energy transfer from the *d*-block organometallic chromophores so as to achieve long-lived NIR lanthanide luminescence with high efficiency.

12.3.1.1 d^{10} Metal–Organic Chromophores

The studies on d^{10} organometallic complexes as light-harvesting antenna chromophores for sensitization of lanthanide luminescence have been relatively less well explored to date. Incorporating zinc(II) complexes of phenylene- or ethylene-bridged Schiff bases **63** or **64** with an equimolar amount of Ln^{3+} , Jones and Wong and coworkers prepared a series of *d*-*f* heterobimetallic complexes [111–121]. It was demonstrated that the zinc(II) complexes with Schiff bases **63** and **64** are effective emitters and could serve as light-harvesting antenna chromophores for sensitization of lanthanide luminescence. Modifying the electronic effect of the substituents and the nature of the spacers (ethylene versus phenylene) of the Schiff bases significantly influence the luminescence properties of the corresponding zinc(II) and their Zn–Ln Schiff base complexes.

Typical NIR luminescence from the corresponding lanthanide(III) ions were detected in these Zn–Ln (Ln = Nd, Er, Yb) Schiff base complexes, apart from the ligand-centered emission in the UV–vis region. For the ethylene-bridged Zn–Ln complexes with **64**, the NIR emission for Er^{3+} species is rather weak and is at least one order of magnitude weaker than the corresponding Nd^{3+} and Yb^{3+} species. The NIR emission of Er^{3+} species for the phenylene-bridged Zn–Er complexes with **63**, however, was not detected, probably due to the fact that the quantum yield of the Zn complex with **63** is much higher for the ethylene-bridged than the corresponding phenylene-bridged Schiff base Zn complex with **64**. It was suggested that for these Zn–Ln complexes, sensitized NIR luminescence from the lanthanide ion was achieved via the ligand-centered triplet (^3LC) state with ethylene-bridged complexes and most probably via the ligand-centered singlet (^1LC) state with phenylene-bridged complexes.



Binuclear gold(I) acetylide diphosphine complexes of 5-ethynyl-2,2'-bipyridine were incorporated with $\text{Ln}(\text{hfac})_3$ ($\text{Ln} = \text{Nd}, \text{Eu}, \text{Er}, \text{Yb}$) subunits through 2,2'-bipyridyl chelation, giving a series of $\text{Au}(\text{I})_4\text{Ln}(\text{III})_4$ or $\text{Au}(\text{I})_2\text{Ln}(\text{III})_2$ heteropolynuclear complexes [122]. Upon formation of $\text{Au}(\text{I})_4\text{Ln}(\text{III})_4$ or $\text{Au}(\text{I})_2\text{Ln}(\text{III})_2$ heteronuclear arrays by associating binuclear gold(I) units with $\text{Ln}(\text{hfac})_3$ fragments, dramatically *cis*–*trans* conformational changes take place due to creating or breaking of ligand-supported or unsupported Au–Au interactions (Figure 12.2). Upon excitation of the gold(I) alkynyl chromophores at $\lambda_{\text{ex}} \geq 350 \text{ nm}$, these Au–Ln heteropolynuclear complexes show luminescence characteristics of the corresponding lanthanide ions with microsecond range of lifetimes in both solid states and fluid dichloromethane at ambient temperature. In addition, the gold(I) acetylide chromophore-based emission in the visible region is remarkably attenuated but does not disappear entirely. This suggests that energy transfer from the $^1(\pi \rightarrow \pi^*)$ singlet state of the alkynyl ligand in gold(I) chromophores to the lanthanide(III) center is not complete even if $\text{Au} \cdots \text{Ln}$ separation is shorter than $9.0 \text{ \AA}$ through the bridging 5-ethynyl-2,2'-bipyridine. The less efficient Au $\rightarrow$ Ln energy transfer in these Au–Ln bimetallic species is probably ascribed to energy mismatching or less spectral overlap between the emission spectra of gold(I) alkynyl chromophores and the lanthanide(III) absorption spectra from f–f transitions.

12.3.1.2 d^8 Metal–Organic Chromophores

Platinum(II) complexes with π -conjugated ligands frequently display intense MLCT absorption in the near-UV to visible spectral region and can serve as excellent light-harvesting organometallic antenna chromophores for sensitization of NIR luminescence from lanthanide ions by $d \rightarrow f$ energy transfer [123–136]. A family of Pt–Ln heteronuclear complexes have been described by Ward and coworkers [123–125, 128] and by our group [129–136] utilizing bifunctional bridging ligands such as bis(diimine) and ethynyl-functionalized polypyridine, achieving long-lived NIR luminescence from Nd(III), Er(III), Yb(III), and so on.

Ward and coworkers [123–125] reported a general synthetic approach for a variety of Pt–Ln heterodinuclear complexes (**65**–**76**) by incorporating a Pt(diimine) fragment, $[\text{Pt}(\text{pdo})(\text{PPh}_3)_2]$, $[\text{Pt}(\text{dppz})\text{Cl}_2]$, $[\text{Pt}(\text{dppz})(\text{C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{CF}_3-4)_2]$, or $[\text{Pt}(\text{bpym})(\text{C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{CF}_3-4)_2]$ with a $\text{Ln}(\beta\text{-diketonate})_3$ fragment to the two binding sites of a bis(diimine) bridging ligand. Excitation of the Pt(II)-based MLCT absorption band at 420–520 nm results in characteristic NIR luminescence from the Nd(III), Yb(III), or Er(III) centers with lifetimes on the microsecond timescale in both solid state and in dichloromethane, comparable to those of other NIR-emitting

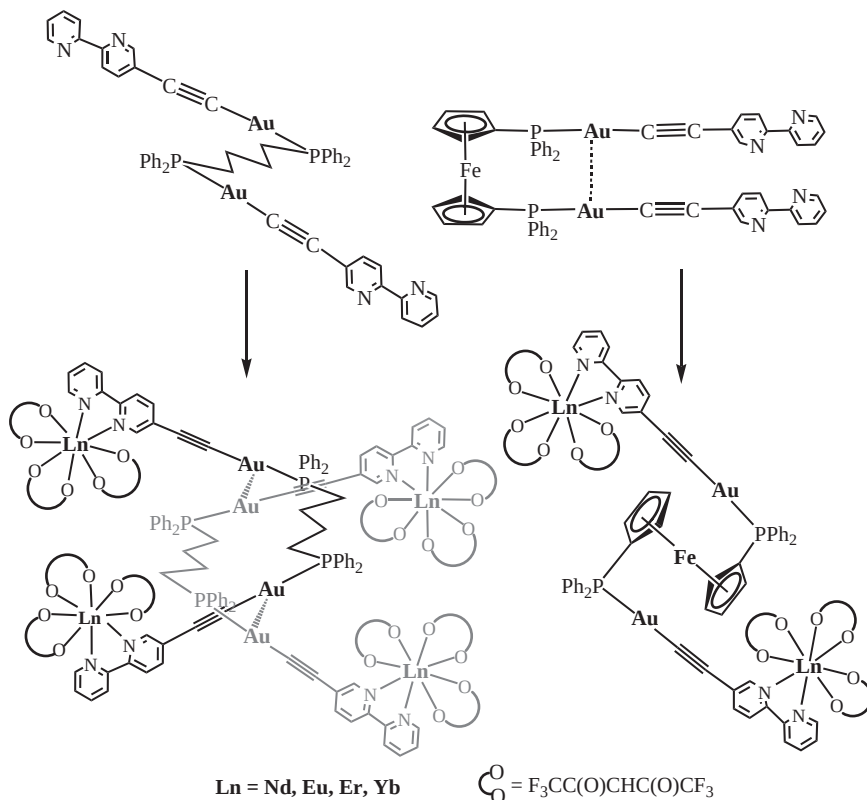
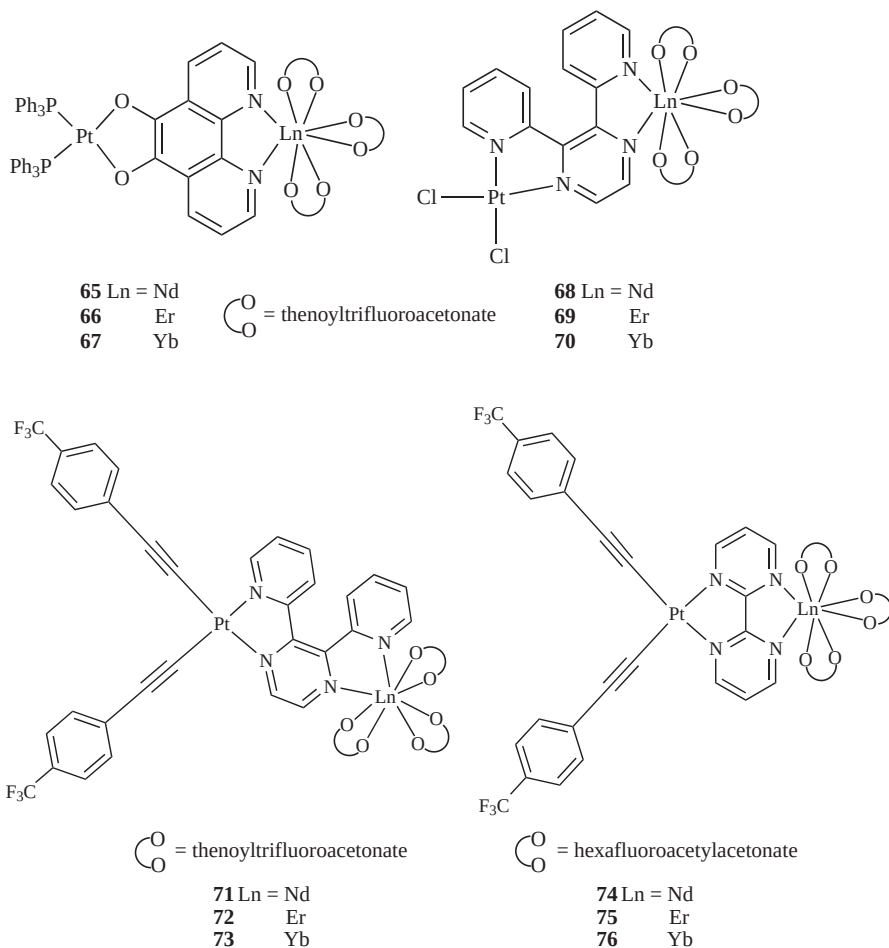


Figure 12.2 *cis-trans* conformational conversion upon formation the Au–Ln arrays by incorporating gold(I) acetylide diphosphine complexes with $\text{Ln}(\text{hfac})_3$ units [122]. (Redrawn from H.B. Xu *et al.*, “Conformation changes and luminescent properties of Au–Ln (Ln = Nd, Eu, Er, Yb) arrays with 5-ethynyl-2,2′-bipyridine,” *Inorganic Chemistry*, **47**, 10744, 2008.)

complexes for which excitation through a directly coordinated ligand is used. The characteristic $^3\text{MLCT}$ luminescence from a $\text{Pt}(\text{II})$ organometallic chromophore, however, is completely quenched. This suggests that the $\text{Pt}(\text{II})$ -based organometallic chromophores in these Pt –Ln complexes serve as feasible sensitizers for achieving lanthanide luminescence due to effective $\text{Pt} \rightarrow \text{Ln}$ energy transfer from the Pt -based organometallic chromophore to the emissive excited state of the lanthanide ion.

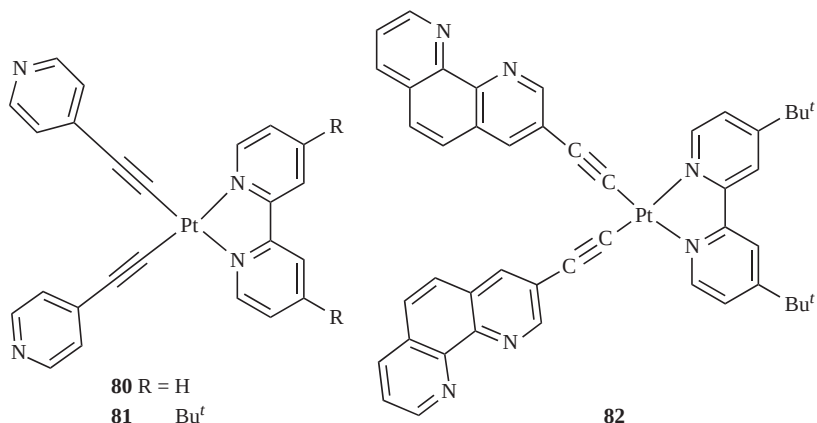
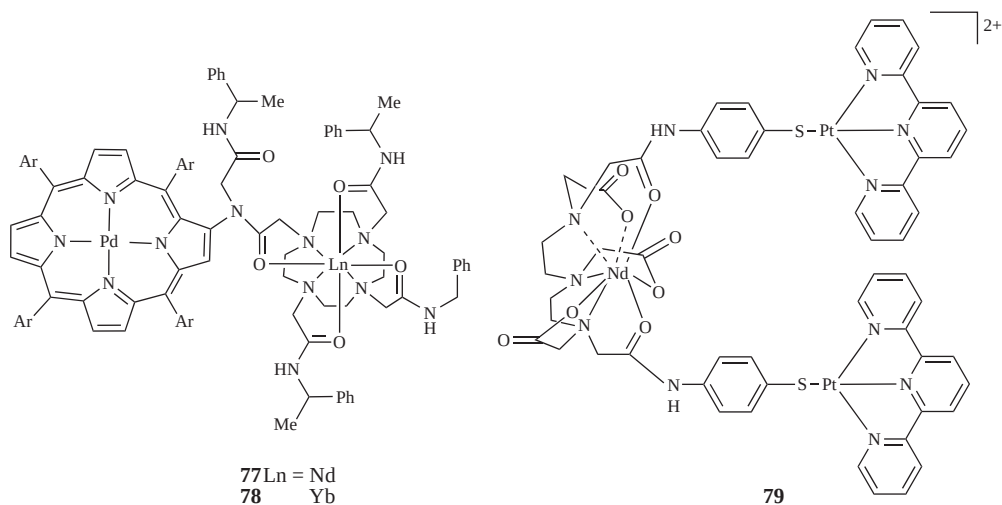
Beeby and Parker and coworkers [126] described the preparation of Pd –Nd (**77**) and Pd –Yb (**78**) heteronbinuclear complexes by covalently linking a palladium porphyrin to a chiral lanthanide complex. Upon excitation of the Pd –porphyrin chromophore absorption at 529 nm, sensitized NIR luminescence from a $\text{Nd}(\text{III})$ or $\text{Yb}(\text{III})$ center was successfully detected in aerated and degassed MeOH and CD_3OD . The sensitization of NIR luminescence from $\text{Nd}(\text{III})$ or $\text{Yb}(\text{III})$ ion is enhanced in the absence of oxygen and in the presence of a nucleic acid. Pikramenou and coworkers [127] reported the use of a $\text{Pt}(\text{terpyridyl})$ unit to link with $\text{Nd}(\text{III})$ polyaminocarboxylate complex to give a Pt_2Nd heterotrinnuclear complex **79**. Upon excitation at 515 nm, which is the absorption of the MLCT/LLCT state from the $\text{Pt}(\text{terpyridyl})$ chromophore, the Pt_2Nd complex **79** showed an NIR emission characteristic of the $\text{Nd}(\text{III})$ ion



at 1060 and 1340 nm due to $^4F_{3/2} \rightarrow ^4I_{11/2}$, $^4I_{13/2}$ transitions with a lifetime of 0.67 μ s. The relative quantum yield of NIR emission in this Pt₂Nd species is unchanged upon the formation of a complex with calf-thymus DNA.

Incorporating Pt(II) acetylide complexes **80–82** with Ln(β -diketonate)₃ fragments resulted in formation of one-dimensional Pt–Ln heterometallic coordination polymers for **80** and **81**, whereas **82** formed PtLn₂ heterotrimeric adducts [128]. On the one hand, long-lived NIR luminescence characteristic of the corresponding lanthanide(III) ions were detected with the lifetimes in the microsecond range in these Pt–Ln complexes containing Yb(III), Nd(III), Er(III), or Pr(III). On the other hand, the Pt(II)-based ³MLCT/³MMLCT luminescence is mostly quenched because of effective Pt→Ln energy transfer in these Pt–Ln complexes. Depending on the ability of the different Ln(III) ions to act as energy acceptors, the extent of the quenching of the Pt(II)-based emission and the Pt→Ln energy-transfer rates can vary over a wide range. The Yb(III) usually provides the least quenching with the slower Pt→Yb energy transfer, whereas either Nd(III) or Er(III) provide the most quenching with the faster Pt→Ln

energy transfer, depending on whether the Pt(II)-based emission comes from an $^3\text{MLCT}$ state [better overlap with the absorption spectrum of Er(III)] or a lower-energy $^3\text{MMLCT}$ state [better overlap with the absorption spectrum of Nd(III)].



Incorporating Pt(II) complexes **83–85** with Ln(hfac)₃ units, a series of PtLn₂ heterotrinnuclear complexes were prepared in a stepwise synthetic approach using HC≡Cbp_y, HC≡CC₆H₄tp_y or HC≡CC₆H₄C≡Cbp_y as a bridging ligand through Pt–acetylide σ -coordination and 2,2'-bipyridyl or 2,2':6',2''-terpyridyl chelating the lanthanide(III) centers [129]. Upon excitation of these PtLn₂ complexes at 350 nm $\leq \lambda_{\text{ex}} \leq$ 500 nm, NIR luminescence (Figure 12.3) from lanthanide(III) ions with microsecond ranges of lifetimes is achieved through effective Pt $\rightarrow$ Ln energy transfer from the $^3[\text{d}(\text{Pt}) \rightarrow \pi^*(\text{Bu}_2^t\text{bpy})]$ $^3\text{MLCT}$ excited state of the Pt(Bu₂^tbpy)bis(acetylide) antenna chromophore. By successive insertion of phenylene or ethynyl between acetylide and 2,2'-bipyridyl/2,2':6',2''-terpyridyl in the bridging ligands, the rate and efficiency of Pt $\rightarrow$ Ln energy transfer can be controlled and modulated. For

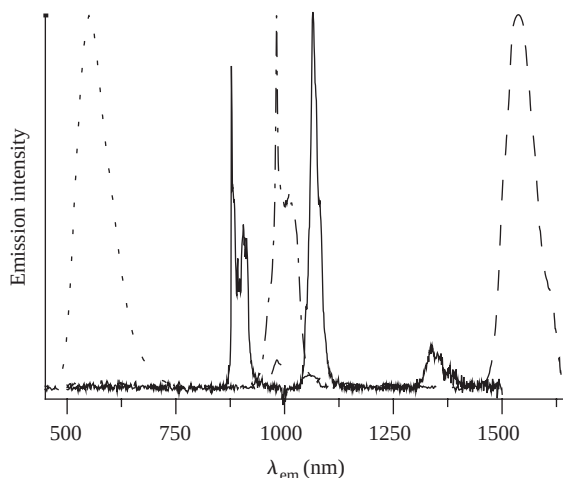
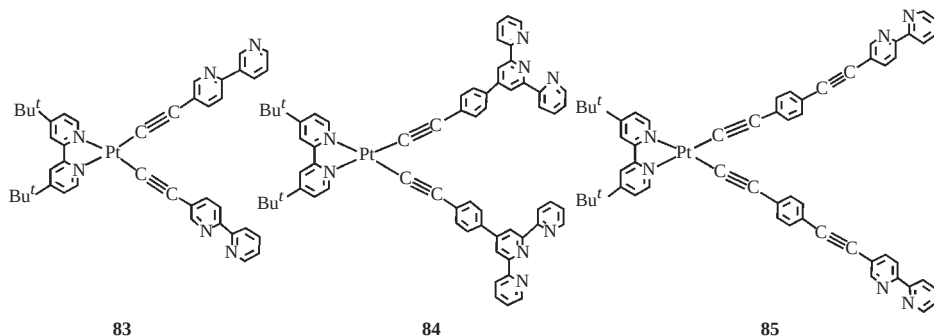
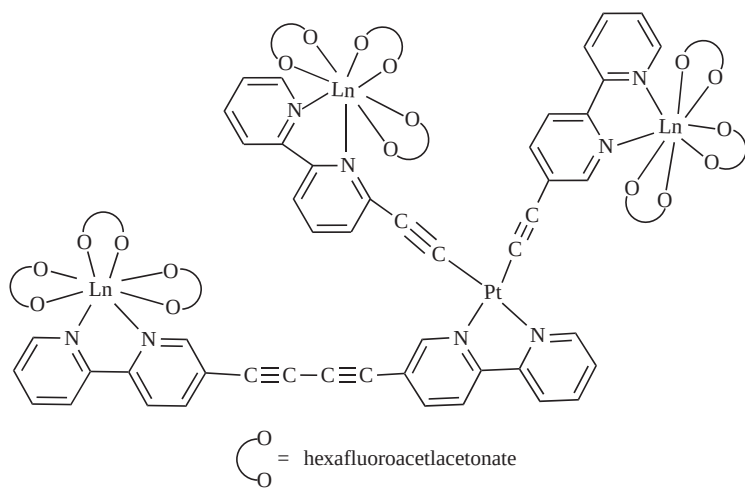


Figure 12.3 Emission spectra of Pt(II) complex **84** (dotted line) and its PtNd₂ (solid line), PtEr₂ (dashed line), and PtYb₂ (dash-dotted line) adducts in dichloromethane solutions at 298 K [129]. (Reprinted with permission from H.B. Xu *et al.*, “Modulation of Pt → Ln energy transfer in PtLn₂ (Ln = Nd, Er, Yb) complexes with 2,2′-bipyridyl/2,2′:6′2′′-terpyridyl ethynyl ligands,” *Crystal Growth and Design*, **9**, 569, 2009. © 2009 American Chemical Society.)

the PtLn₂ species derived from **85**, Pt → Er energy transfer in PtEr₂ complex is fairly fast ($k_{ET} > 10^8 \text{ s}^{-1}$) and more effective than the corresponding Pt → Nd or Pt → Yb energy transfer in PtNd₂ ($k_{ET} = 1.24 \times 10^8 \text{ s}^{-1}$) or PtYb₂ ($k_{ET} = 1.40 \times 10^7 \text{ s}^{-1}$) species. The rate orders $k_{ET}(\text{PtEr}_2) > k_{ET}(\text{PtNd}_2) > k_{ET}(\text{PtYb}_2)$ were rationally elucidated by spectroscopic overlapping between Pt-based MLCT emission and lanthanide(III) f–f absorption.

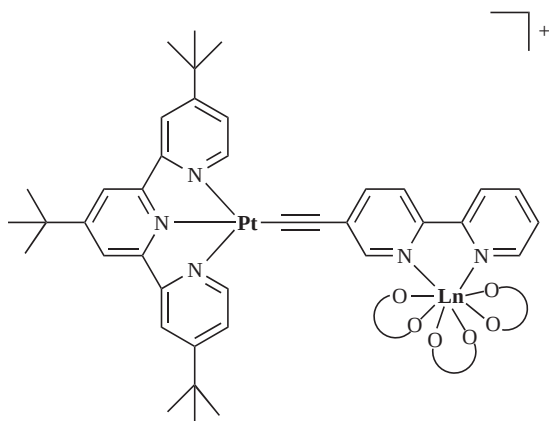


PtLn₃ (Ln = Nd **86**, Yb **87**) heterotetranuclear complexes were prepared using bis(2,2′-bipyridin-5-yl)-butadiyne (bpyC≡CC≡Cbpy) as connectors for fabrication of the Pt–Ln linkages through Pt–acetylide σ-coordination and 2,2′-bipyridyl chelating of the lanthanide(III) centers [130]. With excitation at $360 \leq \lambda_{ex} \leq 480 \text{ nm}$, which is the MLCT absorption region of the Pt(2,2′-bipyridyl)(acetylide)₂ chromophore, sensitized lanthanide luminescence is successfully attained by efficient Pt → Ln energy transfer from the Pt(II) antenna chromophores. In contrast to the complete Pt → Ln energy transfer through the Pt–C≡Cbpy–Ln array with Pt ⋯ Ln = 8.4 Å, energy transfer across the Pt–bpyC≡C–C≡Cbpy–Ln array is long-range



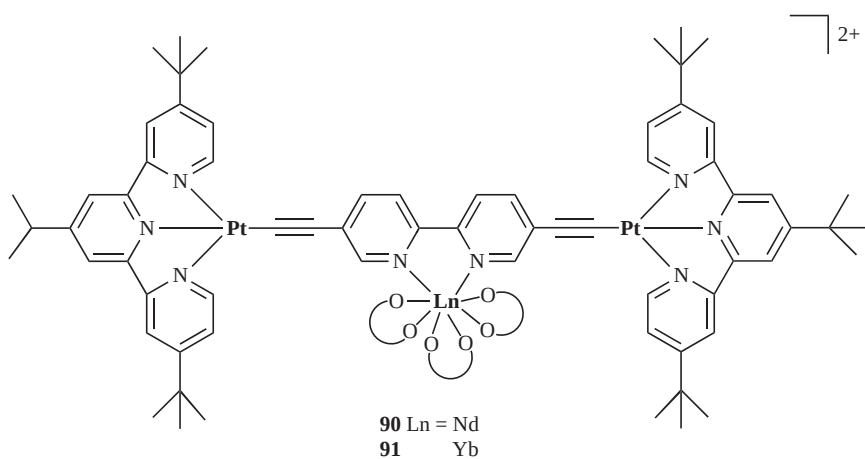
86 Ln = Nd

87 Yb



88 Ln = Nd

89 Yb

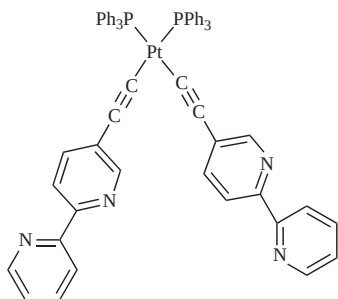


90 Ln = Nd

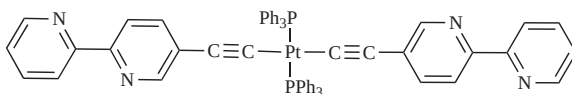
91 Yb

and less effective in view of the Pt $\cdots$ Ln distance being as long as 13.3 Å. The Pt $\rightarrow$ Ln energy transfer rates k_{ET} are $5.64 \times 10^7 \text{ s}^{-1}$ for PtNd₃ (**86**) and $2.82 \times 10^6 \text{ s}^{-1}$ for PtYb₃ (**87**) species.

Mono- or dinuclear platinum(II) complex capped with one or two [Pt(Bu^ttpy)]⁺ units can be incorporated with Ln(hfac)₃ units to produce a series of PtLn (Ln = Nd **88**, Yb **89**) and Pt₂Ln (Ln = Nd **90**, Yb **91**) heteronuclear complexes [131]. With excitation at 350 nm < λ < 550 nm, sensitized NIR lanthanide luminescence was detected in these Pt–Ln heteronuclear complexes with microsecond ranges of lifetimes, whereas Pt-based luminescence from the ³MLCT and ³LLCT states was mostly quenched. This reveals that fairly effective Pt $\rightarrow$ Ln energy transfer is operating from the platinum(II) terpyridyl alkynyl chromophores to the lanthanide(III) centers.



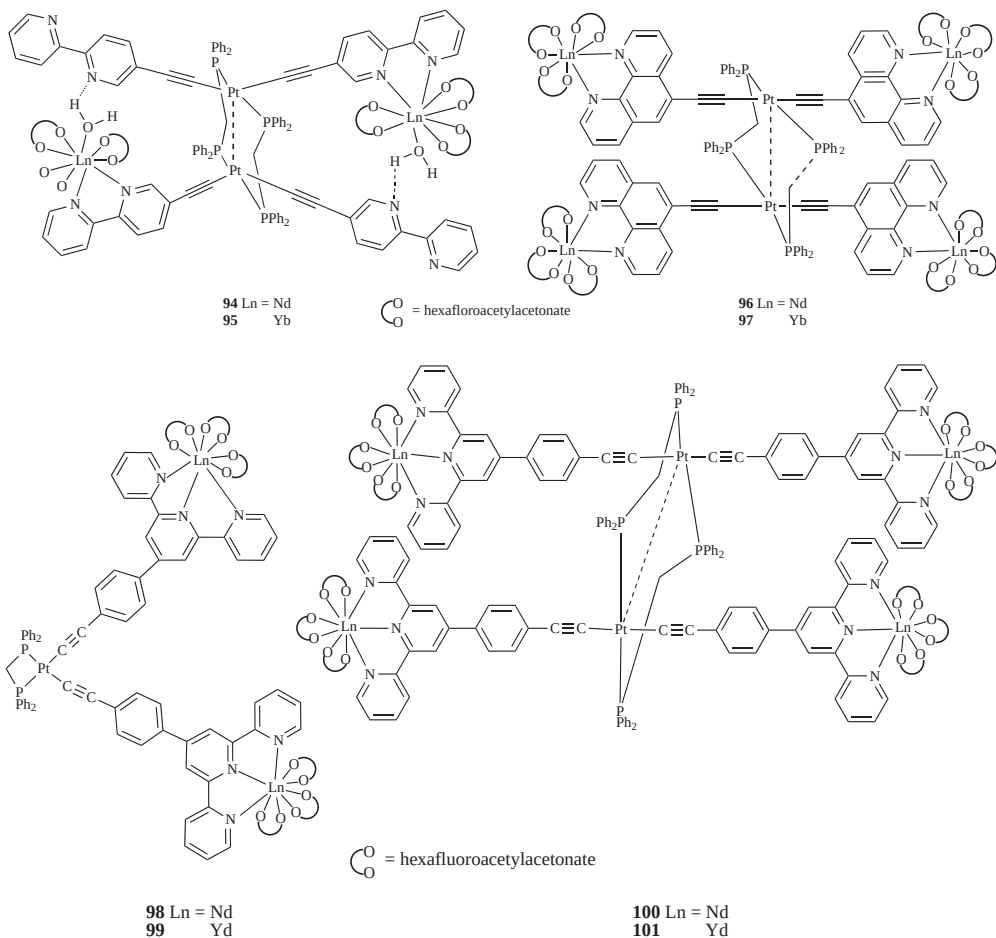
92



93

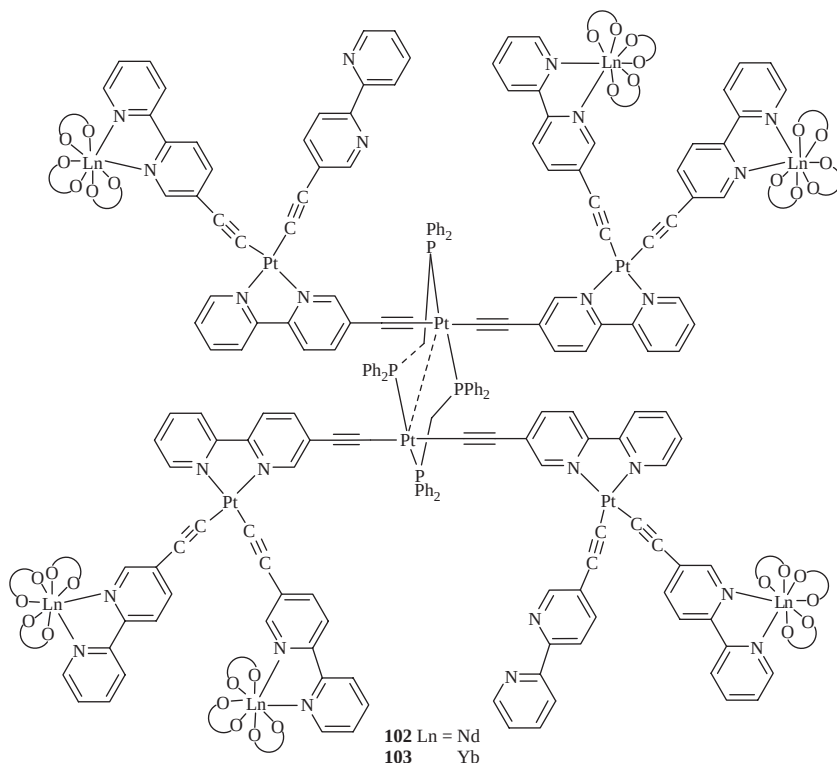
Incorporating *cis*- (**92**) or *trans*-Pt(PPh₃)₂(C≡Cbpy)₂ (**93**) with Ln(hfac)₃ gave the corresponding isomeric *cis*- or *trans*-PtLn₂ heterotrinnuclear complexes, which are kinetically stable to be able to resist thermal and photoinduced isomerization [132]. With excitation at 360 < λ_{ex} < 450 nm, which is the absorption region of the metal-perturbed $\pi \rightarrow \pi^*$ (C≡C) transitions and d(Pt) $\rightarrow$ π^* (C≡Cbpy) MLCT transitions, sensitized lanthanide luminescence was detected with microsecond ranges of lifetimes in both *cis*- and *trans*-arranged PtLn₂ complexes. The low-energy phosphorescence from a Pt-based chromophore is entirely quenched because of the effective Pt $\rightarrow$ Ln energy transfer, whereas high-energy fluorescence from a ligand-centered singlet state is still detected in these PtLn₂ complexes. It was demonstrated that geometrical orientation of the central platinum(II) bis(σ -acetylide) antenna chromophore exerts a slight influence on the Pt $\rightarrow$ Ln energy transfer and on the NIR lanthanide luminescence in these *cis*- and *trans*-PtLn₂ isomeric complexes.

Incorporating diplatinum(II) complexes of 5-ethynyl-2,2'-bipyridine or 5-ethynyl-1,10-phenanthroline with Ln(hfac)₃ (Ln = Nd, Yb) through 2,2'-bipyridyl or 1,10-phenanthroline chelating afforded Pt₂Ln₂ (Ln = Nd **94**, Yb **95**) or Pt₂Ln₄ (Ln = Nd **96**, Yb **97**) arrays [133]. Upon irradiation of the MLCT absorption of the diplatinum alkynyl moiety at λ_{ex} = 350–450 nm, these Pt₂Ln₂ and Pt₂Ln₄ complexes exhibit emission characteristic of these lanthanide ions with lifetimes in the microsecond range in both solid states and dichloromethane at 298 K. By contrast, ³MLCT and ligand-centered emissions from a diplatinum alkynyl chromophore disappeared entirely in both the solid states and dichloromethane, indicating that the Pt-based luminescence was completely quenched because of fairly efficient and fast energy transfer from the d(Pt₂) $\rightarrow$ π^* (C≡C–R) ³MMLCT excited state to the f–f emissive state.



Using 4'-(4-ethynylphenyl)-2,2':6',2''-terpyridine ($\text{HC}\equiv\text{CPhtpy}$) as a connector for Pt–Ln arrays, either PtLn_2 heterotrimeric complexes (Ln = Nd **98**, Yb **99**) or Pt_2Ln_4 heterohexanuclear complexes (Ln = Nd **100**, Yb **101**) were accessible [134, 135]. With excitation at $\lambda_{\text{ex}} = 360\text{--}450$ nm (PtLn_2) or $\lambda_{\text{ex}} = 360\text{--}500$ nm (Pt_2Ln_4), which is the absorption region of the Pt(II) alkynyl antenna chromophores, sensitized lanthanide luminescence was successfully achieved in these PtLn_2 and Pt_2Ln_4 complexes, suggesting that efficient $\text{Pt} \rightarrow \text{Ln}$ energy transfer indeed occurred across the bridging $\text{C}\equiv\text{CPhtpy}$, with intramolecular $\text{Pt} \cdots \text{Ln}$ distances being about 14.2 Å. The $\text{Pt} \rightarrow \text{Ln}$ energy transfer rate (k_{ET}) is $6.07 \times 10^7 \text{ s}^{-1}$ for Pt_2Nd_4 (**100**) and $2.12 \times 10^5 \text{ s}^{-1}$ for Pt_2Yb_4 (**101**) species.

Using emissive $\text{Pt}(\text{Me}_3\text{SiC}\equiv\text{Cbp})_2$ as an alkynyl bridging “ligand,” heterododecanuclear Pt_6Ln_6 (Ln = Nd **102**, Yb **103**) complexes of 4-ethynyl-2,2'-bipyridine were accessible in a stepwise synthetic approach [136]. The Pt_6Yb_6 array in **103** (Figure 12.4) consists of $\text{Pt}_6(\mu\text{-dppm})_2(\text{C}\equiv\text{Cbp})_{12}$ incorporating six $\text{Ln}(\text{hfac})_3$ components through 2,2'-bipyridyl chelating. The $\text{Pt} \cdots \text{Yb}$ separations across bridging $\text{C}\equiv\text{Cbp}$ are in the range 8.41–8.80 Å. Other intramolecular $\text{Pt} \cdots \text{Yb}$ distances are in the range 10.48–16.73 Å. Upon irradiation at



$360 < \lambda_{\text{ex}} < 470 \text{ nm}$, Pt_6Ln_6 complexes **102** and **103** exhibited characteristic NIR luminescence by $\text{Pt} \rightarrow \text{Ln}$ energy transfer from both $\text{Pt}(\text{bpy})(\text{acetylide})_2$ and $\text{Pt}_2(\text{dppm})_2(\text{acetylide})_2$ chromophores. While the $\text{Pt} \rightarrow \text{Ln}$ energy transfer from $\text{Pt}(\text{bpy})(\text{acetylide})_2$ antenna chromophore is rapid and complete, that from the $\text{Pt}_2(\text{dppm})_2(\text{acetylide})_2$ cluster chromophore is indirect, long-range, and incomplete, inducing some residual $\text{Pt}(\text{II})$ -based emission in the Pt_6Ln_6 species. The energy transfer rates k_{ET} are $1.02 \times 10^7 \text{ s}^{-1}$ for Pt_6Nd_6 (**102**) and $1.83 \times 10^5 \text{ s}^{-1}$ for Pt_6Yb_6 (**103**) species. The faster $\text{Pt} \rightarrow \text{Ln}$ energy transfer for the Pt_6Nd_6 complex than that for Pt_6Yb_6 species was rationalized by the better spectroscopic overlap between the emission spectrum of the $\text{Pt}(\text{II})$ -based antenna chromophore and the absorption spectrum of the $\text{Nd}(\text{III})$ ion.

12.3.1.3 d⁶ Metal–Organic Chromophores

Veggel and coworkers [137, 138] first reported the use of ruthenium(II) tris(2,2'-bipyridine) complexes ($[\text{Ru}(\text{bpy})_3]^{2+}$) and ferrocene as light-harvesting chromophores for sensitization of NIR luminescence from $\text{Nd}(\text{III})$ and $\text{Yb}(\text{III})$ ions. The $\text{Ru}-\text{Ln}$ complexes ($\text{Ln} = \text{Nd}$ **104**, Yb **105**) resulted from incorporating $[\text{Ru}(\text{bpy})_3]^{2+}$ with m-terphenyl-based lanthanide complexes. Upon excitation of the $\text{Ru}(\text{bpy})_3$ chromophore absorption with visible light up to 500 nm, both $\text{Ru}-\text{Nd}$ and $\text{Ru}-\text{Yb}$ complexes exhibited typical NIR luminescence because of effective $\text{Ru} \rightarrow \text{Ln}$ energy transfer with the rates of $1.1 \times 10^6 \text{ s}^{-1}$ for $\text{Ru}-\text{Nd}$ complex and $\leq 1.0 \times 10^5 \text{ s}^{-1}$ for $\text{Ru}-\text{Yb}$ species.

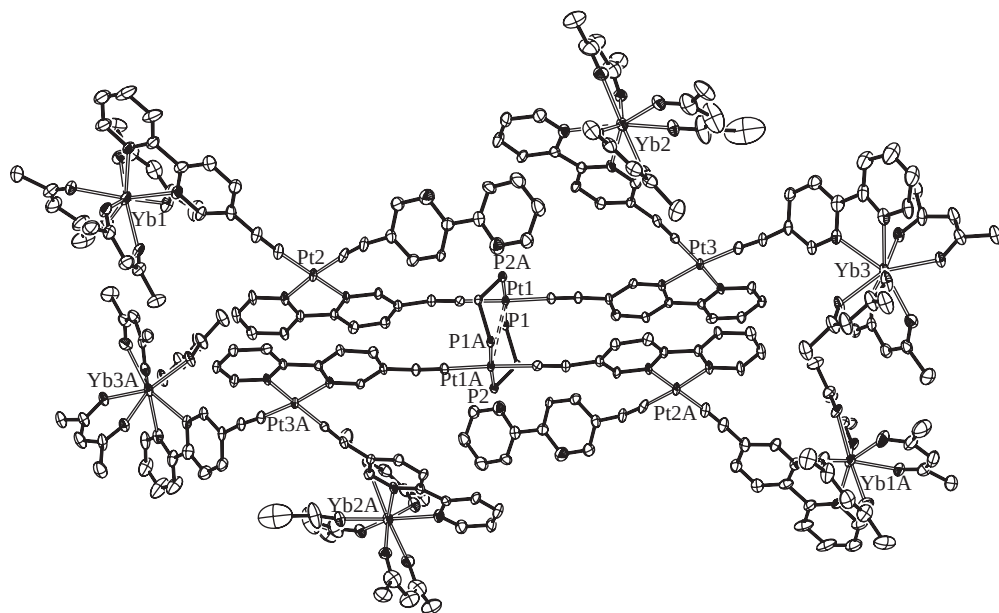
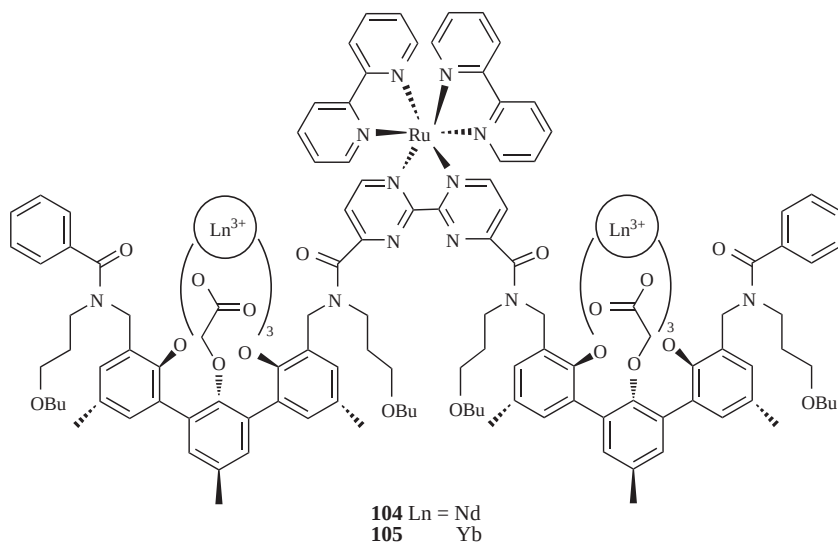
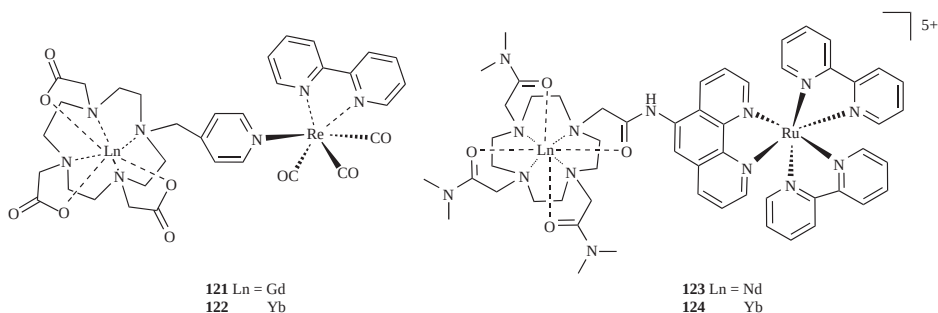
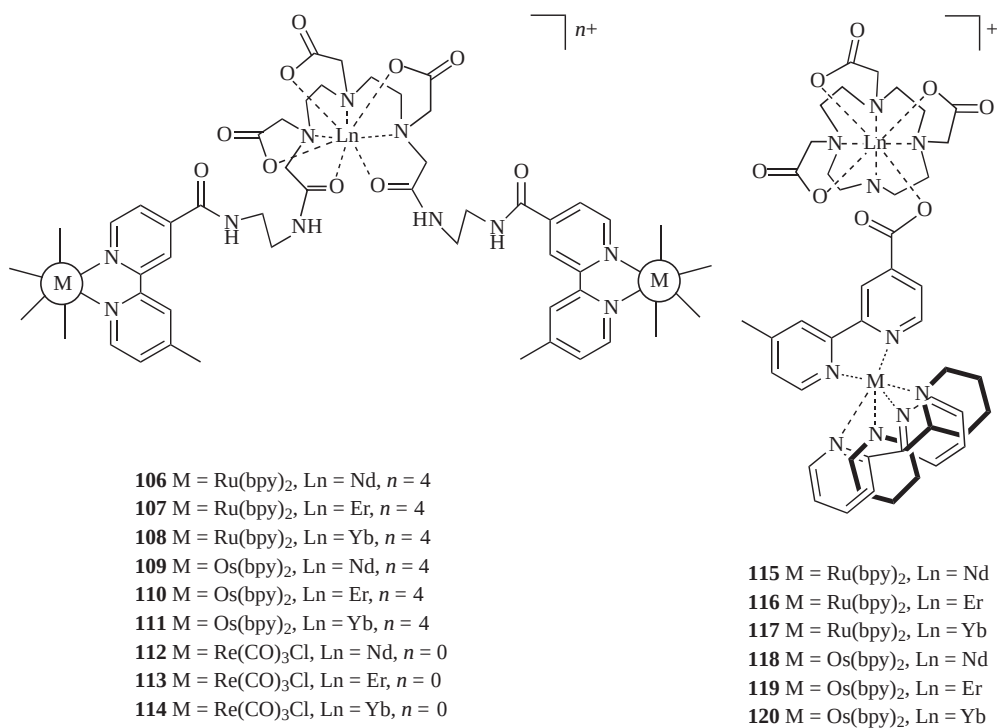


Figure 12.4 ORTEP drawing of Pt_6Yb_6 complex **103** [136]. (Reproduced from H.B. Xu *et al.*, “Heterododecanuclear Pt_6Ln_6 ($\text{Ln} = \text{Nd}, \text{Yb}$) arrays of 4-ethynyl-2,2'-bipyridine with sensitized near-IR lanthanide luminescence by Pt–Ln energy transfer,” *Chemical Communications*, 2744, 2007, by permission of The Royal Society of Chemistry.)

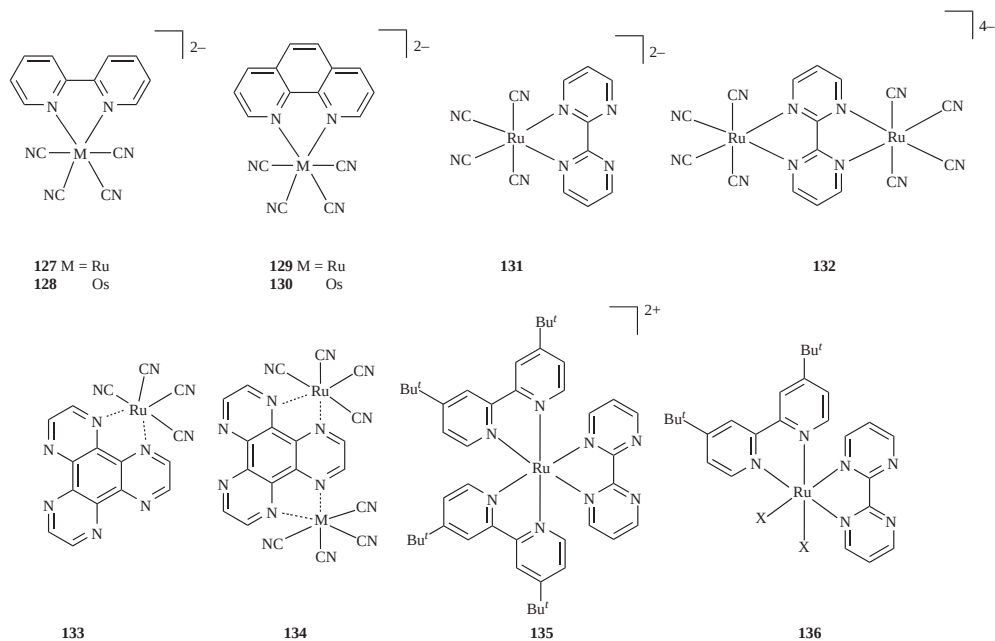


Using functionalized DTPA- or cyclen-based ligands, Faulkner and coworkers, and other groups [139–143], described a series of kinetically stable $\text{Ln}-\text{M}$ ($\text{M} = \text{Ru}, \text{Os}, \text{Re}$) heterobinuclear or heterotrinnuclear complexes **106–124**, where the $\text{Ln}(\text{III})$ ion is bound in a DTPA-derived or cyclen-derived coordination environment and the $\text{Ru}(\text{bpy})_2$, $\text{Os}(\text{bpy})_2$, or $\text{Re}(\text{CO})_3\text{Cl}$ unit

is held in close proximity through a chelating 2,2'-bipyridyl or 1,10-phenanthroline moiety. In these water-soluble Ln–M complexes, the MLCT state of a d-block metal chromophore acts as an effective sensitizer for NIR luminescence from Ln(III) ions. Excitation of the Ru(II), Os(II) or Re(I)-based metal-to-ligand charge-transfer band, which absorbs strongly in the near-UV to visible spectral region, gives rise to typical NIR luminescence from Nd(III), Er(III) or Yb(III) ions with sub-microsecond to microsecond ranges of lifetimes in methanol solutions at ambient temperature.



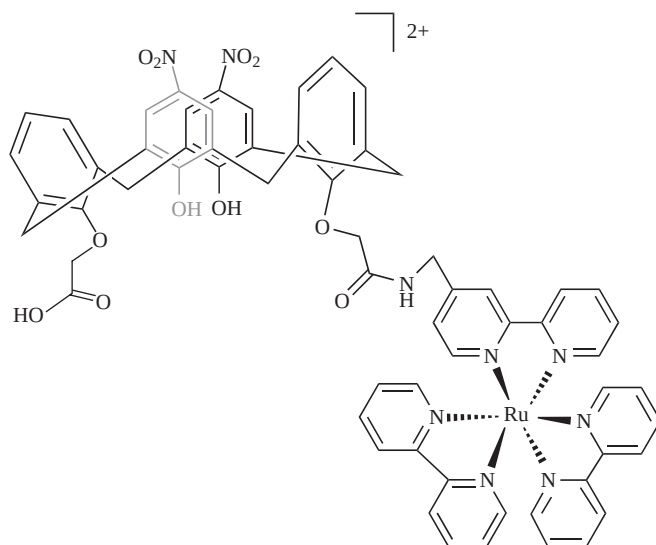
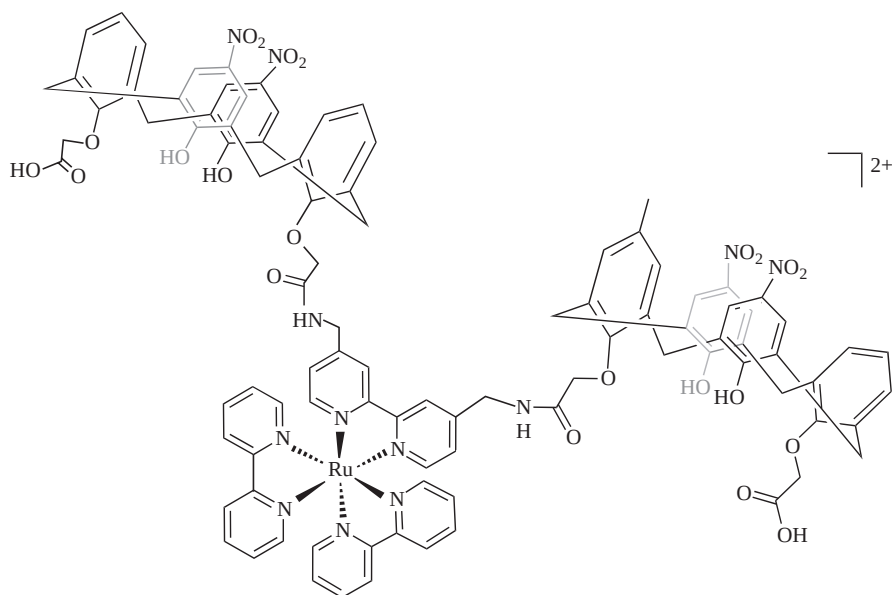
Ward and coworkers [144–151] used a series of simple ruthenium(II) or osmium(II) complexes **127–136** containing cyanide and/or bpym to serve as precursors for fabrication of Ru–Ln or Os–Ln heteronuclear complexes. Reactions of these cyanide- and/or bpym-anions



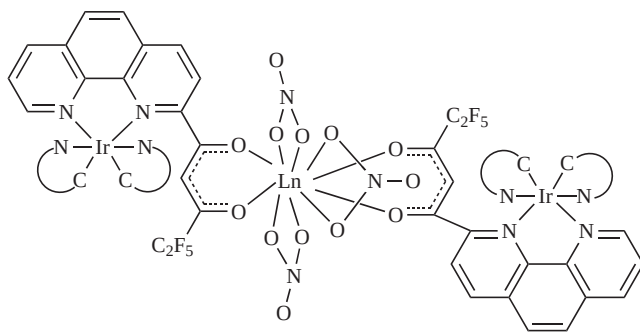
or with lanthanide(III) salts resulted in isolation of a family of discrete polynuclear complexes or coordination polymers based on Ru(Os)–CN–Ln or Ru–bpy–Ln linkages. Upon excitation of the Ru- or Os-based MLCT absorption bands in the visible spectral region, the Ru–Ln or Os–Ln heteronuclear species exhibited sensitized NIR luminescence from the corresponding lanthanide ions in every case. The intensity and lifetimes of Ru- or Os-based $^3\text{MLCT}$ emission, however, were highly diminished because of Ru(Os) $\rightarrow$ Ln photoinduced energy transfer to low-lying emissive states of the lanthanide ions. From the degree of quenching of the Ru/Os-based emission, the Ru(Os) $\rightarrow$ Ln energy-transfer rates (k_{ET}) were estimated, which generally follow the order k_{ET} (Yb) $<$ k_{ET} (Er) $<$ k_{ET} (Pr) $<$ k_{ET} (Nd). This k_{ET} order was rationalized on the basis of the availability of excited f–f levels on the lanthanide ions at energies that overlap with the Ru/Os-based emission spectra.

Beer *et al.* [152] described the synthesis and photophysical properties of ruthenium(II) bipyridyl complexes containing one (**137**) or two (**138**) rim acid-amide-modified calix[4]arene moieties covalently linked to the 2,2'-bipyridine groups, which were designed to coordinate to Nd^{3+} with formation of adducts of variable stoichiometry. Upon formation of the Ru–Nd arrays, the Ru-based $^3\text{MLCT}$ luminescences were largely quenched due to Pt $\rightarrow$ Ru energy transfer and the electronic energy of the excited calixarene was mostly transferred to the Nd^{3+} ion. Typical NIR luminescence from the Nd(III) ion was observed during titration of **137** or **138** with the Nd^{3+} ion in fluid solution at 298 K, suggesting that sensitization of Nd(III) luminescence resulted from the Ru(bpy) $_3$ -based $^3\text{MLCT}$ triplet state with the rate of Pt $\rightarrow$ Ru energy transfer being about $2.4 \times 10^6 \text{ s}^{-1}$.

With a 1,10-phenanthroline functionalized β -diketone ligand, Ir_2Ln (Ln = Nd **139**, Er **140**, Yb **141**) heterotrinnuclear complexes were recently prepared by Bian and Huang and coworkers in a stepwise approach [153, 154], in which the Ir(ppy) $_2$ chromophore is chelated by 1,10-phenanthroline and the lanthanide bound to β -diketone and to nitrates. Upon irradiation

**137****138**

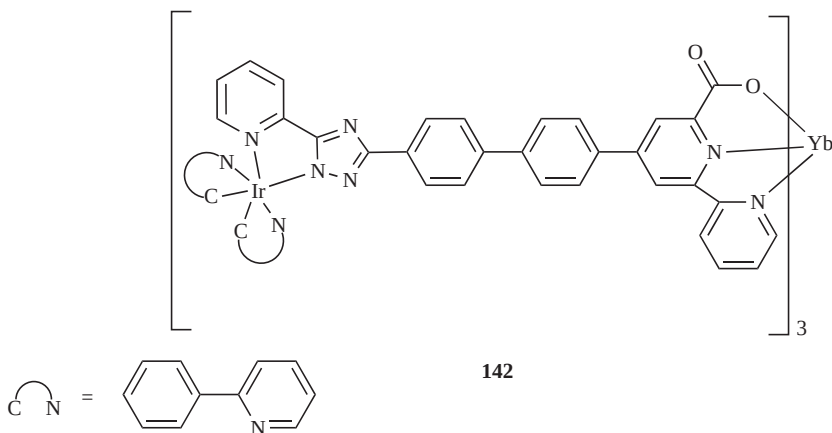
of the Ir(III)-based MLCT absorption at an excitation wavelength from 380 to 490 nm, the Ir₂Ln complexes displayed characteristic NIR emission from the corresponding lanthanide ions with lifetimes of 17.9 μ s (solid state) and 22.1 μ s (acetonitrile) for the Ir₂Yb complex **141** at ambient temperature. Kottas and De Cola *et al.* [155] described recently the preparation and photophysical properties of the Ir₃Yb heterotetranuclear complex **142**. Upon excitation of Ir(III)-based MLCT absorption in the visible region (400 nm), a strong quenching ($\geq 95\%$)



139 Ln = Nd

140 Er

141 Yb



of the Ir(III)-based $^3\text{MLCT}$ emission was observed along with intense NIR emission from the Yb(III) ion at 976 nm with a quantum yield of 0.7% ($\lambda_{\text{ex}} = 300$ nm), suggesting an efficient energy transfer from the Ir(III) units to the Yb(III) ion. The relatively high quantum yield of NIR luminescence from f–f transition is probably due to the exclusion of solvent molecules from the inner coordination sphere of the Yb(III) ion due to the nine coordination sites occupied by the bipyridine-carboxylate ligand.

12.3.1.4 d^3 Metal–Organic Chromophores

Incorporation of the bidentate–terdentate ligand **143** with $\text{Cr}(\text{CF}_3\text{SO}_3)_2$ and $\text{Ln}(\text{CF}_3\text{SO}_3)_3$ by self-assembly led to isolation of heterobimetallic triple-stranded helicates $[\text{Cr}(\text{III})\text{Ln}(\text{III})(\text{143})_3]^{6+}$ (Ln = Nd, Er, Yb) [156–159]. From the crystal structural determination (Figure 12.5), it was demonstrated that metal ions of different sizes could be accommodated in the helical structure without sizeable changes in the intermetallic $\text{Cr} \cdots \text{Ln}$ distances. Upon irradiation of the $\text{Cr}(\text{III})\text{N}_6$ chromophores by visible light, these helicates $[\text{Cr}(\text{III})\text{Ln}(\text{III})(\text{143})_3]^{6+}$ produced NIR emission characteristic of the corresponding Ln^{3+} ion through $\text{Cr} \rightarrow \text{Ln}$ energy

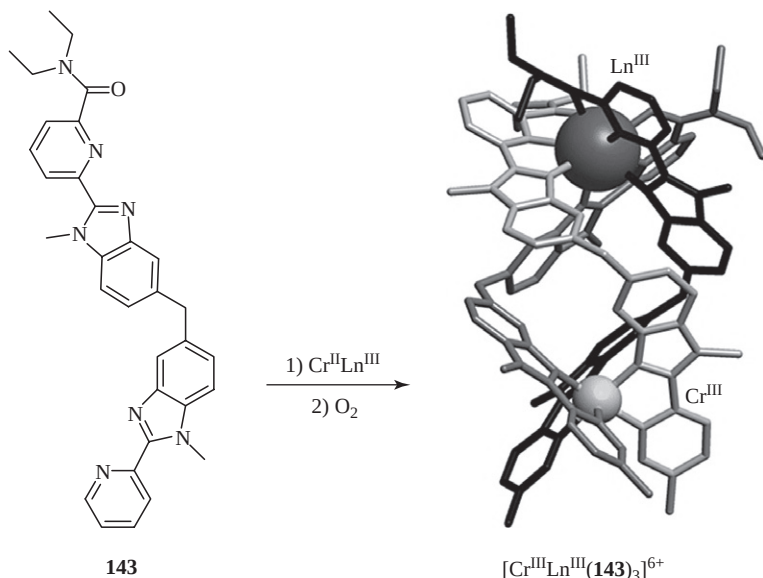


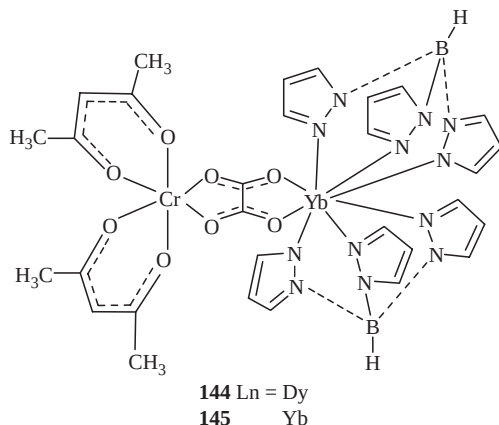
Figure 12.5 Self-assembly of the triple-stranded helicates $[Cr(III)Ln(III)(143)_3]^{6+}$ and the crystal structure of $[Cr(III)Yb(III)(143)_3]^{6+}$ [156]. (Reprinted with permission from D. Imbert *et al.*, “Extending lifetimes of lanthanide-based near-infrared emitters (Nd, Yb) in the millisecond range through Cr(III) sensitization in discrete bimetallic edifices,” *Journal of the American Chemical Society*, **125**, 15698, 2003. © 2003 American Chemical Society.)

migration from the $Cr(III)N_6$ chromophore to the lanthanide center. The lanthanide-based NIR luminescence decay times could be tuned from micro- to milliseconds. The lifetimes are 120 μs for $CrNd$ and 240 μs for $CrYb$ complexes in the solid state at 295 K. The yields of the $Cr \rightarrow Ln$ energy transfer are 62(11)% for $CrNd$ and 21(11)% for the $CrYb$ species in the solid state, and become 0.8(1) for $CrNd$ and 0.2(1) for $CrYb$ complexes in acetonitrile solution. This result is evidence for sizable $Cr \rightarrow Ln$ intramolecular energy transfers taking place both in the solid state and in solution.

Reaction of $Na[Cr(acac)_2(ox)]$ with $Ln(CF_3SO_3)_3$ and $KHBpz_3$ gave rise to formation of the chiral heterodinuclear $Cr(III)Ln(III)$ complexes $(\Lambda-\Delta)-[\{ (acac)_2Cr(ox) \} \{ Ln(HBpz_3)_2 \}]$ ($Ln = Dy$ **144**, Yb **145**, where $(\Lambda-\Delta)$ denotes the absolute configuration around the octahedral Cr and square-antiprismatic Ln moiety [160]. The NIR circular dichroism (CD) spectra for the $4f \rightarrow 4f$ transitions of the $(\Lambda-\Delta)-Cr(III)(ox)Ln(III)$ complexes **45** and **46** revealed the configurational chirality around the Ln ion without an asymmetric carbon in dichloromethane. This represents the first example of the stereospecific $(\Lambda-\Delta)-Cr(III)(ox)Dy(III)$ assembly with configurational chirality of the lanthanide complexes in solution without asymmetric carbon atoms. The solution NIR magnetic circular dichroism (MCD) of the racemic $Cr(III)(ox)Dy(III)$ and $Cr(III)(ox)Yb(III)$ complexes was also investigated.

On incorporating $[Cr(CN)_6]^{3-}$ or $[Co(CN)_6]^{3-}$ with $Ln(III)$ salts ($Ln = Nd, Gd, Yb$) in aqueous DMF, a series of cyanide-bridged discrete $Cr(Co)-Ln$ dinuclear species or coordination polymers were isolated by Ward and coworkers [161]. In these $Cr(Co)-Ln$ complexes, the d-block luminescence was completely quenched due to fast ($> 10^8 s^{-1}$) energy transfer to

the Ln(III) center, resulting in the characteristic emission from Yb(III) and Nd(III) in the NIR region. It was suggested that the long-lived spin-forbidden d–d excited states of $[M(CN)_6]^{3-}$ ($M = Cr, Co$) acted as effective sensitizers of NIR luminescence from Yb(III) and Nd(III) in these cyanide-bridged arrays.



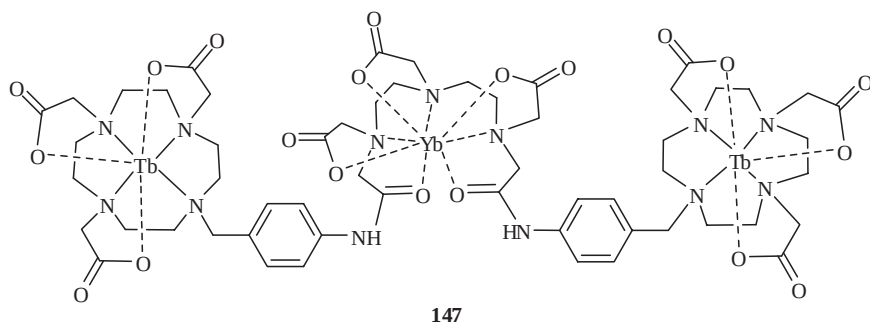
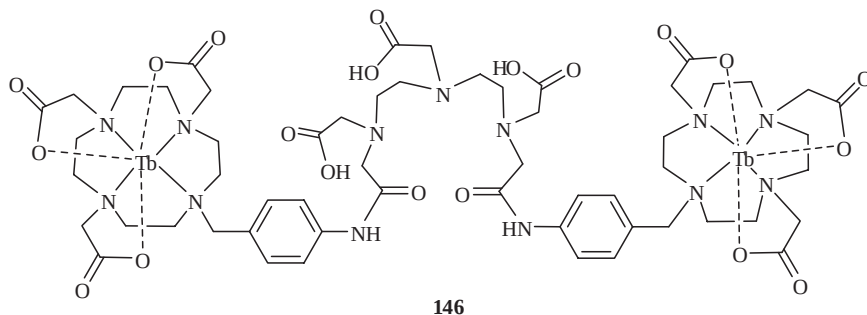
12.3.2 *f*-Block Chromophores

Because of the difficulty in controlling the f–f mixed metal arrays from synthetic procedures, studies on lanthanide centered NIR emission sensitized by another lanthanide ion has been relatively less well explored. Faulkner *et al.* [162] described a synthetic and luminescence study on a Tb_2Yb heterotrinnuclear complex **147** by complexation of the Tb_2 species **146** with Yb^{3+} ion. The bridging ligand contains a DTPA-like binding site suitable for Yb(III) coordination and two tricarboxylate functionalized 1,4,7,10-tetraazacyclododecanes with two Tb(III) ions encapsulated in the coordination environment. The synthetic strategy used allows the incorporation of a DTPA-like binding site as a bridge between two kinetically stable terbium complexes.

Upon excitation of the Tb_2Yb complex **147** at 337 nm, both the green luminescence at 545 nm from the Tb^{3+} center and NIR emission at 980 nm from the Yb^{3+} center due to the $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition were detected. The emission from the Tb^{3+} center in **147**, however, was obviously reduced in intensity relative to the Tb-centered luminescence in **146**. The observation of Yb-centered emission at 980 nm by direct excitation of the Tb^{3+} absorption band at 488 nm suggests unambiguously that Tb→Yb energy transfer is indeed operating from the Tb to the Yb center in Tb_2Yb complex **147**, because neither Yb nor the ligand-centered chromophore have any absorption bands at 488 nm. This represents the first report of an NIR emitting lanthanide centered near-IR emission sensitized by a visible emitting lanthanide ion.

The preparation, characterization and luminescence properties of binuclear Yb and/or Er complexes $Er_2(Ba)_6(phen)_2$ (**148**), $Yb_2(Ba)_6(phen)_2$ (**149**), and $Er_{1.4}Yb_{0.6}(Ba)_6(phen)_2$ (**150**) were recently described [163]. With excitation at both 320 and 975 nm, the emission intensity around 1000 nm from the Yb(III) center decreased significantly, whereas the emission intensity around 1535 nm from the Er center was obviously enhanced in $Er_{1.4}Yb_{0.6}$ species (**150**) compared with that in Er_2 (**148**) and Yb_2 (**149**) complexes. This suggests that an efficient Yb→Er energy transfer occurs most probably from Yb^{3+} to Er^{3+} in the $Er_{1.4}Yb_{0.6}$ species.

This is an excellent binuclear complex model with a short metal-to-metal distance (about 4 Å) to facilitate the intramolecular Yb→Er energy transfer process.



12.4 Outlook

This chapter summarizes recent progresses in NIR luminescence from lanthanide(III) complexes focusing on synthetic strategy, photophysical properties, and correlation between the structures and NIR emitting properties. To attain long-lived NIR lanthanide(III) luminescence with high efficiency, it is necessary to minimize the deactivation processes through O–H, N–H, and C–H vibration excitation. One of feasible approaches is to make lanthanide(III) ions encapsulated with polydentate ligands so as to prevent any solvent molecules and anions getting close to the lanthanide centers. On the other hand, fluorinated ligands and deuterated solvents are frequently adopted to eliminate vibrational deactivation induced by O–H, N–H, and C–H oscillators in close proximity to the lanthanide(III) centers. Apart from the systems with organic ligands as light harvesting antenna chromophores, transition metal complexes that display intense MLCT/LLCT absorptions in the visible spectral region can act as excellent energy donors for sensitization of NIR luminescence from lanthanide(III) ions through efficient d→f energy transfer. Current challenges in developing NIR lanthanide luminescence include: (i) design of better complexation agents (both organic chelators and d-block organometallic “ligands”) for light-harvesting chromophores, (ii) finding new approaches for sensitization of NIR luminescence, (iii) eliminating as much as possible the radiationless deactivation processes, and (iv) finding new applications of NIR lanthanide emission in medical diagnosis and biological imaging and also in organic light-emitting devices.

List of Abbreviations

acac
acetylacetonate
Ba
benzoate
bpy
2,2'-bipyridine
 $\text{bpyC}\equiv\text{CC}\equiv\text{Cbpy}$
bis(2,2'-bipyridin-5-yl)-butadiyne
bpym
2,2'-pyrimidine
 Bu_2^tbpy
4,4'-di-*tert*-butyl-2,2'-bipyridine
 Bu_3^ttpy
4,4',4''-tri-*tert*-butyl-2,2' : 6',2''-terpyridine
dbm
dibenzoylmethane
DO3A
1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid
DOTA
1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid
dppm
diphenylphosphinomethane
dppz
2,3-bis(2-pyridyl)pyrazine
DTTA
diethylenetriamine tetracarboxylic
DTPA
diethylenetriamine pentaacetic acid
 HBpz_3
hydrotris(pyrazol-1-yl)borate
 $\text{HC}\equiv\text{Cbpy}$
5-ethynyl-2,2'-bipyridine
 $\text{HC}\equiv\text{CC}_6\text{H}_4\text{tpy}$
4'-(4-ethynylphenyl)-2,2' : 6',2''-terpyridine
hfac
hexafluoroacetylacetonate
ILCT
intraligand charge transfer
 $\text{Me}_3\text{SiC}\equiv\text{Cbpy}$
5-[2-(trimethylsilyl)-1-ethynyl]-2,2'-bipyridine
MLCT
metal-to-ligand charge transfer
MMLCT
metal-metal-to-ligand charge transfer

ox
oxalate
H₂pdo
5,6-dihydroxyphenanthroline
pdon
1,10-phenanthroline-5,6-dione
phen
1,10-phenanthroline
ppy
2-phenylpyridine
tpy
2,2' : 6',2''-terpyridine

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13

Luminescent Rare Earth Complexes as Chemosensors and Bioimaging Probes

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13.1 Introduction

Lanthanide ions have numerous energy levels because their 4f orbitals are buried beneath their 6s, 5p, and 5d orbitals and the coupling between the 4f orbitals and the surrounding ligands is weak. Moreover, the f–f transitions of lanthanide ions have a low absorption coefficient, and thus sensitized emission is often used to achieve high luminescence (Figure 13.1). For a lanthanide complex, a chromophore incorporated into the ligand (called a sensitizer) absorbs excitation light with a large absorption coefficient and transfers its energy to the lanthanide ion by intersystem crossing, whereby the lanthanide ion attains the emissive state. By choosing an appropriate sensitizer, it is possible to obtain a highly emissive lanthanide complex [1].

As luminescent materials, lanthanide complexes exhibit unique photoluminescence properties, such as sharp absorption and luminescence bands, large Stokes shifts (>200 nm), and long luminescence lifetimes ($\sim$ ms). These long lifetimes clearly offer an advantage as they allow time-resolved fluorescence (TRF) spectroscopy and microscopy (Figure 13.2). The introduction of a time delay (for example, 1 or 100 μ s), prior to detection of the emitted light, eliminates interference from light scattering and autofluorescence, and hence greatly enhances the signal to noise ratio and the reliability of detection and monitoring. Time-resolved luminescence bioassay techniques using luminescent lanthanide complexes as probes have been exploited in various fields, especially immunoassays and high-throughput screenings, since the first application was reported in 1983 [2–4]. There are two types of assays: homogeneous assays

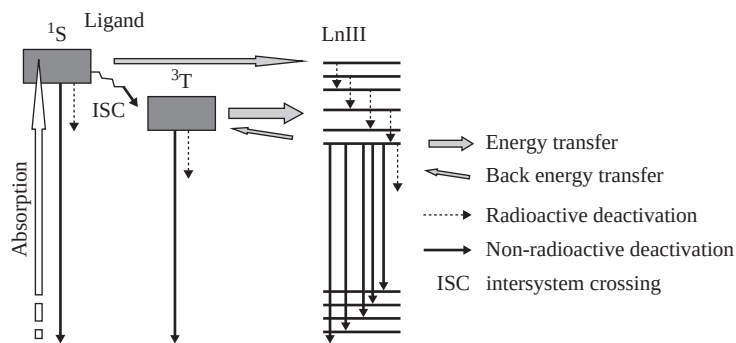


Figure 13.1 Simplified diagram showing the main energy flow paths during sensitization of lanthanide luminescence via its surroundings (ligands).

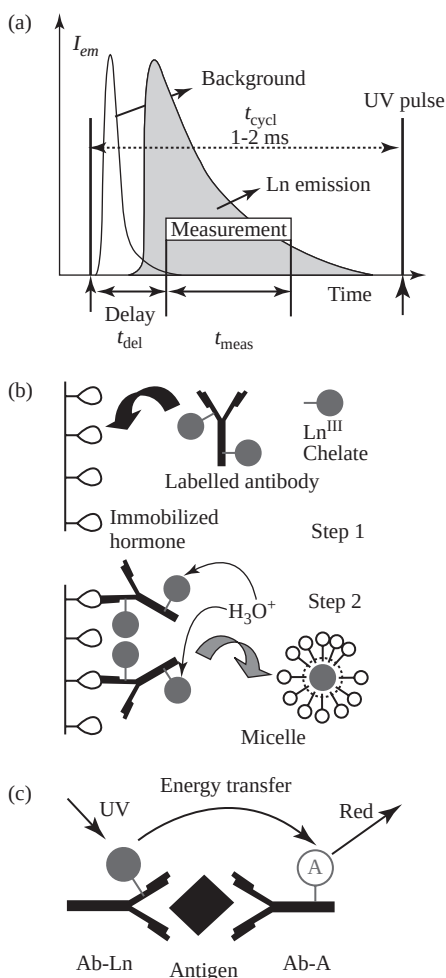


Figure 13.2 Principles of (a) time-resolved spectroscopy, (b) heterogeneous immunoassays, and (c) homogeneous immunoassays [1]. (Reproduced from J.C.G. Bunzli and C. Piguet, "Taking advantage of luminescent lanthanide ions," *Chemical Society Reviews*, **34**, 1048–1077, 2005, by permission of The Royal Society of Chemistry.)

and heterogeneous assays. In homogeneous assays (immunoassays, nucleic acid hybridization assays, or enzyme assays), the binding or chemical reaction changes the properties of the label (Figure 13.2c), enabling its specific detection in solution without any separation or washing steps. However, the lack of separation steps can cause problems arising from interfering species in the sample. Heterogeneous assay formats are the most common owing to their reliable assay performance. In the noncompetitive assay format, analyte is immobilized on the solid surface by a direct binding reaction with an activated surface, or through an unlabeled specific binding reagent that is already bound to the support. The labeled specific binding reagent then binds to the immobilized analyte, and the signal arising from the label is detected after washing the unbound label-specific binding reagent. Alternatively, in a competitive format, labeled analyte is added to compete with the unlabeled-specific binding reagent in the sample for binding sites on the solid support; bound labeled analyte is then detected after washing [1].

Because there are many reports concerning TRF measurement in immunoassays [5–9], we focus herein on the use of rare earth complexes as luminescent chemosensors and bioimaging probes.

13.2 Rare Earth Complexes as Luminescent Chemosensors

13.2.1 Basic Concept

As a light-based analytical method, luminescent chemosensing offers many advantages, such as high sensitivity, low cost, submillisecond temporal resolution, and possible remote sensing by using optical fibers [10]. As shown in Figure 13.3, luminescent chemosensors usually consist of a signaling moiety (chromophore) and a recognition moiety (receptor). The signaling moiety converts the recognition information into a fluorescent signal, which is expressed as a change in the photophysical properties of the chromophore. The recognition moiety is responsible for the selectivity and efficiency of binding, which depend on the properties of the guest. The signaling moiety can be linked to the recognition moiety via a spacer [11]. On the basis of the principles of photoinduced electron transfer, electronic energy transfer, monomer–excimer formation, charge transfer, the rigidity effect, and special chemical reaction, a series of luminescent chemosensors based on organic dyes and metal–ligand charge-transfer (MLCT)-based complexes has been developed [12–27].

Owing to the unique process of ligand-sensitized lanthanide luminescence emission, the design principle of lanthanide complex-based chemosensors is distinct from that of organic chemosensors [28]. As shown in Figure 13.4, lanthanide-based luminescent chemosensors

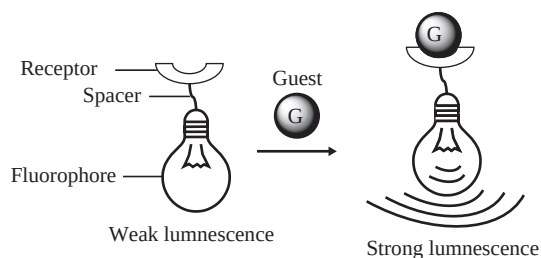


Figure 13.3 Scheme of the luminescent chemosensor.

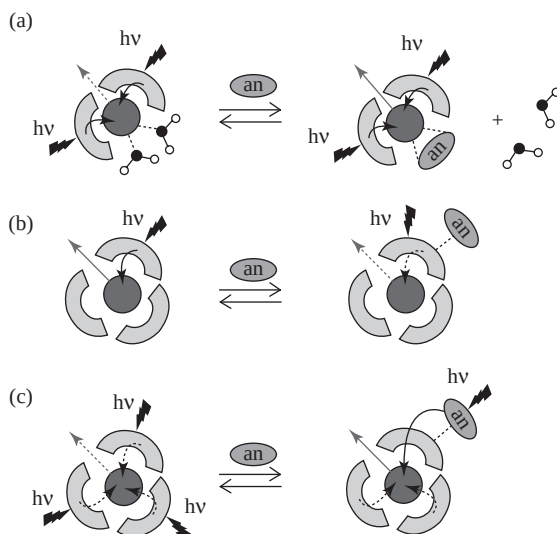


Figure 13.4 Typical design principle of lanthanide complex-based chemosensors based on binding of an analyte (an): (a) directly influencing the Ln(III) luminescence, (b) influencing photophysical properties of the ligand, and (c) addition of a sensitizing analyte onto a poorly luminescent lanthanide-containing sensor [1]. (Reproduced from J.C.G. Bunzli and C. Piguet, "Taking advantage of luminescent lanthanide ions," *Chemical Society Reviews*, **34**, 1048–1077, 2005, by permission of The Royal Society of Chemistry.)

have been designed on the basis of three main mechanisms [1]. (i) One mechanism may act directly on the Ln(III) ion and directly influence the Ln(III) luminescence. For a lanthanide complex with an unsaturated coordination environment, the lanthanide ion will allow water binding, resulting in weak luminescence emission. When these quenching water molecules are displaced with an analyte by ligand exchange, emission intensity of the lanthanide complex is restored (Figure 13.4a). (ii) Another mechanism may influence the photophysical properties of the ligand, either of its singlet state or of its triplet state and, consequently, the efficiency of the inter-system crossing transfer. (iii) The analyte itself may be used as either a sensitizer for the Ln(III) luminescence or possibly as a quencher. For example, addition of a sensitizing analyte onto a poorly luminescent lanthanide-containing sensor induces the enhancement in the Ln(III) luminescence of the complex (Figure 13.4c).

13.2.2 Rare Earth Complexes as Luminescent pH Chemosensors

pH is an essential parameter of physiological processes. For example, the activity of enzymes is switched on or off depending on the pH. It is therefore not surprising that many pH-sensitive luminescent systems have been developed based on lanthanide complexes. In particular, a series of lanthanide complexes (Figure 13.5) based on the cyclen macrocycle ligands with pendent arms such as amides, carboxylates or phosphinate esters were reported as pH-sensitive luminescent chemosensors [29, 30]. The change in lanthanide luminescence can be depicted as

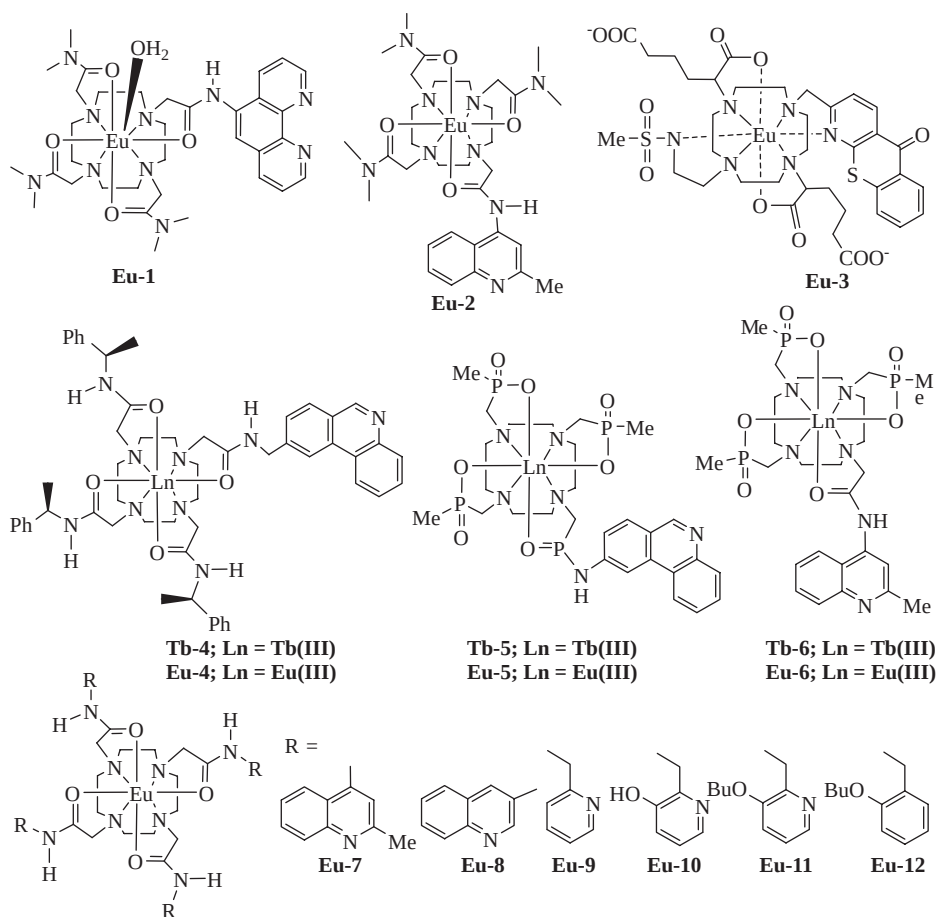


Figure 13.5 Chemical structures of the Ln(III) complexes.

shown in Figure 13.6, where the Ln(III) luminescence is only “switched on” upon protonation. Moreover, these Ln(III) complexes are also kinetically and thermodynamically stable [31, 32].

For example, Gunnlaugsson *et al.* reported the Eu(III) complex **Eu-1** (Figure 13.5) containing a 1,10-phenanthroline (phen) moiety as a pH-responsive chemosensor [33]. In alkaline solution in the pH range 12–8.5, the Eu(III) emission was found to be weak upon excitation at 266 nm. However, upon acidification, the Eu(III) emission of **Eu-1** was gradually “switched on,” reaching a maximum in the physiological pH range. Upon further addition of acid, the Eu(III) emission of **Eu-1** decreased until about pH 3, being pH-independent between a pH of about 1–2.5. The emission can be described as being switched “off–on–off” as a function of pH. Moreover, this pH dependence was fully reversible. From these changes, two pK_a values of 3.8 and 8.1 were determined. These were assigned to protonation of the phen nitrogen moiety and deprotonation of the aryl amide. In addition, for **Eu-4** and **Eu-5**, protonation of

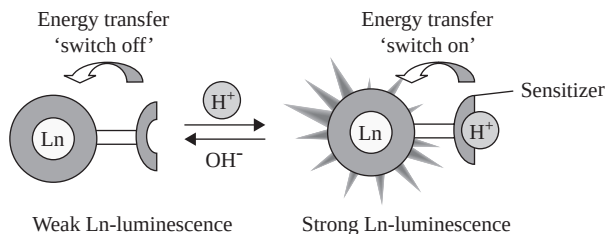


Figure 13.6 The mechanism of pH probe based on the complexes **Ln-4**, **Ln-5**, and **Ln-6** (Ln = Tb, Eu).

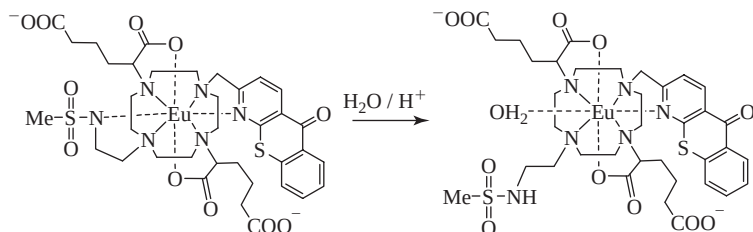


Figure 13.7 The possible protonation mechanism of the complex **Eu-3**.

the phenanthridine moiety gave rise to a large 500-fold enhancement in the Eu(III) emission, suggesting specific sensitivity of the Eu(III) emission to the local environment of the sensitizer.

For some Eu(III) complexes incorporating an *N*-methylsulfonamide moiety, the binding of a europium(III) center to a sulfonamide N atom is weak and can be switched by ligation with water or a carboxylate group, resulting in the changes in the Eu(III) emission. On basis of this strategy, Pal and Parker designed and synthesized a macrocyclic Eu(III) complex **Eu-3** containing an *N*-methylsulfonamide moiety (Figure 13.7) as a ratiometric pH probe. Plots of the change in the emission intensity ratio (680 : 587 nm) versus pH revealed an 80% change in this ratio (pH 4.5 to 8), and a protonation constant of 6.15 for **Eu-3** was estimated [34].

13.2.3 Rare Earth Complexes as Luminescent Chemosensors for Cations

Metal ions (such as Zn^{2+} or Cu^{2+}) at the trace level are often essential to biochemical reactions, for example, in catalysis, transport, or biosynthesis. However, at higher concentrations, accumulation of these ions in an organism can lead to unhealthy interactions such as biochemical redox processes and inhibition of enzyme activity. Therefore, the detection of metal cations is of great interest to many scientists [10, 16, 18, 24].

A typical example of a cation-selective chemosensor based on a lanthanide complex was reported by Nagano and coworkers. Based on Zn^{2+} induced switch-on of absorption-energy transfer-emission (A-ET-E), a Tb^{3+} complex **Tb-13** (Figure 13.8) was developed to serve as a sensitive luminescent sensor for Zn^{2+} [35]. For **Tb-13**, a diethylenetriaminepentaacetic acid (DTPA)-bisamide moiety was used as the coordination ligand of Tb^{3+} , and two di-(2-pyridinylmethyl)amine groups were designed as both sensitizers of Tb^{3+} and binding sites of

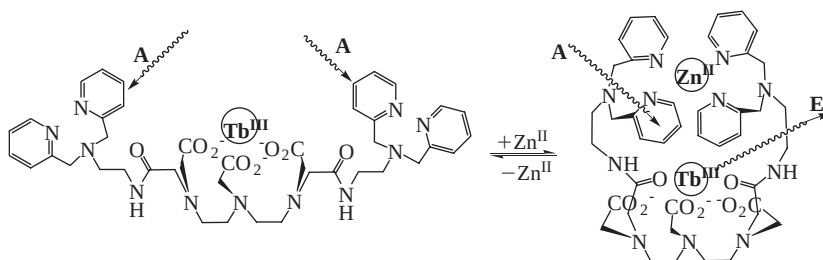


Figure 13.8 Schematic of absorption–energy transfer–emission (A–ET–E) process and proposed conformational alteration of **Tb-13** in the presence of Zn^{2+} .

Zn^{2+} . In 100 mM HEPES [*N'*-(2-hydroxyethyl)piperazine-*N*-ethanesulfonic acid)] buffer at pH 7.4, the time-resolved emission intensity of Tb^{3+} increased upon addition of Zn^{2+} from 0 to 1 equiv. The enhancement of the emission intensity of **Tb-13** upon Zn^{2+} binding appears to be the result of efficient intramolecular energy transfer from the pyridyl group to the Tb^{3+} ion, as shown in Figure 13.8. Moreover, **Tb-13** exhibited a high selectivity for Zn^{2+} over other metal ions.

It is well known that copper ion (Cu^{2+}) is able to quench Eu(III) emission. Recently, the Eu(III)–cyclen–*phen* conjugate **Eu-1** (Figure 13.5) has been reported as a luminescent copper sensor. The addition of Cu^{2+} to the solution of **Eu-1** at pH 7.4 induced the quenching of Eu(III) luminescence at 615 nm [36].

Lanthanide luminescence is strongly dependent on the coordination environment of the lanthanide ion, and some lanthanide coordination polymers with supramolecular structures have recently been introduced as luminescent chemosensors of cations. Liu *et al.* reported three-dimensional lanthanide coordination polymers $\{\text{Na}[\text{Ln}(\text{L14})(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}_n$ [$\text{Ln} = \text{Eu}$ (**Eu-14**), Gd (**Gd-14**)] (Figure 13.9) using a 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetrapropionic acid (L14) as a ligand [37]. Complex **Eu-14** exhibits three emission bands at 592, 615, and 696 nm corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 1, 2, 4$) transitions. Interestingly, Ag^+ can modulate the luminescent properties of **Eu-14**. As shown in Figure 13.9, upon addition of Ag^+ , the emission intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition for Eu^{3+} increased 4.9 times, while the other $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 1, 4$) transitions largely decreased. Moreover, the emission spectrum changed from displaying multiple peaks to displaying a single peak. Furthermore, the titrations of **Eu-14** with AgNO_3 suggest the fit to a 1 : 1 binding model. These results strongly suggest that Ag^+ enters the empty coordination site of **Eu-14**.

Chen and coworkers have reported that a series of multidimensional porous polymers with 3d–4f mixed metals could recognize some specific cations. For example, two 3d–4f heterometallic coordination polymers $\{\text{Ln}(\text{L15})_3\text{Mn}_{1.5}(\text{H}_2\text{O})_3\} \cdot 3.25 \text{H}_2\text{O}\}_\infty$ [$\text{L15} = \text{pyridine-2,6-dicarboxylic acid}$; $\text{Ln} = \text{Eu}$ (**Eu-15**); $\text{Ln} = \text{Tb}$ (**Tb-15**)] with 1D-channels could recognize Zn^{2+} to some extent [38]. The emission intensity of **Eu-15** gradually increased upon addition of 1–3 equiv of Zn^{2+} . The highest peak at 618 nm was at least twice as intense as the corresponding band in a solution without Zn^{2+} . Although the lanthanide ions in **Eu-15** and **Tb-15** are different, the luminescent intensity of **Tb-15** changed in essentially the same way as that of **Eu-15**. Therefore, **Eu-15** and **Tb-15** could be considered to be luminescent probes of Zn^{2+} . In addition, Chen and coworkers also reported two Dy–Mn polymers $\{\text{Dy}(\text{L15})_3\text{Mn}_{1.5}(\text{H}_2\text{O})_3\} \cdot 3.125\text{H}_2\text{O}\}_n$

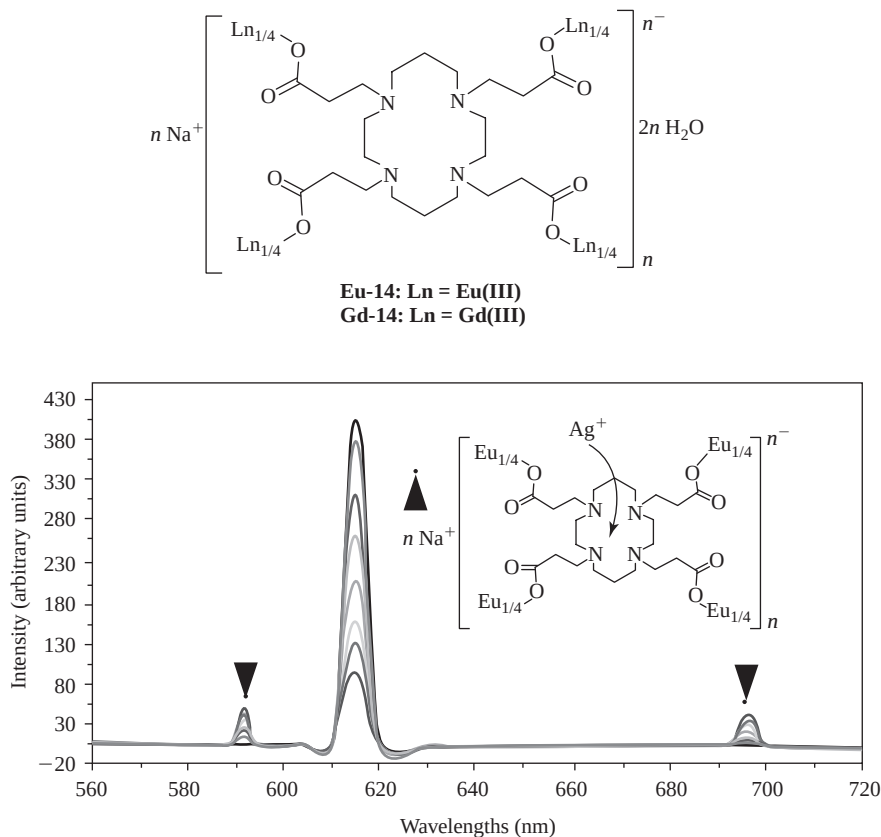


Figure 13.9 Scheme for the complexes $\{\text{Na}[\text{Ln}(\text{L14})(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}_n$, and increase in luminescence intensity of a 100 μM solution of **Eu-14** in H_2O upon addition of Ag^+ [37]. (Reproduced with permission from W.S. Liu *et al.*, “Lanthanide coordination polymers and their Ag^+ -modulated fluorescence,” *Journal of the American Chemical Society*, **126**, 2280–2281, 2004. © 2004 American Chemical Society.)

(**Dy-15**) and $\{[\text{Dy}(\text{L16})_3\text{Mn}_{1.5}(\text{H}_2\text{O})_6] \cdot 8.25\text{H}_2\text{O}\}_n$ (**Dy-16**, L16 = 4-hydroxypyridine-2,6-dicarboxylic acid) as emissive systems for detecting Mg^{2+} [39]. The emission spectra of **Dy-15** and **Dy-16** in DMF (*N,N'*-dimethylformamide) exhibit characteristic transitions of the Dy^{3+} ion from $^4\text{F}_{9/2}$ to $^6\text{H}_{15/2}$ and $^6\text{H}_{13/2}$, respectively. Interestingly, the emission intensities of **Dy-15** and **Dy-16** increase significantly upon addition of Mg^{2+} over other metal cations.

In addition, Qian and coworkers reported a luminescent lanthanide-based metal–organic framework (MOF) $[\text{Eu}(\text{L16})_{1.5}(\text{dmf})] \cdot (\text{DMF})_{0.5}(\text{H}_2\text{O})_{0.5}$ (**Eu-17**, L17 = pyridine-3,5-dicarboxylate) with Lewis basic pyridyl sites for the sensing of metal ions (Cu^{2+} , Co^{2+} , and so on) [40]. Under excitation at 321 nm, **Eu-17** shows characteristic emission bands of the Eu^{3+} ion at 590, 616, and 698 nm, which were ascribed to transitions from the $^5\text{D}_0$ state to $^7\text{F}_1$, $^7\text{F}_2$, and $^7\text{F}_4$, respectively. The luminescence intensity of **Eu-17** was strongly dependent on the identity of the metal ion, with Cu^{2+} having the most significant quenching effect. Moreover,

the fluorescence lifetime was significantly reduced from 898.9 to 494.6 μs in the presence of 10 mM Cu^{2+} , indicating the potential of **Eu-17** for the sensing of Cu^{2+} .

13.2.4 Rare Earth Complexes as Luminescent Chemosensors for Anions

Anions, such as fluoride, chloride, and phosphate, play critical roles in a range of biological processes and are implicated in a number of diseased states, ranging from fluorosis to cystic fibrosis [41]. Therefore, the exploitation of new luminescent chemosensors for anions is very important. The main design approach for lanthanide complexes as luminescent chemosensors for anions is to utilize the specific interaction between the anions and the lanthanide ion to realize the detection of the anions.

The first example of an anion-selective chemosensor based on a lanthanide complex was developed by Ziessel and coworkers. In 2001, they reported a europium complex (**Eu-18**, Figure 13.10) with a bis(bipyridine)phenylphosphine oxide ligand as a chemosensor of nitrate (NO_3^-) [42, 43]. In **Eu-18**, two bipyridine fragments act as efficient sensitizers while providing, together with the phosphoryl group, considerable coordination strength. However, the coordination sphere is unsaturated, allowing further coordination of anions. The luminescent properties of **Eu-18** drastically depend on the nature of the anion in solution, with binding of nitrate, fluoride, chloride, and acetate being stronger than that of other anions. In particular, adding two equivalents of nitrate to a solution of **Eu-18** resulted in an 11-fold enhancement of the Eu(III) emission intensity. In the case of nitrate, the first anion expels the solvent molecules while further binding results in successive decomplexation of the bipyridyl units.

Parker's group reported a series of cationic, zwitterionic, and anionic lanthanide complexes for the analysis of anions [44, 45]. Figure 13.11 shows the chemical structures of six europium complexes-based sensors (**Eu-19–Eu-24**) of hydrogencarbonate (HCO_3^-) [46]. In a simulated extracellular ionic background [0.1 M NaCl, 2.3 mM lactate, 0.13 mM citrate, 0.9 mM phosphate, pH 7.4, 0.1 M MOPS (3-morpholinopropanesulfonic acid)], changes in the 618 : 588 nm intensity ratio as a function of the concentration of NaHCO_3 (from 0 to 40 mM) were recorded for each complex. The cationic complex **Eu-20** was found to bind HCO_3^- more avidly than the corresponding zwitterionic complex **Eu-23**, whilst the anionic complex **Eu-24** bound HCO_3^- most weakly.

In addition, the triply-charged and coordinatively unsaturated europium complex (**Eu-25**, Figure 13.11) was also reported as a pH-insensitive, ratiometric chemosensor for citrate [47]. Addition of citrate at very low concentrations into an aqueous solution of **Eu-25** (5 μM) resulted

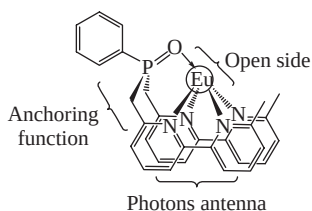


Figure 13.10 Chemical structure of the Eu(III) complex **Eu-18**.

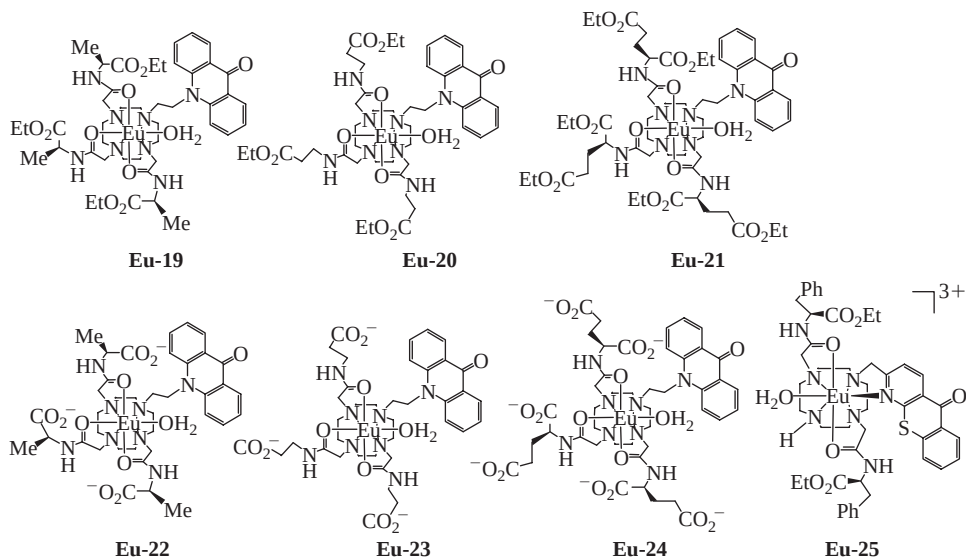


Figure 13.11 Structure of anion sensors **Eu-19–Eu-25** published by Parker's group.

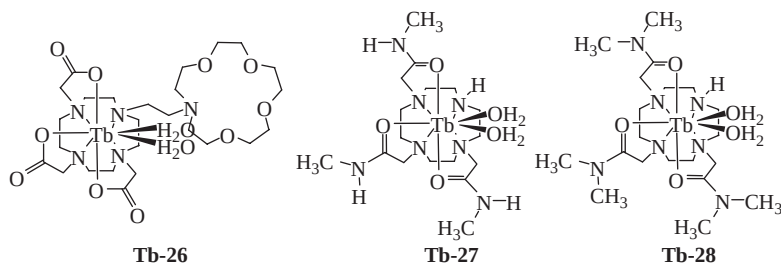


Figure 13.12 Chemical structures of the Tb(III) complexes **Tb-26**, **Tb-27**, and **Tb-28**.

in highly significant changes in the Eu(III) luminescence, with the integrated band intensity of the $\Delta J = 2$ manifold increasing and the relatively sharp $\Delta J = 0$ transition decreasing.

Li and Wong reported a Tb³⁺ complex **Tb-26** with pendant aza-15-crown-5 (Figure 13.12) that showed recognition of two important bio-active anions, lactate and salicylate, in aqueous solution [48]. The luminescence lifetime of **Tb-26** in H₂O was dependent on the nature of the ratio in solution. Upon addition of 3.0 equiv of lactate, the luminescence lifetime of **Tb-26** increased from 1.45 ms to its maximum of 2.15 ms. Moreover, **Tb-26** shows a high selectivity of lactate over other anions such as HCO₃[−], H₂PO₄[−], AcO[−], and Cl[−]. In addition, two coordinatively unsaturated terbium complexes **Tb-27** and **Tb-28** (Figure 13.12) could be displaced upon metal chelation to aromatic carboxylic anions, such as salicylate, in water [49].

Recently, we reported a terbium complex Tb(PMIP)₃(PhCN) (**Tb-29**, PMIP = 1-phenyl-3-methyl-4-isobutyl-5-pyrazolone; PhCN = pyrazino[2,3-*f*][1,10] phenanthroline-2,3-dicarbonitrile, Figure 13.13) as a reagent for anions [50]. Interestingly, the luminescent

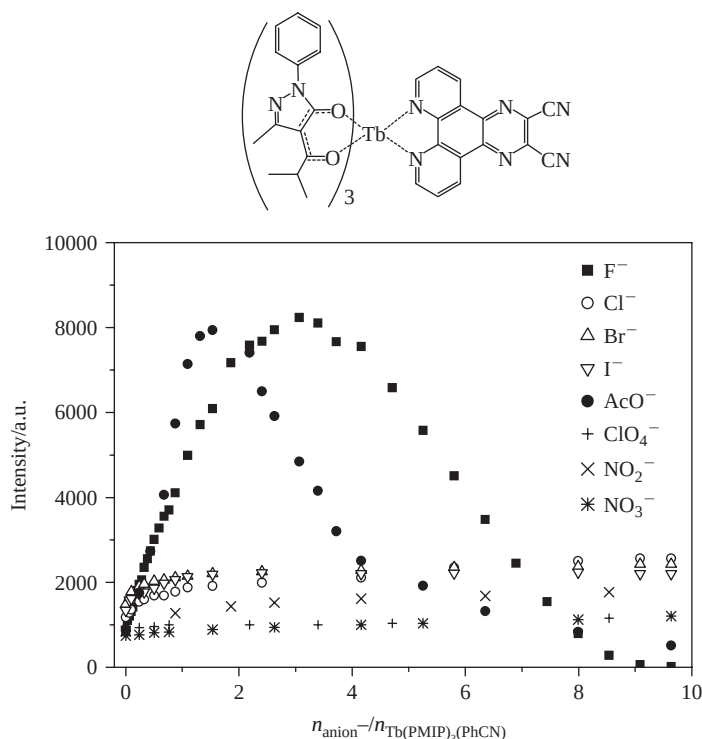


Figure 13.13 Chemical structure of **Tb-29** and luminescent titrations of **Tb-29** (10 μM) in CH₃CN upon addition of F⁻, Cl⁻, Br⁻, I⁻, ClO₄⁻, NO₃⁻, NO₂⁻, and AcO⁻ [50]. (Reproduced with permission from D.Q. Zhang *et al.*, “The luminescence modulation of a terbium complex with fluoride anion and its application for chemodosimeter”, *European Journal of Inorganic Chemistry*, 2006, no. 11, 2277–2284. © Wiley-VCH Verlag GmbH & Co. KGaA.)

behavior of **Tb-29** drastically depends on the nature of the anions added into the solution. For **Tb-29**, the triplet energy level of PhCN (20920 cm⁻¹) is lower than that of PMIP (23000 cm⁻¹) and a little higher than that for ⁵D₄ of Tb³⁺ (20400 cm⁻¹), resulting in a back-energy transfer from Tb³⁺ to PhCN and a weak luminescence emission of **Tb-29**. Upon addition of apropos equivalents of fluoride (or acetate) anions, the replacement of PhCN with fluoride (or acetate) anions was observed and the above back-energy transfer was inhibited, resulting in a significant enhancement in luminescence emission of **Tb-29** (Figure 13.13). After excessive equivalents of fluoride (or acetate) anions were added, the replacement of PMIP with fluoride (or acetate) anions inhibited the PMIP ligand-sensitized-energy transfer, resulting in the luminescence quenching of the system. Moreover, in aqueous solution, **Tb-29** shows high sensitivity of ~10⁻⁸ mol L⁻¹ and a remarkable selectivity of F⁻ over the other anions [50]. In addition, we also demonstrated a europium complex Eu(NO₃)₃(L30)₃ [**Eu-30**, L30 = tri-(4-methoxyphenyl)phosphine oxide)] as a time-resolved luminescence-based chemosensor for the fluoride anion [51].

In addition, Qian and coworkers reported a luminescent MOF, $\text{Tb}(\text{L31})\cdot\text{G}$ (**Tb-31**: L31 = benzene-1,3,5-tricarboxylate, G = guest solvent) for the recognition of fluoride anion [52]. MOF **Tb-31** was immersed in methanolic solutions of NaX ($\text{X} = \text{F}^-$, Cl^- , and Br^-) and Na_2X ($\text{X} = \text{CO}_3^{2-}$ and SO_4^{2-}) to form anion-incorporating **Tb-31** microcrystalline solids. The most interesting observation was that the luminescence intensity of the anion-incorporating **Tb-31** was significantly enhanced, particularly in the case of the F^- -incorporating MOF. Fourfold enhancement in $\text{Tb}(\text{III})$ luminescence intensity was measured for the F^- -incorporated **Tb-31** activated by a 10^{-2} M solution of NaF in methanol.

13.2.5 Rare Earth Complexes as Luminescent Chemosensors for Small Molecules

As a widespread exopeptidase, microsomal leucine aminopeptidase (LAP) can remove N-terminal amino acids (primarily leucine and alanine) from almost all unsubstituted oligopeptides and plays important roles in tumor-cell invasion, tumor metastasis, and maturation of MHC class I epitopes. Recently, Nagano and coworkers synthesized a Tb complex **Tb-32** (Figure 13.14) as a photoinduced electron transfer (PeT) based luminescence probe to monitor the enzymatic activity of LAP [53]. As shown in Figure 13.14, the ligand of **Tb-32** consists of three moieties: diethylenetriaminepentaacetic acid (DTPA) derivative as a chelator, a (1*H*)-quinolinone derivative as an antenna, and a moiety that is reactive towards LAP as a luminescence on/off switch. The substrate peptide sequence of LAP, L-Leu, was attached through a peptide bond to the amino group of the luminescence on/off switch moiety of **Tb-32** (Figure 13.14). Clear dependence of terbium luminescence on the HOMO level of the switch was observed for **Tb-32**. The free **Tb-32** showed strong luminescence, as the HOMO energy level of its switch moiety was -5.89 eV and the quinolinone moiety could sensitize the Tb^{3+} ion. Upon addition of LAP, the peptide was cleaved and **Tb-32** was converted into **Tb-33**. As a result, intramolecular PeT within the ligand took place and the luminescence of **Tb-33** was quenched. The drastic change in the $\text{Tb}(\text{III})$ emission in response to the enzymatic activity of LAP confirms that **Tb-32** was indeed an intramolecular PeT-based luminescence probe of LAP [53].

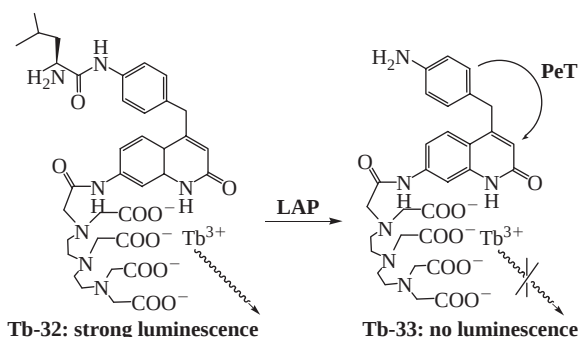


Figure 13.14 Schematic representation of the probe **Tb-32** for LAP.

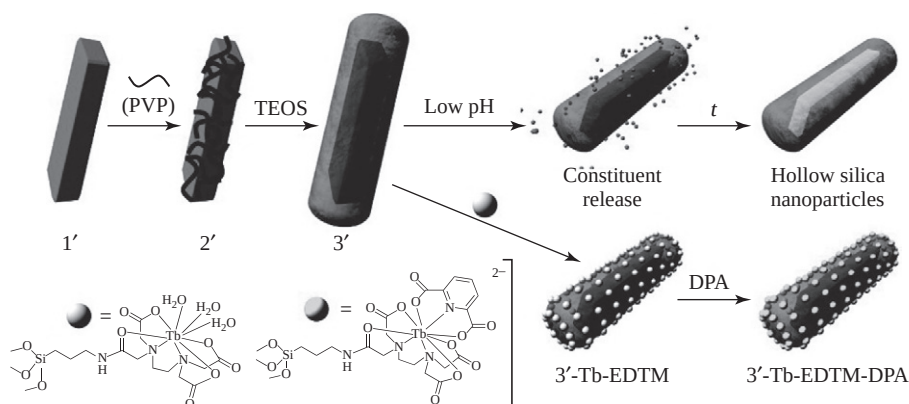


Figure 13.15 Schematic representation of synthesis and surface modification of nanoparticles [54]. (Reproduced with permission from W.J. Rieter *et al.*, “Surface modification and functionalization of nanoscale metal-organic frameworks for controlled release and luminescence sensing,” *Journal of the American Chemical Society*, **129**, 9852–9853, 2007. © 2007 American Chemical Society.)

Dipicolinic acid (DPA) is a unique biomarker and a major constituent of bacterial spores. Lin and coworkers reported the use of silica-coated nanoscale lanthanide-organic frameworks (NMOFs) **3'**-Tb-EDTM (EDTM = ethylenediamine triacetic acid) to detect DPA [54]. As shown in Figure 13.15, **3'**-Tb-EDTM was prepared from Eu-doped Gd(L34)_{1.5}(H₂O)₂@SiO₂ nanoparticles (L34 = 1,4-benzenedicarboxylate) and further surface functionalized with a silylated Tb-EDTM monoamide derivative. Upon excitation at 278 nm, **3'**-Tb-EDTM exhibited only Eu luminescence, as the Tb-EDTM moiety is essentially nonemissive. As DPA was added to an ethanolic dispersion of **3'**-Tb-EDTM, intense Tb(III) luminescence was observed, suggesting the formation of the Tb-EDTM-DPA complex. The Tb(III) luminescence signal provides a sensitive probe for DPA detection, while the Eu(III) emission from the NMOF core serves as a non-interfering internal calibration. The relationship between the ratio of Tb(III) to Eu(III) emission intensities and DPA concentration displayed normal saturation behavior. Such a ratiometric detection works well in Tris buffer solution and can selectively detect DPA in the presence of biologically prevalent interfering species such as amino acids. The DPA detection limit for this system was estimated to be about 48 nM [54].

The emissive lanthanide complexes can also be used to detect vapors of volatile organic compounds such as alcohols, acetone, aldehydes, and esters [55, 56]. For example, Rocha and coworkers reported a novel europium(III)-organic framework [Eu₂(L35)₃] (**Eu-35**) [L35 = 4,4'-(hexafluoroisopropylidene)-bis(benzoic acid)] as an efficient sensor of ethanol in the presence of water and under ambient conditions [56]. Single-crystal diffraction analysis indicated that three symmetrically independent ligands give rise to a microporous hydrophobic structure with both strongly hindered fluorinated channels and relatively free channels surrounded by the aromatic groups. As shown in Figure 13.16, a rapid decrease in emission intensity at 619 nm was measured for **Eu-35** in the presence of ethanol, and a rapid recovery (almost to the initial value) was observed when the **Eu-35** sample was exposed to air. Moreover, **Eu-35** exhibits a similar sensing behavior when exposed to a gaseous mixture containing water and ethanol.

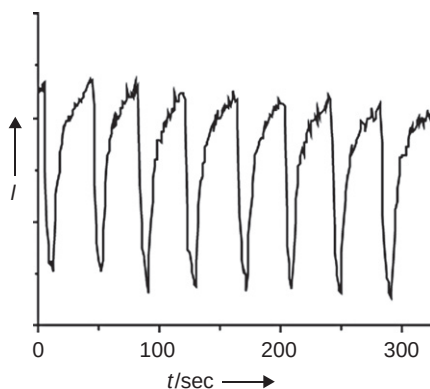


Figure 13.16 Variation of the fluorescence intensity of **Eu-35** at 619 nm under alternating streams of air saturated with ethanol (signal intensity decreases) and ethanol-free air (signal intensity increases) [56]. (Reproduced with permission from B.V. Harbuzaru *et al.*, “Metal-organic nanoporous structures with anisotropic photoluminescence and magnetic properties and their use as sensors,” *Angewandte Chemie International Edition*, 2008, **47**, no. 6, 1080–1083. © Wiley-VCH Verlag GmbH & Co. KGaA.)

13.3 Bioimaging Based on Luminescent Rare Earth Complexes

13.3.1 Time-Resolved Luminescence Imaging

The earliest use of lanthanide ions in imaging arose from the need for high-sensitivity probes for use in bioassays. As lanthanide ions have much longer luminescence lifetimes than conventional fluorescent probes, the emissive signals they produce can be separated from background biological fluorescence (autofluorescence) using a time-resolved technique (as illustrated in Figure 13.2) [57].

Time-resolved luminescence imaging requires a special experimental set-up whereby a time-gated image intensifier is synchronized with a laser pulse and is used to control the time interval over which measurements are made. In 2007, Nagano and coworkers demonstrated a new system for time-resolved luminescence microscopy (TRLM), as shown in Figure 13.17a [58]. In this system, the excitation light from a xenon flash lamp passes through the excitation filter and is focused onto the samples with dichroic mirrors. The emission light passes through the emission filter and is separated from the excitation light, and then is collected by a charge-coupled device (CCD) camera. It should be noted that the I.I. unit passes the long-lived luminescence signal to the CCD camera, controlling the delay time, the gate time, and the gain. By varying the degree of synchronization between the excitation pulse and the time-gate, it is possible to apply a time delay to the intensifier, and hence to exclude short-lived processes. As a result, the complete elimination of short-lived background fluorescence can be achieved.

An example of the utility of the time-resolved technique in eliminating the interference from background fluorescence in bioimaging is shown in Figure 13.17b. Nagano and coworkers compared time-resolved luminescence microscopy with conventional microscopy using live cultured HeLa cells injected with a Eu^{3+} complex **Eu-36** (or **Eu-37**). In the prompt fluorescence images, both the luminescence of **Eu-36** (or **Eu-37**) and weak autofluorescence from

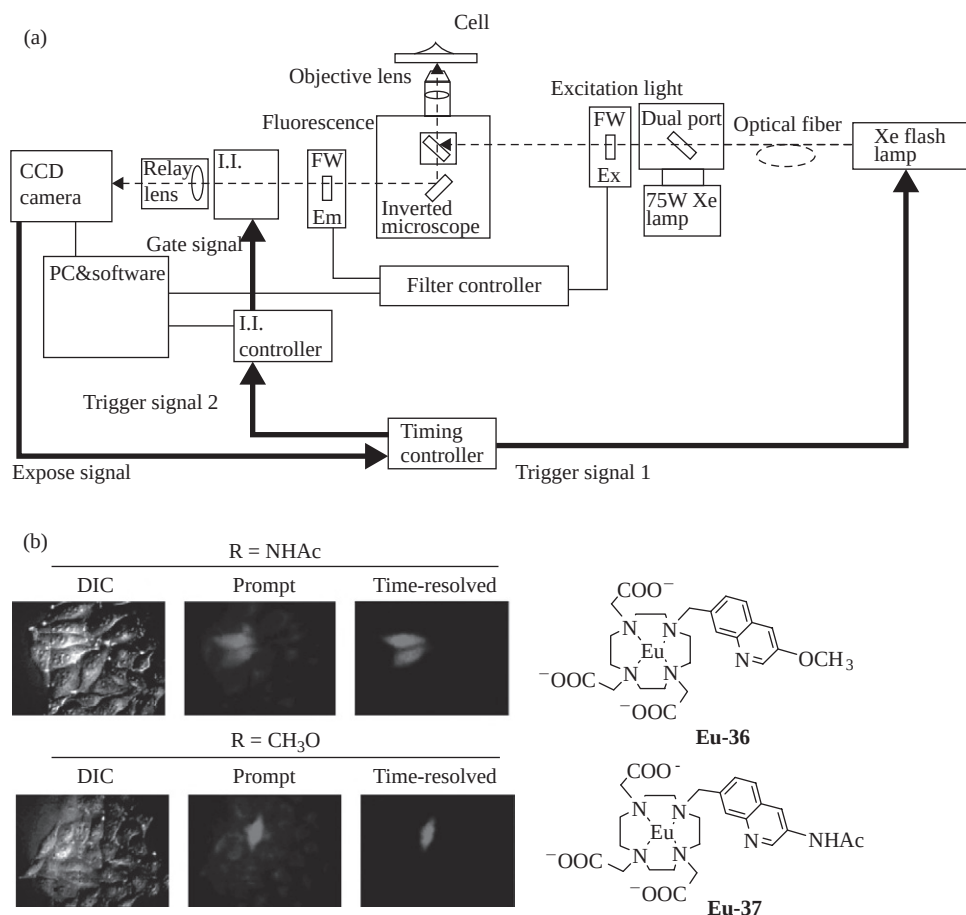


Figure 13.17 (a) Schematic diagram of the optical apparatus used for the time-resolved luminescence microscopy system. (b) Bright-field transmission images (DIC), prompt fluorescence images (Prompt), and time-resolved luminescence images of living cells injected with **Eu-36** (or **Eu-37**) in HBSS buffer. The fluorescence was measured at 617 ± 37 nm, with excitation at 360 ± 40 nm [58]. (Reproduced with permission from K. Hanaoka *et al.*, “Time-resolved long-lived luminescence imaging method employing luminescent lanthanide probes with a new microscopy system,” *Journal of the American Chemical Society*, **129**, 13502–13509, 2007. © 2007 American Chemical Society.)

untreated cells was visible (Figure 13.17b). In the TRLM images, the short-lived autofluorescence from the cells was gated out, leaving only **Eu-36** (or **Eu-37**)-injected cells clearly distinguishable [58].

13.3.2 Types of Luminescent Rare Earth Complexes for Bioimaging

A viable luminescent bioprobe has to meet several stringent requirements, among which are adequate photophysical properties, thermodynamic stability and kinetic inertness at physiological

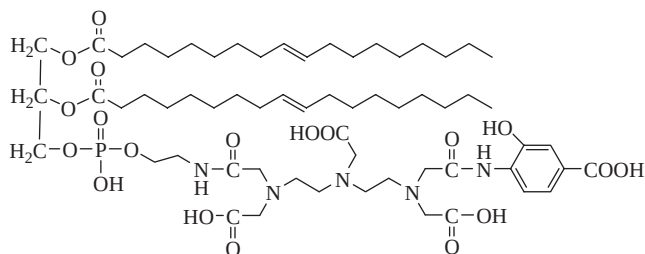


Figure 13.18 Chemical structure of the ligand L38.

pH, and non-cytotoxicity. An early use of lanthanide complexes in time-resolved microscopy imaging was reported by Saavedra and coworkers. In 1995, they examined the use of two Tb chelates as staining agents for time-resolved total internal reflection fluorescence microscopy (TIRFM) of substrate-adherent cells [59]. Furthermore, they demonstrated another Tb(III) chelate **Tb-38** with a ligand L38 of dioleoylphosphatidylethanolamine conjugated to diethylenetriaminepentaacetyl-4-aminosalicylic acid (Figure 13.18) as a long-lived probe for time-resolved TIRFM of cells. Under excitation at 310 nm, **Tb-38** exhibited characteristic Tb³⁺ emission with a lifetime of 1.57 ms. The investigation with time-resolved TIRFM of Swiss albino mouse 3T3 cells stained with **Tb-38** confirmed the suitability of **Tb-38** as a membrane-staining agent [60].

The majority of work on lanthanide-based bioprobes has focused on the emissive complexes of Eu(III) and Tb(III). Transitions between the f–f electronic states of lanthanide(III) ions are symmetry-forbidden, resulting in extremely low molar extinction coefficients for direct excitation. This problem is averted by incorporating a sensitizing moiety into the ligand structure. The moiety needs to possess a triplet energy at least 2000 cm^{−1} above the Eu ⁵D₀ (17 200 cm^{−1}) or Tb ⁵D₄ (20 400 cm^{−1}) excited states in order to avoid back energy transfer from the excited lanthanide ion to the triplet state of the sensitizer (Figure 13.1). Therefore, the sensitizer must be selected carefully. Eu or Tb sensitization requires a sensitizing moiety that possesses a small singlet–triplet energy gap of <7000 cm^{−1}, with an S₁ excited state lying <29 000 cm^{−1} above the ground state [61].

13.3.3 Luminescent Rare Earth Complexes with “Privileged” Cyclen Core Structures as Bioimaging Probes

Parker’s group undertook systematic studies of more than 60 emissive Eu and Tb complexes with “privileged” cyclen core structures, examining the time dependence of cellular uptake and compartmentalization, cellular toxicity, protein affinity, and quenching sensitivity [34, 62–75]. Each complex consisted either of a different chromophore with a common ligand core structure or was based on the same chromophore with varying ligand donors. Sensitizers used included acridones, tetraazatriphenylenes, azaxanthenes, azathi-axanthenes, and pyrazoyl-azaxanthenes, these being amenable to excitation in the range 337–410 nm.

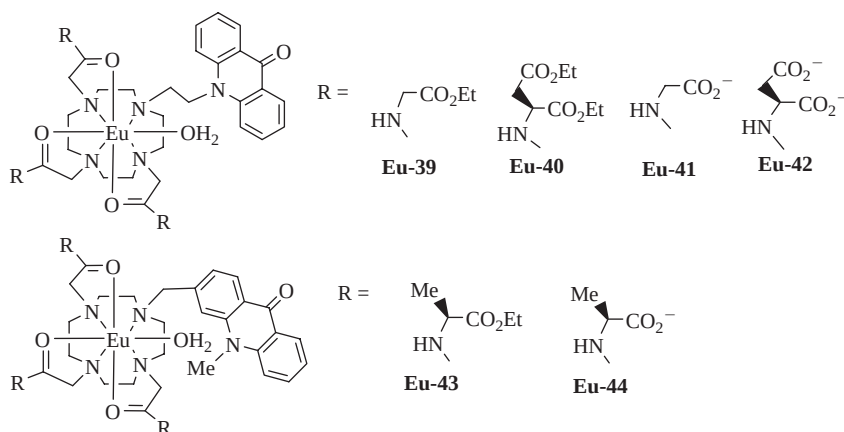


Figure 13.19 Chemical structures of the europium complexes incorporating an N- or C-linked acridone chromophore.

13.3.3.1 Acridones as Sensitizers

The acridone chromophore allows sensitization of Eu emission following excitation at 390–410 nm. Parker and coworkers reported a series of cationic, zwitterionic, and anionic macrocyclic europium complexes incorporating N- or C-linked acridone chromophores (Figures 13.11 and 13.19) [46]. Among these Eu complexes, **Eu-19**, **Eu-22**, and **Eu-24** (Figure 13.11) were selected as the cationic, zwitterionic, and anionic complexes, respectively, and their interaction with living cells were investigated in detail. Interestingly, the charged complexes **Eu-19**/**Eu-24** showed no evidence of toxicity [same number of live cells ($95 \pm 2\%$) as a control with no added complex], while the neutral complex **Eu-22** showed only a slight toxic effect (87% live cells). By selectively examining the Eu(III) emission by fluorescence microscopy under excitation at 400 nm, each complex displayed a similar distribution of staining, resembling an endosomal/lysosomal localization. Indeed, localization and staining appeared to be independent of the period of incubation or the nature of the complex.

13.3.3.2 Azaxanthenes and Azathiaxanthenes as Sensitizers

Being similar in structure to acridone, azaxanthenes and azathiaxanthenes can also be used as sensitizers of luminescent lanthanide complexes. Figure 13.20 shows these chemical structures of some europium(III) complexes with heptadentate macrocyclic ligands bearing azaxanthone or azathiaxanthone chromophores [66, 67]. Parker and coworkers investigated the usefulness of these complexes as responsive probes of the intracellular environment. For example, the localization behavior of **Eu-46** with an azathiaxanthone moiety in both CHO and NIH-3T3 cells was examined by microscopy. As shown in Figure 13.21, localization in the mitochondria was observed after 4 h of incubation with **Eu-46** (50 μM) solution, which was consistent with co-localization studies using Mitotracker GreenTM. Further investigation of the intracellular trafficking indicated that **Eu-46** appeared to migrate from the mitochondria to late endosomes/lysosomes (Figure 13.21) when longer incubation times were used [68]. Moreover,

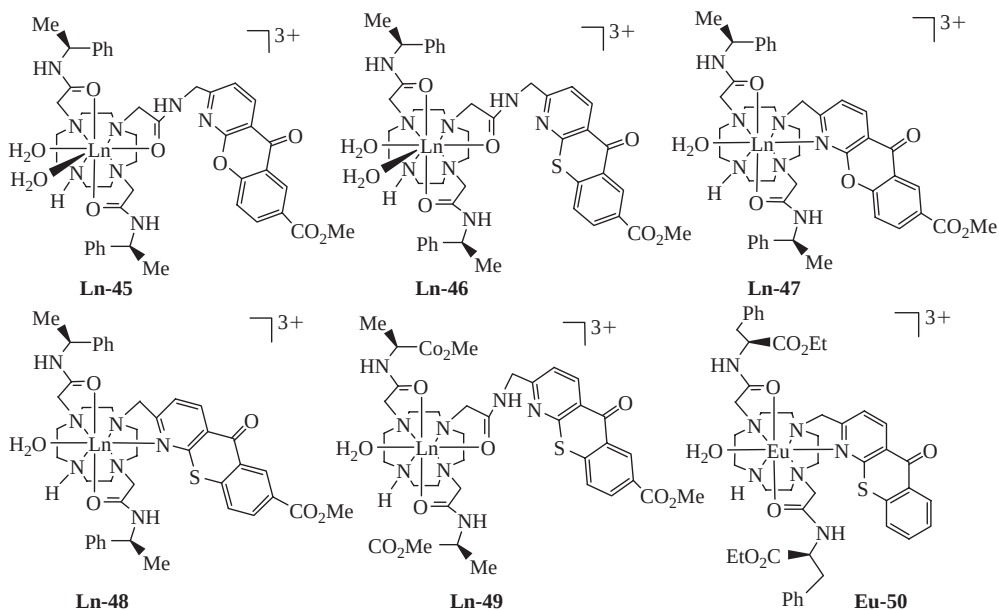


Figure 13.20 Chemical structures of lanthanide complexes **Ln-45**–**Ln-50** incorporating an N- or C-linked azaxanthone and azathioxanthone chromophore.

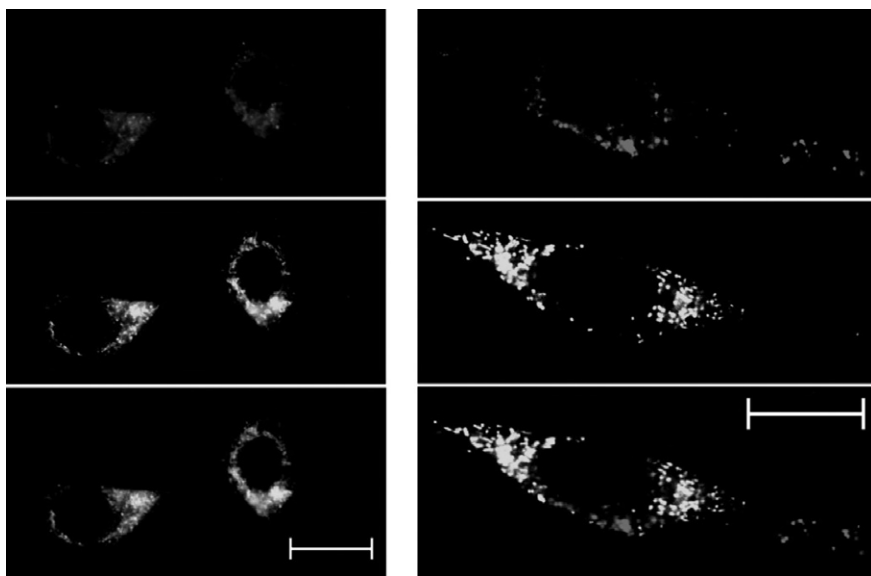


Figure 13.21 Epifluorescence microscopy images (left, 4 h incubation; right, 24 h; 50 μ M **Eu-46**) showing (left) at 4 h amitochondrial localization profile (upper, Eu emission; center, Mitotracker Green; lower, merged imaged; scale bar 20 μ m) and (right) at 24 h a lysosomal profile [61]. (Reproduced with permission from C. P. Montgomery *et al.*, "Cell-penetrating metal complex optical probes: targeted and responsive systems based on lanthanide luminescence," *Accounts of Chemical Research*, **42**, 925-937, 2009. © 2009 American Chemical Society.)

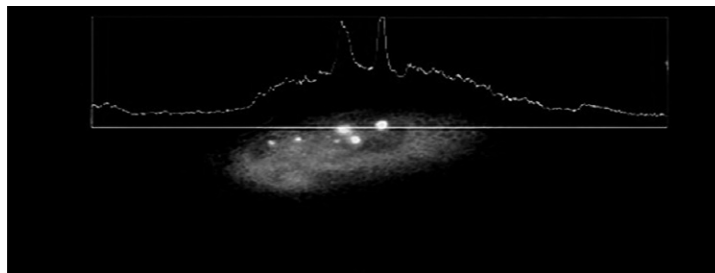


Figure 13.22 Luminescence image of NIH/3T3 cells loaded with **Eu-50** (500 μM , 1 h) in DMEM ($\lambda_{\text{ex}} = 450 \pm 30 \text{ nm}$; $\lambda_{\text{em}} = 510 \pm 25 \text{ nm}$). Scale bar: 10 μm [69]. (Reproduced with permission from J. Yu *et al.*, “A europium complex that selectively stains nucleoli of cells,” *Journal of the American Chemical Society*, **128**, 2294–2300, 2006. © 2006 American Chemical Society.)

the egress of **Eu-49** from CHO cells was investigated. When CHO cells were incubated with 100 μM **Eu-49** for 4 h, there was obvious luminescence originating from endosomes or lysosomes in the perinuclear region. After removing the growth medium, washing the cells with phosphate buffered saline (PBS) and incubating them in fresh medium for 1 h, the localization profile changed significantly. A lysosomal/endosomal profile was still manifest, but a more even distribution throughout the cytoplasm was apparent.

Interestingly, the europium complexes **Eu-50** (Figure 13.20) [69] and **Eu-3** (Figure 13.7) [70] containing an azathioxanthone moiety can selectively stain the nucleolus of live cells. For example, as shown in Figure 13.22, **Eu-50** can selectively stain the nucleolus of live cells and fixed cells, which was confirmed by co-localization experiments using live cells simultaneously loaded with both **Eu-50** and the commercially available nucleolar stain SYTO RNA-Select. When **Eu-50** was loaded at 4°C, europium luminescence was still clearly observed, indicating that the cell staining mechanism of **Eu-50** is unlikely to be endocytosis. The selective staining of the nucleolus may be correlated with strong binding to serum albumin [69].

13.3.3.3 Tetraazatriphenylene as a Sensitizer

As a bidentate ligand, the tetraazatriphenylene chromophore possesses a fast rate of inter-system crossing and a triplet energy in the order of 24 000 cm^{-1} (singlet energy about 29 000 cm^{-1}), higher than the lowest energy (20 400 cm^{-1}) of $^5\text{D}_4$ of the Tb(III) ion. Therefore, the tetraazatriphenylene chromophore is an effective sensitizer of lanthanide luminescence [71]. Moreover, the tetraazatriphenylene moiety may intercalate between the base pairs of DNA [72]. Therefore, some Eu(III) and Tb(III) complexes containing a tetraazatriphenylene moiety have attracted more attention.

Parker and coworkers also reported a series of cationic, neutral, and anionic europium and terbium complexes containing a tetraazatriphenylene moiety (Figure 13.23) and investigated the interaction of these Eu(III) complexes with various living cells [66, 73, 74]. Interestingly, cellular uptake of either of the cationic complexes **Tb-52** and **Tb-57** is favored over uptake of the related neutral complex (**Tb-53**) and anionic complexes (**Tb-54** and **Tb-56**) [66]. The cationic lanthanide complexes are taken up by mouse skin fibroblast (NIH/3T3) cells and tend

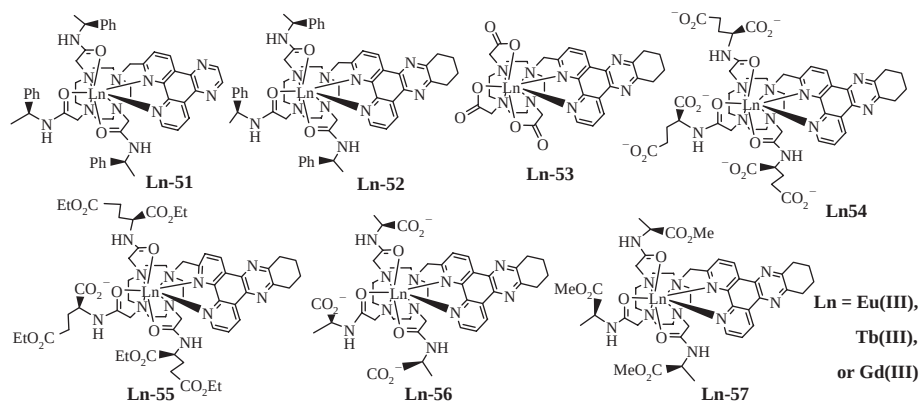


Figure 13.23 Chemical structures of the lanthanide-based complexes **Ln-51–Ln-57** containing a tetraazatriphenylene moiety.

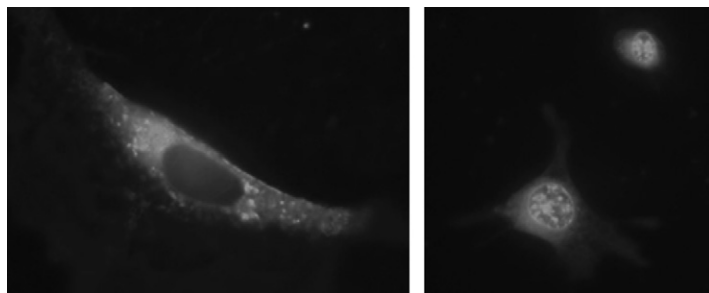


Figure 13.24 (Left) Fluorescence microscope image showing a live NIH/3T3 cell stained with **Tb-52** (0.3 mM) for 4 h. (Right) Fluorescence microscope image revealing the localization of **Tb-52** (1 mM in medium, 24 h post-incubation) in the cell nucleus [73]. (Reproduced from R.A. Poole *et al.*, “Synthesis and characterisation of highly emissive and kinetically stable lanthanide complexes suitable for usage ‘in cellulo’,” *Organic & Biomolecular Chemistry*, **3**, 1013–1024, 2005, by permission of The Royal Society of Chemistry.)

to localize inside the cell nucleus. Furthermore, the spatio-temporal localization of **Tb-52** in NIH/3T3 cells was investigated in detail using a time-course series of images of NIH/3T3 cells incubated with **Tb-52** for from 1 to 48 h. As shown in Figure 13.24 (left), the image of a cell incubated with a 0.3 mM solution complex for 4 h clearly highlights the localization of **Tb-52** in the cytoplasm. Upon continuous exposure to **Tb-52**, most of the luminescence is observed in the cell nucleus and nuclear membrane with a residual diffuse luminescence in the cytosol (Figure 13.24, right) [73]. After removal of unbound complex by washing with phosphate-buffered saline solution, the luminescence in the cell nucleus becomes progressively less intense and **Tb-52** is found to be distributed mostly in the cytosol once more. The data reveal that transport into and out of the cell nucleus is reversible and requires a favorable concentration gradient of the complex [74].

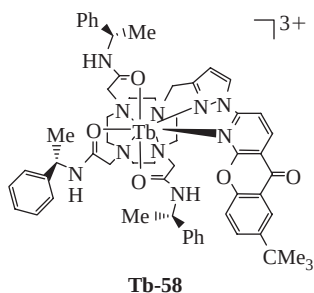


Figure 13.25 Chemical structure of complex **Tb-58**.

In addition, pyrazoyl-azaxanthone can also be used as a sensitizer of lanthanide complexes. An emissive terbium complex **Tb-58** incorporating a pyrazoyl-1-aza-xanthone chromophore (Figure 13.25) exhibits cellular uptake and possesses a much lower sensitivity to excited state quenching. For example, **Tb-58** was incubated for varying periods of time (from 1 to 12 h; 50 or 100 μM complex) with CHO or NIH/3T3 cells. Examination of the loaded cells by luminescence microscopy revealed complex uptake, and localization within endosomes in the cytoplasm, presumably following receptor mediated endocytosis, but no tendency to nuclear localization [75].

13.3.4 Luminescent Rare Earth Complexes with Bis(benzimidazole)pyridine Tridentate Units as Bioimaging Probes

The bis(benzimidazole)pyridine tridentate unit makes up an entire class of novel and versatile building blocks [76]. In particular, the bis(benzimidazole)pyridine tridentate unit, which has a strongly coordinating group of a carboxylic acid, as shown in Figure 13.26, can induce nine-coordinate, tricapped trigonal prismatic environments around the lanthanide ions [77]. This environment is especially protective against interaction of the lanthanide ion with water, providing remarkable luminescent properties. Bünzli and coworkers developed a series of bis(benzimidazole)pyridine tridentate ligands (Figure 13.26) to produce stable mono- and bimetallic lanthanide complexes displaying programmed functionalities [76–84].

Recently, Bünzli and coworkers reported that neutral homobimetallic helicate $[\text{Eu}_2(\text{L59})_3]$, containing the dicarboxylic acid ligand **L59** (Figure 13.26), was very stable in water, and showed a high luminescence quantum yield of 24% and long lifetime of 2.43 ms [80]. However, the water solubility of $[\text{Eu}_2(\text{L59})_3]$ is limited, particularly at $\text{pH} < 4.27$. Introduction of a short polyoxyethylene side chain, either on the 4-position of the pyridines (**L60**) [81] or on the benzimidazoles (**L61**) [82, 83], improves water-solubility of their helicates. The conditional stability constants $\log \beta_{23}$ of the **L60** and **L61** helicates are in the range 22–25, revealing high thermodynamic stability of the helicates at physiological pH. The ligand triplet state (0-phonon transition of **L60** and **L61** at around $20\,800\text{ cm}^{-1}$ and $21\,900\text{ cm}^{-1}$, respectively) has an adequate energy for sensitizing the Eu(III) luminescence (quantum yield $> 11\%$) in aerated water at pH 7.4. Determined by means of the WST-1 assay, no significant effect of $[\text{Eu}_2(\text{L60})_3]$ or $[\text{Eu}_2(\text{L61})_3]$ on the viability of several cell lines is observed. Moreover, the cell staining properties of $[\text{Eu}_2(\text{L60})_3]$ and $[\text{Eu}_2(\text{L61})_3]$ are demonstrated by counterstaining

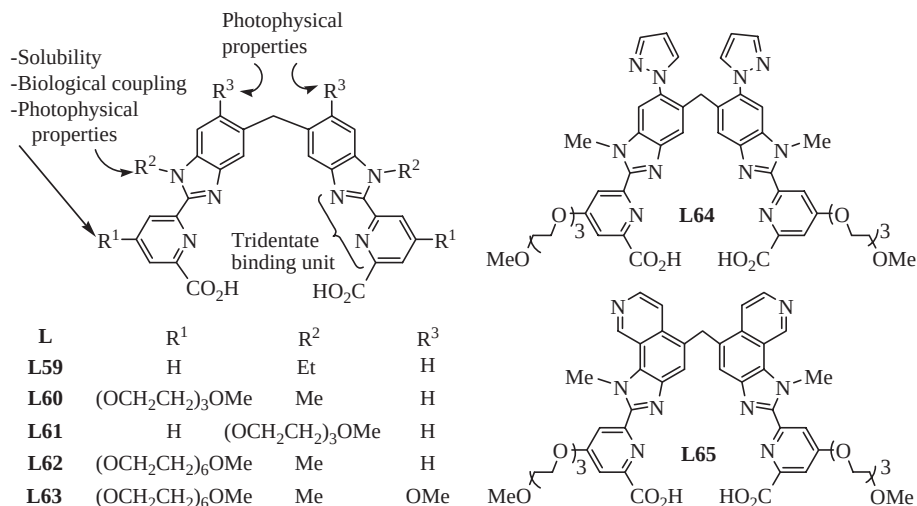


Figure 13.26 Chemical structures of some bis(benzimidazole)pyridine tridentate ligands reported by Bünzli *et al.*

experiments with the commercially available nucleus stain acridine orange. After incubation with [Eu₂(L60)₃] or [Eu₂(L61)₃] as early as 15–30 min, the red Eu(III) emission is clearly visible in the cytoplasm of the cells while the green acridine orange emission originates from the cell nucleus. Further investigation suggested that the helicates probably permeate into the cytoplasm of HeLa cells by endocytosis.

Furthermore, a new ligand **L62** was synthesized by introduction of six (OCH₂CH₂) units into R² (Figure 13.26) [77]. At physiological pH, log β₂₃ of [Eu₂(L62)₃] is around 28, resulting in the speciation of the Eu(III) helicate being >92% for a total ligand concentration of 1 mM. The 0–phonon transition at about 21 800 cm⁻¹ of **L62** features adequate energy for sensitizing the Eu(III) luminescence and [Eu₂(L62)₃] displays high luminescence quantum yield of 19% and a long lifetime of 2.43 ms. Upon incubation with up to 500 μM [Eu₂(L62)₃] for 24 h, the viability of HeLa cells is unaffected. As shown in Figure 13.27, [Eu₂(L62)₃] clearly permeates into HeLa cells and stains the cytoplasm in a concentration dependent manner, the higher the concentration, the brighter the image. Even a loading concentration of [Eu₂(L62)₃] as low as 10 μM still produced distinct luminescent cell images (Figure 13.27, top). Further counter-staining with acridine orange highlighted the red emission of the helicate in the cytoplasm of the cells and the green acridine orange emission in the nucleus (Figure 13.27 middle), confirming the cell localization of [Eu₂(L62)₃] in the cytoplasm. Furthermore, co-staining experiments with [Eu₂(L62)₃] and a commercially available marker for endocytosis (BIODIPY FL labeled transferrin or LDL), revealed that [Eu₂(L62)₃]-stained cell compartments also contain the organic marker (Figure 13.27 bottom, third column), as evidenced by the appearance of bright yellow spots (Figure 13.27 bottom, fourth column) after merging the images. These observations strongly suggest that the uptake of [Eu₂(L62)₃] occurs via a lysosomally directed and/or a recycling endosomal pathway [77].

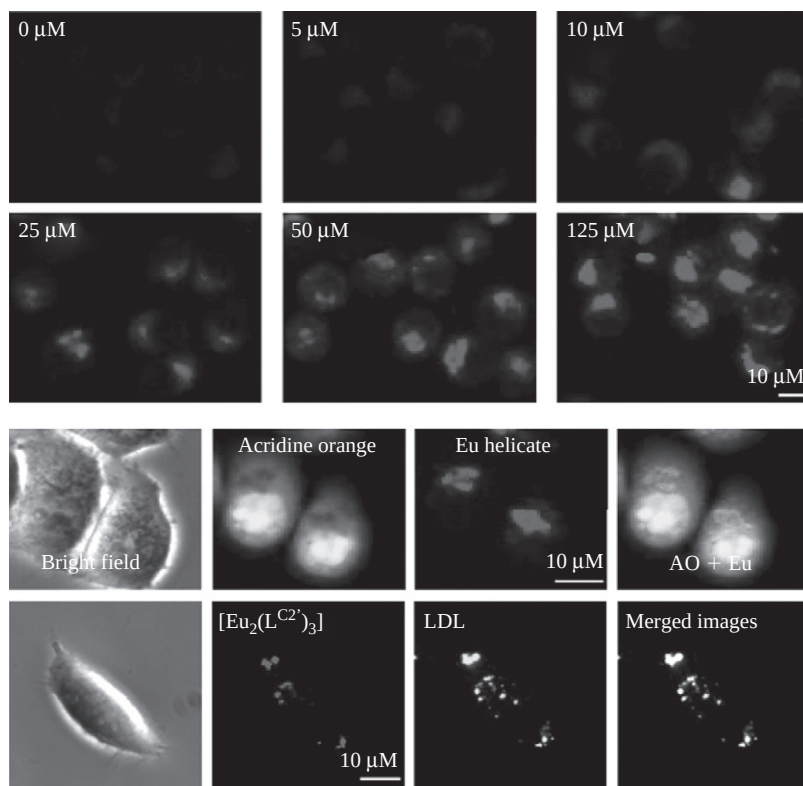


Figure 13.27 (Top) Luminescence images of HeLa cells loaded with different concentrations of [Eu₂(L62)₃] in RPMI-1640 for 7 h at 37°C. ($\lambda_{\text{ex}} = 330$ nm, $\lambda_{\text{em}} > 585$ nm, exposure time 60 s). (Middle) Images of HeLa cells loaded with 250 μM [Eu₂(L62)₃] (5 h at 37°C, exposure time 10 s), then incubated with 40 mg mL⁻¹ acridine orange ($\lambda_{\text{ex}} = 450$ –490 nm; $\lambda_{\text{em}} = 515$ –565 nm, exposure time 10 ms) in PBS (5 min at room temperature). (Bottom) Co-localization experiments: cells loaded with 250 μM [Eu₂(L62)₃] and 15 mg mL⁻¹ BIODIPY FL LDL (0.5 h, $\lambda_{\text{ex}} = 470$ nm, 2 s exposure time) [77]. (Reproduced from E. Deiters *et al.*, “Effect of the length of polyoxyethylene substituents on luminescent bimetallic lanthanide bioprobes,” *New Journal of Chemistry*, **32**, 1140–1152, 2008, by permission of The Royal Society of Chemistry (RSC) for the Centre National de la Recherche Scientifique (CNRS) and the RSC.)

The only drawback of the above new class of bimetallic lanthanide luminescent bioprobes is the excitation wavelength in the UV range, with an absorption maximum around 320–325 nm. To shift the excitation wavelength towards the visible range, three new ligands **L63**, **L64**, and **L64** (Figure 13.26) were synthesized. These neutral bimetallic helicates [Ln₂(L63)₃], [Ln₂(L64)₃], and [Ln₂(L65)₃] are thermodynamically stable in water ($\log \beta_{23} = 27$ at pH 7.4) and display a metal–ion environment with pseudo-D₃ symmetry and are devoid of coordinated water molecules. These helicates are considered non-cytotoxic, with IC₅₀ > 500 μM. In particular, [Eu₂(L65)₃] exhibits a high quantum yield of 9% with excitation wavelength into

the visible range. The relatively long excitation wavelength allows easy recording of bright luminescent images on a confocal microscope ($\lambda_{\text{ex}} = 405 \text{ nm}$) [84].

13.3.5 Hybrid Rare Earth Complexes as Luminescent Probes in Bioimaging

A novel strategy for designing lanthanide-based bioprobes is to synthesize luminescent lanthanide nanoparticles [85–87]. For example, Zhang and coworkers reported that an amphiphilic tris(dibenzoylmethanato)europium(III) $[\text{Eu}(\text{DBM})_3]$ coordinated copolymer (Figure 13.28) emitted strong red luminescence [86]. The copolymer self-assembled into body temperature-thermosensitive micelles of around 260 nm size. Cell imaging indicated that the micelles could be internalized into A549 cells. The copolymer was further subjected to an *in vivo* test with zebrafish. After incubation until hatching on the sixth day, micelles were found to exist inside the bodies of the fish. Interestingly, after the larvae were transferred into fresh aqueous media on the third day, the fluorescence in larvae ($n = 24$) had faded completely due to excretion. These results showed that the micelles had good biocompatibility.

In addition, Yuan and coworkers described spherical silica-based luminescent europium nanoparticles with a uniform size of about 10 nm in diameter [87]. Interestingly, the nanoparticles can be excited over a wavelength range from the UV to visible light (200–450 nm) in aqueous solution, and could be used for time-resolved luminescence imaging of an environmental pathogen, *Giardia lamblia*.

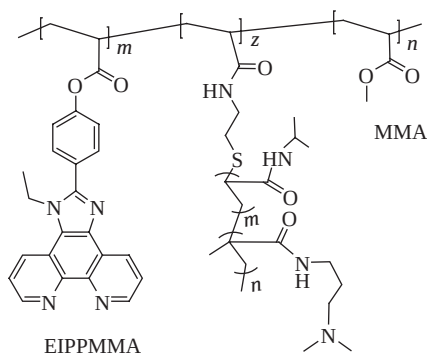


Figure 13.28 Chemical structure of P(MMA-*co*-EIPPMMA)-*co*-P(NIPAAm-*co*-NDAPM) copolymer.

13.4 Rare Earth Luminescent Chemosensors as Bioimaging Probes

To date, about 70 cell-permeable and emissive lanthanide complexes have been investigated as bioimaging probes. Fluorescence microscopy studies have revealed that the uptake and compartmentalization profile was dependent on the structure of the probe. However, the above-mentioned lanthanide complexes cannot recognize functional biomolecules in living cells. In fact, using luminescence microscopy in combination with luminescent chemosensors as bioimaging probes, detecting functional molecules in living cells is of great interest to many scientists [88, 89]. Recently, there have been efforts to design and synthesize lanthanide-based chemosensors for monitoring Zn^{2+} and $^1\text{O}_2$ in living cells.

13.4.1 Rare Earth Luminescent Chemosensors as Bioimaging Probes of Zn^{2+}

Zinc (Zn^{2+}) is the second most abundant metal ion after iron in the human body, and plays critical roles in regulating gene expression, enzyme regulation, and neurotransmission [90]. Zn^{2+} is also known to be responsible for the formation of amyloid plaques during the onset of Alzheimer's disease [91]. At present, there is considerable interest in the development of Zn^{2+} -selective luminescence chemosensors as bioimaging probes [92, 93].

To date, some lanthanide-based luminescent chemosensors for the detection of Zn^{2+} have been reported. In 2000, Parker and coworkers developed two luminescent lanthanide complexes **Ln-66** and **Ln-67** (Figure 13.29) binding Zn^{2+} with a dissociation constant K_d of $0.6\ \mu\text{M}$ (295 K, pH 7.3) [94]. In 2003, Nagano and coworkers demonstrated a lanthanide complex **Tb-13** (Figure 13.8) showing a large enhancement in luminescence upon Zn^{2+} addition with K_d of $2.6\ \text{nM}$ (295 K, pH 7.4) [35]. However, these compounds are unsuitable for biological application, because of their short excitation wavelength and inconvenient pH sensitivity.

Recently, Nagano's group synthesized a novel europium(III)-based sensor **Eu-68** (Figure 13.29) for detecting Zn^{2+} [95]. For **Eu-68**, a quinolyl ligand was employed as both a chromophore and an acceptor of Zn^{2+} . The luminescence emission spectrum of **Eu-68** displayed three bands at 579, 593, and 614 nm, corresponding to the deactivation of the $^5\text{D}_0$ excited state down to the $^7\text{F}_0$, $^7\text{F}_1$, and $^7\text{F}_2$ ground state, respectively. The fluorescence spectra of **Eu-68** ($20\ \mu\text{M}$) upon addition of increasing amounts of Zn^{2+} were measured with and without a delay time of $50\ \mu\text{s}$. Upon addition of 1.0 equiv of Zn^{2+} , the time-resolved luminescence emission intensity of **Eu-68** ($50\ \mu\text{M}$) increased significantly (8.5-fold, Figure 13.30). When an excess of Zn^{2+} was added, the emission intensity remained at a plateau (Figure 13.30), indicating 1 : 1 complex stoichiometry for **Eu-68** and Zn^{2+} . However, when measuring the fluorescence emission spectra without a delay time, the short-lived fluorescence at 397 nm ascribed to direct emission from the quinolyl moiety of **Eu-68** was observed. All these results can be rationalized in terms of the necessity of time-delayed luminescence measurement for **Eu-68** recognition of Zn^{2+} .

In light of its high selectivity for Zn^{2+} over other biologically relevant metal cations, **Eu-68** was further investigated for monitoring Zn^{2+} in cultured living HeLa cells by time-resolved luminescence (TRL) microscopy [57]. The delay and gate time were set at 70 and $808\ \mu\text{s}$, respectively. For a single HeLa cell injected with **Eu-68**, a prompt increase in intracellular luminescence was induced by adding Zn^{2+} ($50\ \mu\text{M}$) and a zinc selective ionophore of

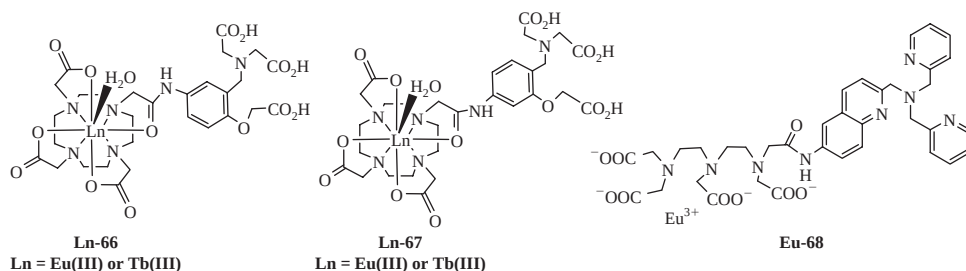


Figure 13.29 Chemical structures of complexes **Ln-66**, **Ln-67**, and **Eu-68**.

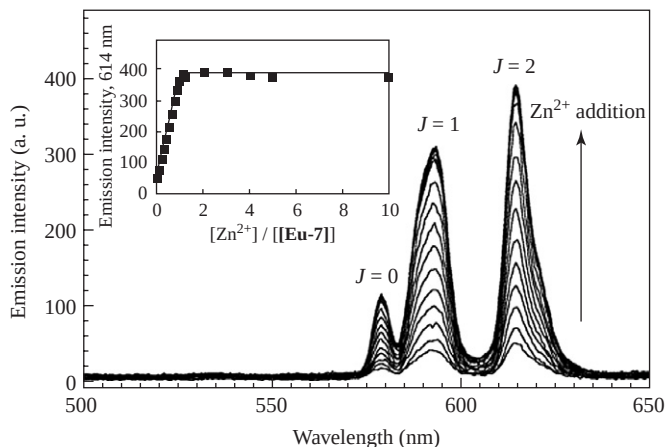


Figure 13.30 Luminescence spectra of **Eu-68** (50 μM) at pH 7.4 (100 mM HEPES buffer) upon addition of increasing amounts of Zn^{2+} (0–10.0 equiv) with a delay time of 50 μs and a gate-time of 1.00 ms ($\lambda_{\text{ex}} = 320 \text{ nm}$). Inset: the changes in luminescence intensity at $\lambda_{\text{em}} = 614 \text{ nm}$ [95]. (Reproduced with permission from K. Hanaoka *et al.*, “Development of a zinc ion-selective luminescent lanthanide chemosensor for biological applications,” *Journal of the American Chemical Society*, **126**, 12470–12476, 2004. © 2004 American Chemical Society.)

2-mercaptopyridine *N*-oxide (pyrithione, 5 μM) to the medium at 5 min (Figure 13.31c). Furthermore, the luminescence intensity decreased immediately upon the extracellular addition of the chelator *N,N,N',N'*-tetrakis(2-picolyl) ethylenediamine (TPEN) (100 μM) at 15 min (Figure 13.31d). As shown in Figure 13.31e, the luminescence intensity data corresponding to TRL images clearly display the intracellular Zn^{2+} concentration changes, indicating that **Eu-68** could be used as a time-resolved luminescent probe for monitoring intracellular Zn^{2+} .

13.4.2 Rare Earth Luminescent Chemosensors as Bioimaging Probes of $^1\text{O}_2$

As a nonradical reactive oxygen species, singlet oxygen ($^1\text{O}_2$) can oxidize various types of biological molecules such as proteins, DNA, and lipids, and is thought to be an important toxic species [96, 97]. $^1\text{O}_2$ probably plays an important role in the cell signaling cascade and in the induction of gene expression [98]. The artificial photochemical generation of $^1\text{O}_2$ has found application in a cancer treatment protocol of photodynamic therapy [99]. Therefore, the development of systems for detecting intracellular $^1\text{O}_2$ is important.

In 2005, Yuan and coworkers demonstrated a Eu(III) complex **Eu-69** (Figure 13.32) as a sensitive and selective time-resolved luminescence probe for $^1\text{O}_2$ [100, 101]. The complex shows a low quantum yield of 0.58%, which was attributed to the triplet–triplet quenching between the terpyridine chromophore and anthracene groups. When **Eu-69** reacts specifically with $^1\text{O}_2$ to yield its endoperoxide (**EP-Eu-69**, Figure 13.32), the triplet–triplet quenching between the chromophore and anthracene groups disappears, which is accompanied by a great increase in luminescence intensity. The product shows a high luminescence quantum yield of

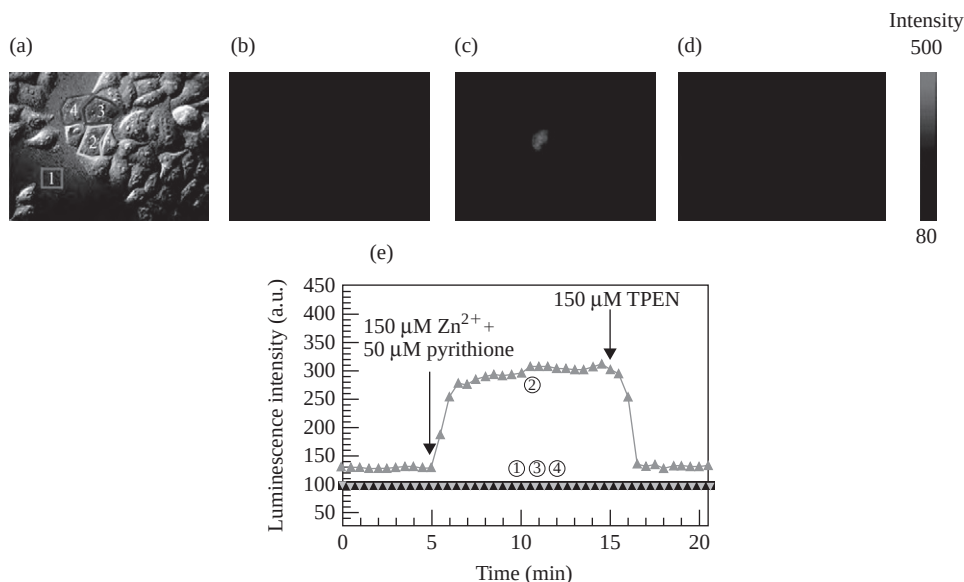


Figure 13.31 (a) Bright-field transmission and (b–d) TRL imaging of intracellular Zn^{2+} in living HeLa cells injected with **Eu-68**, using a delay time of $70 \mu\text{s}$ and a gate time of $808 \mu\text{s}$. The luminescence at $617 \pm 37 \text{ nm}$, excited at $360 \pm 40 \text{ nm}$, was measured at 30 s intervals. (b) TRL image at 0 min. (c) TRL image (7 min) following addition of $5 \mu\text{M}$ pyrithione and $50 \mu\text{M}$ ZnSO_4 to the medium at 5 min. (d) TRL image (17 min) following addition of $100 \mu\text{M}$ TPEN to the medium at 15 min. (e) Luminescence intensity data corresponds to TRL images in (b–d), which shows the average intensity of the corresponding area or cell area in (a) (1, extracellular region; 2, intracellular region of the injected cell; 3, 4, intracellular regions of non-injected cells) [58]. (Reproduced with permission from K. Hanaoka *et al.*, “Time-resolved long-lived luminescence imaging method employing luminescent lanthanide probes with a new microscopy system,” *Journal of the American Chemical Society*, **129**, 13502–13509, 2007. © 2007 American Chemical Society.)

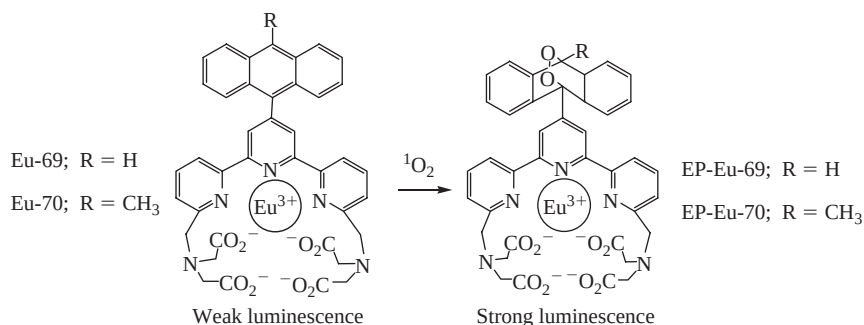


Figure 13.32 Luminescence enhancement accompanying **Eu-69** and **Eu-70** reaction with singlet oxygen ($^1\text{O}_2$).

10.0% and a long luminescence lifetime of 1.21 ms. These features make **Eu-69** a favorable probe for use in highly sensitive time-resolved luminescence detection of $^1\text{O}_2$.

In view of the fast reaction rate of the 10-methyl-9-anthryl moiety with $^1\text{O}_2$, Yuan and coworkers further developed another Eu^{3+} complex, [4'-(10-methyl-9-anthryl)-2,2':6',2''-terpyridine-6,6''-diyl]bis(methylenenitrilo)tetrakis(acetate)- Eu^{3+} (**Eu-70**, Figure 13.32) for monitoring $^1\text{O}_2$ in living cells [102]. **Eu-70** is almost nonluminescent, and will specifically react with $^1\text{O}_2$ over other reactive oxygen species (such as hydroxyl radicals, superoxide, hydrogen peroxide, and peroxyxynitrite) to form highly luminescent endoperoxide (**EP-Eu-70**, Figure 13.32). **Eu-70** was readily taken up by cultured HeLa cells during ordinary incubation together with the photosensitizer 5,10,15,20-tetrakis-(1-methyl-4-pyridinio)porphyrin tetra(*p*-toluenesulfonate) (TMPyP). The TMPyP-**Eu-70**-treated HeLa cells were used for time-resolved luminescence imaging to monitor intracellular $^1\text{O}_2$ generated by irradiation with 450–490 nm light. The luminescence intensities of four selected HeLa cells increased with irradiation time, indicating the increase of $^1\text{O}_2$ formed in the cells during the irradiation. Moreover, the luminescence enhancement of the cell nucleus occurred more rapidly than that of the cytoplasm (fringe of the cell).

13.5 Rare Earth Complexes as Multiphoton Luminescence Probes for Bioimaging

To date, UV light is still needed for the ligand sensitization process of luminescent lanthanide complexes, limiting the depth of investigation and producing some phototoxicity in biological samples, which is a drawback in bioimaging. Two-photon excitation, with simultaneous absorption of two photons of half energy, is an elegant way to circumvent the use of UV light. By using excitation with long-wavelength femtosecond pulses (about 10^{-13} s) at a high repetition rate (typically about 80 MHz), two-photon microscopy (TPM) greatly reduces UV-treatment problems and provides deeper penetration (hundreds of microns) and low photodamage and photobleaching outside of the focal plane [103, 104]. In addition, its intrinsic confocal character makes 3D-resolved microscopy possible. Therefore, two-photon sensitization of lanthanide complexes is an emerging field of research. For example, Wang and coworkers reported a tripyridine-sensitized Eu(III) complex **Eu-71** (Figure 13.33) with a significant two-photon absorption cross-section ($\delta_{2\text{PA}}$) value of 185 GM (GM = Goeppert–Mayer, where $1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$) at 735 nm, however, **Eu-71** is only stable in non-aqueous solvents [105].

Maury and coworkers reported a tricationic complex **Eu-72** (Figure 13.33) with a two-photon antenna effect produced by an alkyloxyphenylacetylene functionalized pyridine dicarboxamide ligand [106]. The complex **Eu-72** is soluble and very stable in aqueous media and shows a broad absorption band at 332 nm assigned to a charge transfer (CT) transition from the alkoxy donor to the pyridinic acceptor. Upon excitation of the ligand CT transition, **Eu-72** exhibits characteristic Eu(III) emission with high quantum yield of 15.7% and a long lifetime of 1.062 ms in water. Its maximal $\delta_{2\text{PA}}$ is high, about 92 GM at 700 nm. Furthermore, the luminescence behavior in fixed T24 cancer cells loaded with **Eu-72** in PBS solution was investigated by two-photon microscopy. Upon femtosecond 760 nm irradiation, red luminescence was observed mainly in the perinuclear region with a distribution appearing to coincident with the endoplasmic

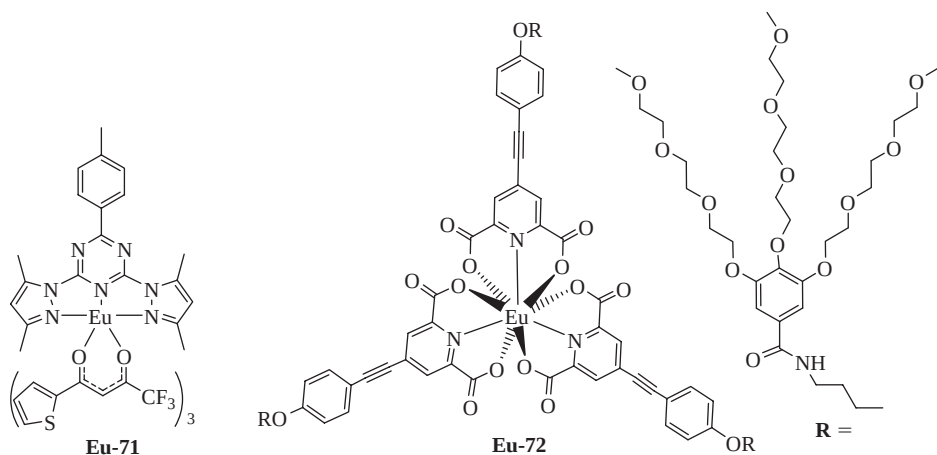


Figure 13.33 Chemical structure of **Eu-71** and **Eu-72**.

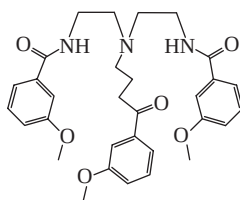


Figure 13.34 Chemical structure of the ligand L73.

reticulum. In addition, other Tb(III) complexes incorporating an N-coordinated azaxanthone group were applied in two-photon microscopy imaging of living cells [107, 108].

Recently, Wong and coworkers reported an emissive Tb(III) complex [Tb(L73)(NO₃)₃] (**Tb-73**, Figure 13.34) based on a ligand of *N*-[2-(bis[2-[(3-methoxybenzoyl)amino]ethyl]amino)ethyl]-3-methoxybenzamide (L73) as a three-photon luminescence probe with low cytotoxicity [109]. The three-photon process of **Tb-73** under excitation at a femtosecond 800 nm laser was confirmed by a power dependence experiment. The three-photon absorption cross section of **Tb-73** is around 1.9 GM. Furthermore, the interaction of three selected cells with **Tb-73** over different durations of time (from 0 to 60 min and 24 h) was investigated. As shown in Figure 13.34, intracellular luminescence increased as the exposure time increased. At an exposure time of 60 min, more than 95% of the cells under 800 nm excitation exhibited green luminescence, as was observed in the cytoplasmic foci around the cell nucleus.

Extension to the use of multi-photon induced luminescence lanthanide-based bioprobes adds new possibilities and challenges to the field. However, there are even fewer examples of multi-photon lanthanide bioprobes because achieving acceptable quantum yields is fairly difficult in view of the numerous nonradiative deactivation pathways created by a wealth of vibrations, including high energy oscillators located far from the emitting lanthanide ion.

13.6 Rare Earth Materials with Upconversion Luminescence for Bioimaging

13.6.1 General Concept of Upconversion Luminescence

The photoluminescence of the above lanthanide complexes may be classified as down-conversion luminescence (DCL). Through the technique of time-resolved luminescence measurement, these DCL lanthanide complexes can be used as bioprobes for *in vitro* imaging without the interference of autofluorescence. However, these complexes have some limitations in the application to *in vivo* imaging, caused by their short-wavelength excitation. Although two-photon microscopy makes possible the use of long-wavelength excitation, unfortunately, it also has some intrinsic limitations resulting from the utilization of a femtosecond pulse. The enormously high instantaneous power of the excitation light results in accelerated photo-bleaching within the focused sample volume. Therefore, DCL lanthanide complexes are not suitable for use as probes in *in vivo* bioimaging.

Alternatively, lanthanide upconversion luminescence materials have been proposed as a new generation of biological luminescent labels, due to their unique luminescence properties, such as the non-invasive and deep penetration of near-infrared (NIR) radiation, and probable elimination of autofluorescence from biological tissues. Upconversion luminescence (UCL) is a process whereby continuous-wave (CW) low-energy light in the NIR region (typically 980 nm) is converted into higher-energy visible light through multiple photon absorption or energy transfer [110]. Upconversion luminescence is a rather unusual process and can only occur in materials in which multi-phonon relaxation processes are not predominant. In lanthanide compounds, the 4f or 5f electrons are efficiently shielded and are thus not strongly involved in the metal-to-ligand bonding. As a consequence, electron-phonon coupling to f–f transitions is reduced, and multi-phonon relaxation processes become less competitive. Nowadays, Er^{3+} , Tm^{3+} , and Ho^{3+} typically featuring a ladder-like arrangement of energy levels are frequently used as activators (Figure 13.35) [111].

13.6.2 Rare Earth Complexes with Upconversion Luminescence

Recently, some lanthanide complexes with upconversion luminescence (UCL) have been developed by Jin and coworkers. In 2007, they used 2,3-pyrazinedicarboxylic acid (H_2pza) as a ligand to obtain a lanthanide–organic framework $[\text{Ln}(\text{pza})(\text{OH})]_n$ ($\text{Ln} = \text{Y}, \text{Er–Yb}$) with helical chains and novel 2D $(4^3)_2(4^6, 6^6, 8^3)$ topology. Interestingly, the Y : Er–Yb codoped coordination polymer $[(\text{Y} : \text{Er–Yb})(\text{pza})(\text{OH})(\text{H}_2\text{O})]_n$ gives off green and red upconversion emissions upon excitation at 975 nm arising from Er^{3+} transitions of $^4\text{S}_{3/2}^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ [112].

Very recently, Jin's group further used 4,4'-oxybis(benzoic acid) (H_2oba) and oxalic acid (H_2ox) as the mixed ligands in synthesizing new lanthanide coordination polymers $[\text{Ln}(\text{oba})(\text{ox})_{0.5}(\text{H}_2\text{O})_2]_n$ ($\text{Ln} = \text{Y}; \text{Er}; \text{Yb}$) by hydrothermal reactions [113]. The single-crystal X-ray diffraction indicated that the lanthanide ions of these complexes are bridged by oba ligands to form 1D double-stranded chains, which are further connected by ox ligands, resulting in the formation of 2D (4,4) grids. The Y : Er–Yb co-doped coordination polymer showed intense UCL under 975 nm laser excitation. As shown in Figure 13.36, there are four major emission bands in the UCL spectrum of the Y : Er–Yb co-doped coordination polymer. The red

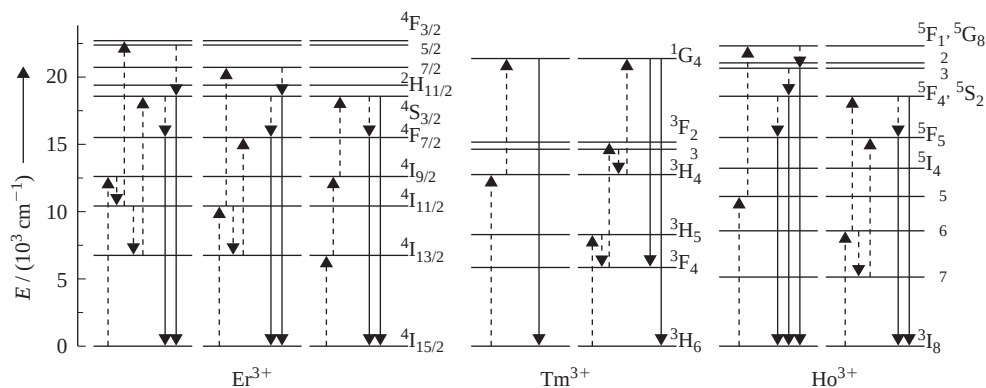


Figure 13.35 Schematic energy level diagrams showing typical UC processes for Er^{3+} , Tm^{3+} , and Ho^{3+} . The dashed–dotted, dotted, and full arrows represent excitation, multi-phonon relaxation, and emission processes, respectively. The $^{2S+1}L_J$ notations used to label the f levels refer to spin (S), orbital (L), and angular (J) momentum quantum numbers, respectively, according to the Russel–Saunders notation [111]. (Reproduced from F. Wang and X. G. Liu, “Recent advances in the chemistry of lanthanide-doped upconversion nanocrystals,” *Chemical Society Reviews*, **38**, 976–989, 2009, by permission of The Royal Society of Chemistry.)

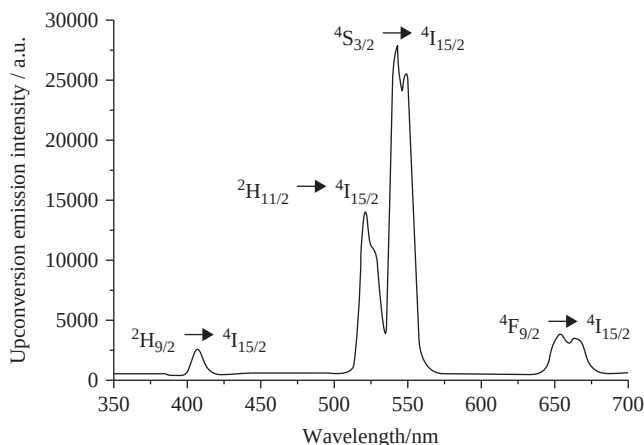


Figure 13.36 Upconversion luminescence spectrum of the Y:Er–Yb co-doped coordination polymer $[(\text{Y:Er–Yb})(\text{oba})(\text{ox})_{0.5}(\text{H}_2\text{O})_2]_n$ [113]. (Reproduced from *Inorganica Chimica Acta*, **362**, C. Y. Sun *et al.*, “Assembly and upconversion luminescence of lanthanide-organic frameworks with mixed acid ligands,” 325–330, 2009, with permission from Elsevier.)

light emission band centered at 653 nm was attributed to $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition of the Er^{3+} ion. The green light emission bands centered at 542 and 520 nm correspond to $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ and $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ transitions of the Er^{3+} ion, respectively. Interestingly, a fourth emission band centered at 407 nm in the blue light region, corresponding to the $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$

transition of the Er^{3+} ion, was also observed. The blue UCL, unusual for Er(III) complexes, can be explained by the three-photon excitation mechanism, which was confirmed by photon-dependent investigation [113].

13.6.3 Rare Earth Nanophosphors with Upconversion Luminescence

The upconversion luminescence of lanthanide complexes is too weak to enable them to be used as bioprobes. Recently, more attention has been paid to lanthanide-based upconversion nanophosphors (UCNPs). To date, many synthetic methods for controlling the size and shape of UCNPs have been developed [114, 115]. For example, Yan and coworkers have developed a thermolysis organo-metallic precursor strategy for synthesis of monodisperse nanocrystals [116], utilizing a high-boiling solvent under elevated pressures and temperatures to decompose the organo-metallic precursor. This strategy requires careful choice of the precursors from among various organic-metallic compounds and the composition of solvent. The most common solvents are oleic acid/oleylamine/1-octadecene (Figure 13.37). This thermolysis method has recently become a popular method for obtaining monodisperse lanthanide nanocrystals [117, 118]. Li and coworkers developed another method for general synthesis of monodisperse nanocrystals, described as a liquid–solid–solution (LSS) phase transfer and separation strategy [119]. By carefully designing the chemical reactions to occur at the interfaces, a series of monodisperse nanocrystals with very different sizes, crystal structures, compositions, and chemical properties have been obtained [120].

Because of hydrophobic organic ligands (such as oleic acid) coating their surface, unfortunately, the above mentioned UCNPs have low solubility in water and cannot be used directly in bioimaging. One strategy is to convert hydrophobic UCNPs into biocompatible ones by encapsulating them with SiO_2 [121, 122], or an amphiphilic copolymer [123, 124], and by surface ligand oxidation [125, 126]. For example, we have recently synthesized an SiO_2 -coated upconversion $\text{NaYF}_4:20\% \text{ Yb}, 2\% \text{ Er}$ nanophosphors (UCNP) capped by the down-conversion luminescence dye of fluorescein (FITC) [abbreviated as $\text{UCNP@SiO}_2(\text{FITC})\text{-NH}_2$] (Figure 13.38) [122]. Yi and Chow [123] reported that oleic acid capped $\text{NaYF}_4:\text{Yb-Er(Tm)}$ UCNPs could be rendered hydrophilic by coating with an amphiphilic layer of 25% octylamine and 40% isopropylamine modified poly(acrylic acid) (PAA). Recently, we have developed two simple and versatile strategies using surface ligand oxidation reactions for converting

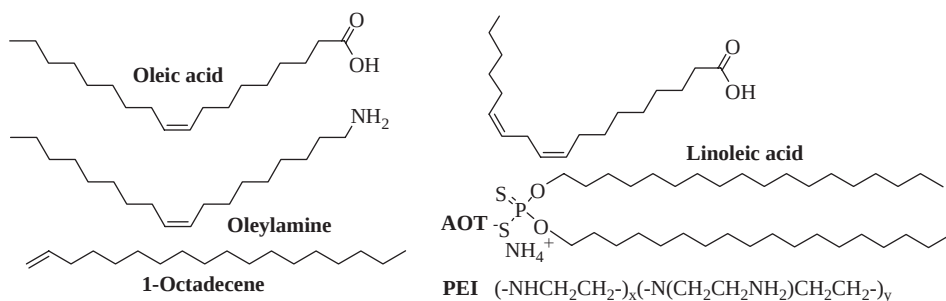


Figure 13.37 Chemical structures of some surfactants.

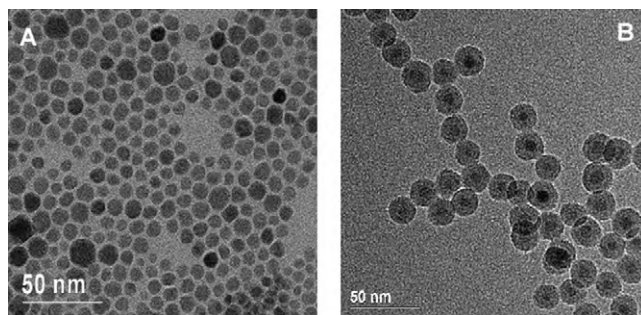


Figure 13.38 TEM images of (A) hydrophobic UCNPs and (B) UCNPs@SiO₂(FITC)-NH₂ nanocomposites.

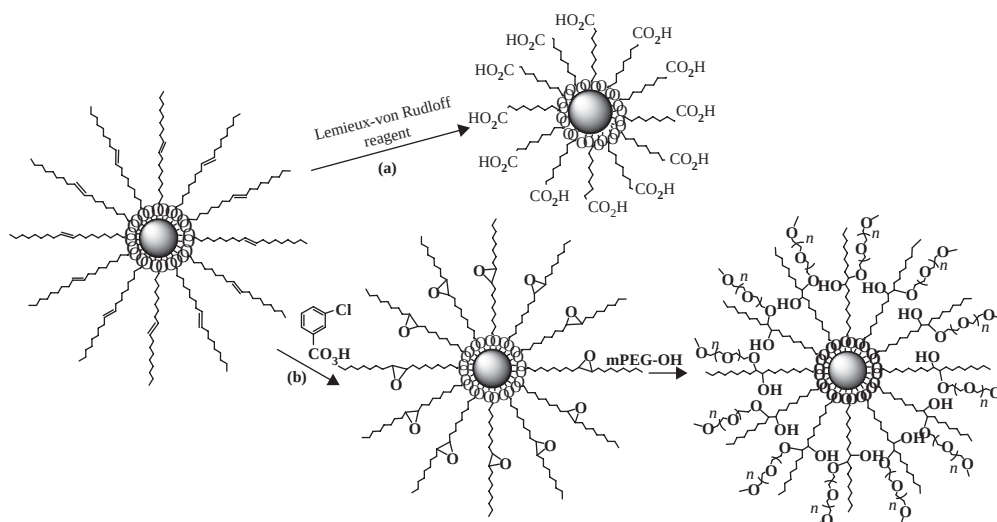


Figure 13.39 Surface ligand oxidation strategy for synthesis of functionalized oleic acid-capped UCNPs. (a) Direct oxidation with the Lemieux-von Rudloff reagent and (b) epoxidation and further coupling with mPEG-OH.

hydrophobic UCNPs into water-soluble and surface-functionalized ones. One of the strategies is to directly oxidize oleic acid ligands with the Lemieux-von Rudloff reagent into azelaic acids [HOOC(CH₂)₇COOH], which results in the generation of free carboxylic acid groups on the surface (Figure 13.39a) [125]. The second strategy is based on epoxidation of the surface oleic acid molecules and further coupling with polyethylene glycol monomethyl ether (mPEG-OH), as shown in Figure 13.39b [126].

However, such two-step conversion strategies for upconversion nanophosphors have some intrinsic limitations, such as complicated preparation and post-treatment procedures. Therefore, one-pot synthesis of water-soluble and surface-functionalized UCNPs has been attracting more attention. The groups working with Zhang [127] and Liu [128] employed

polyethyleneimine (PEI) to synthesize water-soluble nanoparticles and to control crystal growth. Very recently, we reported a new hydrothermal microemulsion synthesis strategy assisted by bi-functional ligand 6-aminohexanoic acid to synthesize amine-functionalized UCNP [129]. When the microemulsion containing lanthanide complexes of 6-aminohexanoic acid was mixed with another microemulsion containing aqueous NaF solution, nanoparticles were formed. By further hydrothermal treatment at 180°C for an appropriate period of time, the reverse micelles could be broken, and larger UCNP could be prepared. The amine content of the UCNP was determined to be about $9.5 \times 10^{-5} \text{ mol g}^{-1}$, confirming the occurrence of amine surface groups on the UCNP. In this system, 6-aminohexanoic acid plays an important role in providing UCNP with a desirable amine surface.

13.6.4 Rare Earth Upconversion Luminescence Nanophosphors as Bioimaging Nanoprobes

The application of UCNP in microscopic imaging demands the development of a novel microscopy technique, namely upconversion luminescence (UCL) microscopy. Recently, we demonstrated that rare earth nanophosphors exhibited unique UCL imaging modality, which was significantly distinct from those of single-photon and two-photon fluorescence imaging. Interestingly, UCL of UCNP was observed along the path of the laser beam. This might be attributed to the unique upconversion mechanism of UCNP. Furthermore, to eliminate the hindrance of out-of-focus UCL, a confocal pinhole was introduced. Finally, a new method of laser scanning upconversion luminescence microscopy (LSUCLM, Figure 13.40) was developed for the three-dimensional visualization of biological samples [130].

Further practical applications of upconversion luminescence nanophosphors (UCNP) in bioimaging has attracted more attention [129–132]. For example, on the basis of the folate receptor (FR) overexpression in some tumor cells (such as HeLa cells) and the high-affinity between FR and folic acid (FA), we fabricated FA-conjugated UCNP for targeted UCL imaging of FR-overexpressing HeLa tumors *in vivo* [129]. To evaluate the FR target recognition of FA conjugated nanophosphors (UCNP-FA), HeLa (FR-positive) and MCF-7 (FR-negative) cells were incubated in a serum-free medium containing UCNP-FA ($67 \mu\text{g mL}^{-1}$) at 37°C for 1 h. For comparison, HeLa cells were also incubated in the presence of non-conjugated

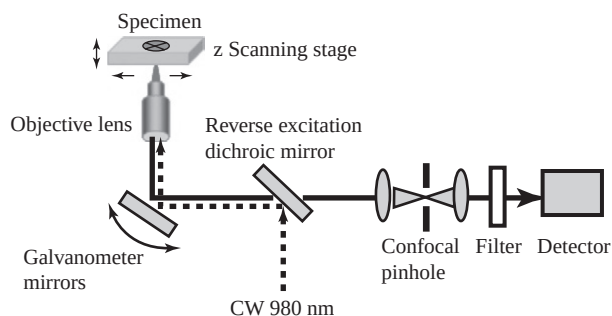


Figure 13.40 Schematic layout of a LSUCLM system set-up. The excitation laser beam path is shown with a dotted line, and the emission pathway is shown in a solid line.

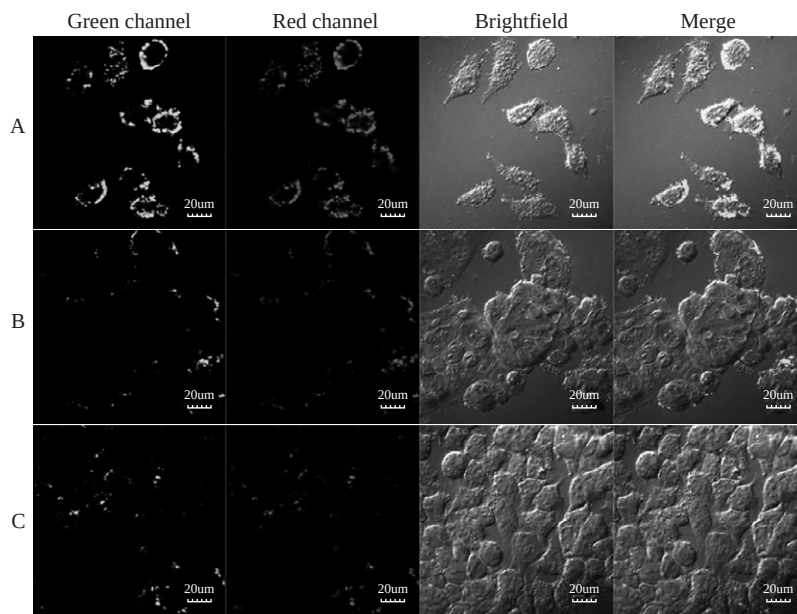


Figure 13.41 Laser scanning UCL images of living cells. (A) HeLa (FR-positive) cells incubated with UCNPs-FA; (B) MCF-7 (FR-negative) cells incubated with UCNPs-FA; (C) HeLa cells incubated with UCNPs-NH₂. Green and red channel images were collected at 500–560 and 600–700 nm, respectively. The merging of green channel and brightfield images is also shown [129]. (Reproduced from *Biomaterials*, **30**, L.Q. Xiong *et al.*, “Synthesis, characterization, and *in vivo* targeted imaging of amine-functionalized rare-earth up-converting nanophosphors,” 5592–5600, 2009, with permission from Elsevier.)

nanoparticles ($67 \mu\text{g mL}^{-1}$ UCNPs-NH₂) under otherwise identical conditions. As displayed in Figure 13.41A, UCNPs-FA-treated HeLa cells showed intense intracellular UCL signals at 500–560 nm (green channel) and 600–700 nm (red channel) under CW 980 nm excitation, indicating the high specific interaction between FA on the UCNPs-FA nanoparticles and FR on the HeLa cells. In contrast, both UCNPs-FA-treated MCF-7 cells (Figure 13.41B) and UCNPs-NH₂-treated HeLa cells (Figure 13.41C) display weak luminescence in the green and red channels, suggesting low-rate non-specific binding of these nanoparticles to the cells. These results establish that UCNPs-FA could be used for targeting and imaging HeLa cells with overexpressed FR.

Further quantification of the UCL signal of UCNPs-FA-treated HeLa cells across the line reveals extremely high UCL intensity (counts > 4095, region-1 and region-3) and no background fluorescence (counts around 0, region-2) as shown in Figure 13.42a. This feature of perfect signal-to-noise ratio in UCL imaging cannot be obtained in single-photon or two-photon fluorescent imaging. Moreover, as shown in Figure 13.42b, the data in the time-sequential scanning reveals no obvious change in the UCL intensity of the cells under continuous illumination (415 s) with a high power CW 980 nm laser (approximately $4.6 \times 10^9 \text{ mW cm}^{-2}$ in the focal plane). This fact reveals that UCNPs are highly resistant to photobleaching compared with conventional luminescent labels [129].

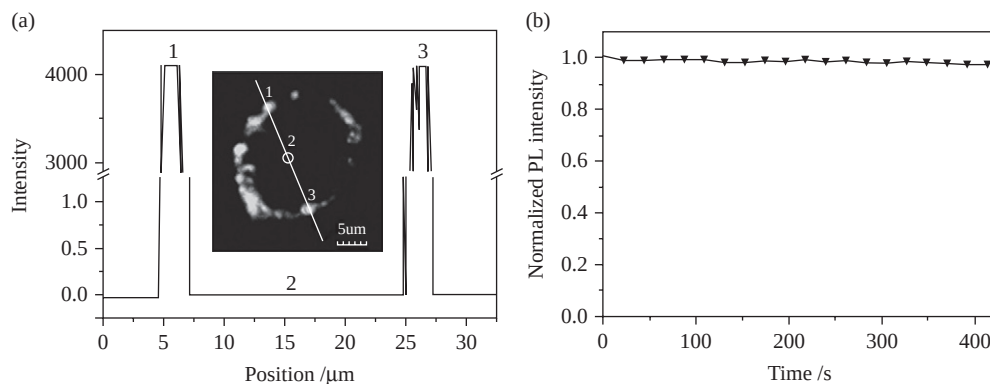


Figure 13.42 (a) UCL intensity along the line shown in UCL image (inset) of UCNPs-FA-treated HeLa cell and (b) the normalized UCL intensity as a function of illumination time [129]. (Reproduced from *Biomaterials*, **30**, L.Q. Xiong *et al.*, "Synthesis, characterization, and *in vivo* targeted imaging of amine-functionalized rare-earth up-converting nanophosphors," 5592–5600, 2009, with permission from Elsevier.)

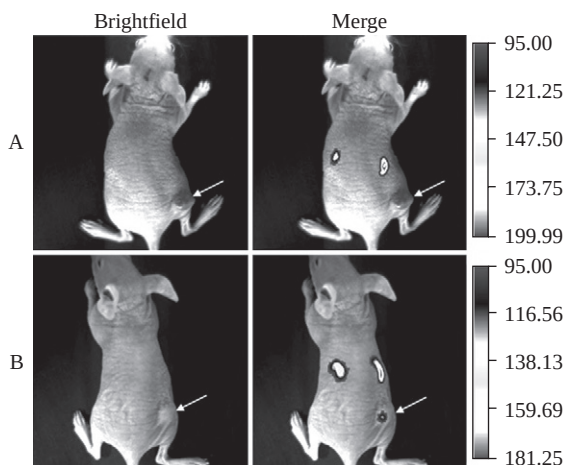


Figure 13.43 *In vivo* upconversion luminescence imaging of subcutaneous HeLa tumor-bearing athymic nude mice (right hind leg) after intravenous injection of (A) UCNPs-NH₂ or (B) UCNPs-FA. All images were acquired under the same instrumental conditions (power density approximately 120 mW cm^{-2} on the surface of the mouse) [129]. (Reproduced from *Biomaterials*, **30**, L.Q. Xiong *et al.*, "Synthesis, characterization, and *in vivo* targeted imaging of amine-functionalized rare-earth up-converting nanophosphors," 5592–5600, 2009, with permission from Elsevier.)

Furthermore, the ability of folic acid conjugated nanophosphors (UCNPs-FA) to target a folic receptor (FR) *in vivo* was evaluated by UCL imaging of mice bearing HeLa (FR-positive) tumors. As shown in Figure 13.43B, a significantly strong UCL signal was measured in the tumor after intravenous injection of UCNPs-FA after 24 h, whereas weak UCL was

observed in the tumor of the UCNPs-NH₂-treated mouse (Figure 13.43A). Furthermore, the UCL signal from the tumor was inhibited in the presence of a blocking dose of FA (10 mg kg⁻¹). The successful tumor imaging described above illustrates the specific *in vivo* FR-targeting of UCNPs-FA [129].

13.7 Outlook

Notwithstanding the significant progress in the lanthanide complexes and nanophosphors as luminescent systems for sensing and bioimaging, there appears to exist tremendous opportunities for further development. Methods for designing and synthesizing of adequate Ln(III) receptors are essentially at hand and will not constitute a handicap any longer in the future. A heavy demand for targeted diagnostic imaging and for monitoring of reactions taking place in living cells will pose the key challenge for future luminescent responsive lanthanide-based systems for bioimaging *in vivo* and mainly *in cellulo*. A combination of polymer techniques and biochemical reactions may be capable of producing new classes of efficient luminescent sensors. Similarly, nanoparticle labels are presently attracting attention for the same reason. Further efforts are starting to emerge to improve several technical aspects, including instrumentation and excitation mode. With respect to the latter, multi-photon absorption is probably a valid option. Considering the advantage of upconversion luminescence of lanthanide-based nanophosphors, one may predict that an ideal luminescent diagnostic assay could feature such a probe with a continuous wave excitation at 980 nm, a wavelength for which cheap laser diodes are available. Further research on upconversion luminescence nanophosphors (UCNPs) will involve: (i) synthesis of monodisperse UCNPs with small size (<30 nm) and high emission quantum efficiency, (ii) the long-term cytotoxicity test, and (iii) targeted localization of these nanophosphors to tumors *in vivo*. In conclusion, there remains a great deal of work to be done.

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Index

- acetic acid, 96, 98–104, 114–115
acetylacetone, 456
acridones, 545
activation
 C–H bond, 319, 328
 C≡N triple bond, 329
 C–O bond, 329
adduct, *see* fullerene, adduct
 bis adduct, 288, 290–291, 293, *see also*
 fullerene, bis adduct
 mono adduct, 288–289, 291–294, *see also*
 fullerene, mono adduct
alcoholysis, 233
aliphatic amide type ligands, 137–138
alkoxide, 246–250, 265
 aliphatic, 230–233, 238
 donor-functionalized, 235–237, 239, 245
 homoleptic, 230, 232, 236
 oxo-, 231
 phosphino-, 236
alkyne dimerization, 338
amide type ligands, 137
amino acid, 92, 122–129
angiography, 422
 gadolinium, 407
anion-incorporating, 540
anions chemosensors, 537–540
antenna effect, 11, 486
 light harvesting antenna, 489, 517
 peripheral antenna, 487
archimedean, 262
architecture, 491
aryloxide, 229–232, 238–240, 242–243, 259
 macrocyclic, 230–231, 233, 237, 242–243
aspartic acid, 126–127, 129
atomic number, 1
atomic radius, 5
azaxanthenes and azathioxanthenes, 545–547

back-energy transfer, 539
background fluorescence, 542
Bath, 439, 445, 449–452, 464–465
BCP, 436, 439, 444–445, 448–449, 452, 454–455,
 461–463, 465
benzoic acid, 96, 101, 103, 114

benzoimidazole, 448
benzyne, 288–289
bidentate ligand, 336
bioimaging, 543–544
bioimaging nanoprobe, 562–565
bioimaging probes, 544, 553–557
 2, 2′-bipyridine type ligands, 148–149
 2, 2′, 2″-bipyridine type ligands, 149–151
 4, 4′-bipyridine type ligands, 148–149
bis(benzimidazole)pyridine tridentate units,
 549–552
bis(benzimidazole)pyridine type ligands,
 156–157
bis(trimethylsilyl)amido, 143
blocking temperature, 382
borate compound, 36
broken symmetry method, 359
butadiene polymerization, 342

cage
 carbon cage, 274, 276–277, 283, 284–287, 297
 fullerene cage, 273–274, 276, 277, 279, 283–286,
 290–291, 295, 297–299
calixarene, 243, 245, 252, 495–496
carbanion, 291, 293
carbazole, 443–444, 449, 462
carbene, 284, 289, 292, 294
carbodiimide, 314, 334, 339
carbon nanotubes (CNTs), 275, 278–279, 297–298
 nano ‘peapods’, 297
carbonate compound, 28
carboxylic acid
 connectivity, 95–97
 coordination model, 95–97
 d–f heteronuclear complex, 112–114
 structure, 94–114
catalysis, 263
 asymmetric, 247
 Dies–Alder reaction, 247
 Meerwein–Ponndorf–Verley reduction, 246
 Michael reaction, 247
 nuclease, 250, 253, 263
 Oppenauer oxidation, 246
 ring-opening polymerization, 247–248
cations chemosensors, 534–536

- cerium
 Ce(OEP)₂, 161
 Ce₂(OEP)₃, 161–162
 tetravalent, 334–336
- charge mobility, 436
- charge transfer, 284–285, 292, 298
- cluster, 230, 283, 285, 287–288
 dinuclear, 245, 253–254, 257
 dodecanuclear, 255
 heptanuclear, 254
 heterometallic, 232, 248–249, 258, 260, 262, 264
 hexanuclear, 240, 258–259
 metal carbide cluster, 284–285
 metal nitride cluster, 284, 286, 288, 291, 294, 297–298
 nonanuclear, 257–260
 nuclearity, 232, 239, 251–254, 262
 octadecanuclear, 255
 octanuclear, 254, 259
 pentanuclear, 233, 237, 239, 257, 259–260, 264
 tetradecanuclear, 235, 241, 259–260, 265
 tetranuclear, 236, 243, 245, 252, 254, 256–257, 264
 trinuclear, 233, 236, 239, 241, 254, 264
- Colo-Colo analysis, 381
- conformational variation, 486, 501, 507
- connectivity, 95–97
- contrast agent, 263–265, 410
 magnetic resonance, 264
 radiographic, 265
- coordination number, 47–71
 coronand, 497–498
 definition, 15
 distribution, 17–18
 eight-coordinated complex, 53–63
 nine-coordinated complex, 63–70
 seven-coordinated complex, 53–55
 six-coordinated complex, 47, 49, 51, 53
 ten-coordinated complex, 70–71
- crown ether, 316, 332
- cryptand, 497–498
- current efficiency, 437, 448, 452, 455, 465
- cyanide compound, 27
- cyclen, 492–495, 510
- cyclen core structures, 544–548
- cycloaddition, 288, 291
- d-block chromophore
 d³ metal–organic, 514–516
 d⁶ metal–organic, 509–514
 d⁸ metal–organic, 501–509
 d¹⁰ metal–organic, 500–501
 f-block, 516–517
 metal–organic, 500–516
 peripheral, 486
- D₂-chiral bis(porphyrinato) complexes, 160
- DBM, 442–454, 464–465
- dc field dependent relaxation, 391
- deactivation, 475–476, 478–480, 482–483, 497, 517
- deactivation process, 467
- delocalization, 477, 497
- dendrimer, 486–489
- deposition, metal–organic chemical vapor, 247
- Diels–Alder reaction, 282, 288
- diene, polymerization, 341–342
 dimeric complex, 101–102, 123
- β-diketone
 bis(β-diketone), 44, 48–49
 dendritic β-diketone, 44, 47, 49–53
 fluorinated β-diketone, 43, 56, 64
 mono(β-diketone), 42–44
 nonfluorinated β-diketone, 44–47
- dimeric and polymeric Ln(III)(La, Sm) complexes, 146
- dimeric Eu(III)-chelated complexes, 146
- dipicolinic acid (DPA), 541
- 1, 3-dipolar addition, 287–288, 290, 299
 azomethine ylides, 287–288
- direct process, 381, 395
- divalent lanthanide complex
 classical, 330
 non-classical, 331, 334
- donor–acceptor dyad, 298–299
- doping, 440, 452
- double- or triple-decker porphyrinato, 159
- downconversion luminescence (DCL), 558
- effect, 500
 heavy atom effect, 482
 nonradiative effect, 478
- effective ionic radius, 19
- electrochemical of
 prophyrin, 164
- electroluminescence of
 Dy, 464–466
 Er, 464, 466
 Eu, 441–455
 Nd, 464, 467
 Sm, 464–465
 Tb, 441, 455–463
 Yb, 464–467
- electron-injection layer, 436
- electron-transporting layer, 436, 442, 449, 456
- electronic absorption spectra
 porphyrin, with, 163
 selection rules, 8
- electronic configuration, 1
- electronic dipole transition, 442
- elimination reaction, 317–318, 323
- emission, 11, 507–509, 512–514
 near-infrared (NIR) emission, 163–164, 464, 473–480, 484, 487, 490–492, 496, 498–500, 502–503, 513–514, 516–517, 558
 visible emission, 473–476, 485, 496, 516
- emission layer, 436, 462
- encapsulation, 273, 276, 299, 486–487, 496–497, 516–517
- energy transfer, 492–493, 495–496, 500–509, 508–512, 514–517
 energy transfer, rate of, 500, 503–504, 507–509, 512
- ethylene copolymerization, 340
- exciplex, 457
- excited singlet state, 441, 477, 487, 498, 500–501, 507

- excited state, 441, 443, 475–478, 482, 487, 498–500, 502, 507, 516
excitons, 436–438, 441, 449
external quantum efficiency, 437, 443, 448, 452–453, 455, 465
external quantum yield, 448–449
extraction, 273, 277, 279–280, 293, 299
- fluorination, 475, 480
folic acid (FA), 564
folic receptor (FR), 564
formation mechanism
 empty fullerene, 275, 281–282, 284, 287, 290, 293, 298
 endofullerene, 275, 284
 endohedral metallofullerene (EMF), 273–278, 283–285, 287, 298–299
 fullerene, 273–279, 283, 295, 298
fullerene
 adduct, 287–288, 290–294, 299
 bis adduct, 288, 290–291, 293
 electronic structure, 283–286, 289–290, 293
 HOMO-LUMO band-gap of, 279, 290
 mono adduct, 288–289, 291–294
- gadolinium break, 25, 115, 128
glutamic acid, 125–127, 129
ground state, 441, 475
- H₄DOTA (1, 4, 7, 10-tetraazacyclododecane-1, 4, 7, 10-tetraacetic acid), 119–120
H₄EDTA (ethylenediaminetetraacetic acid), 115–117, 120–121
H₅DTPA (diethylenetriaminepentacarboxylic acid), 118, 121
H₆TTHA (triethylenetetraaminehexaacetic acid), 118
- halide compound, 26
helicate, 484, 491–492, 514–515
heteroleptic bis(porphyrinato) double-decker complexes, 164–166
high-performance-liquid-chromatography (HPLC), 279–281, 288
high-work-function material, 436
[{(HNdCMe)₂MeCNH₂}Dy(MeCN)₆]₃, 179
hole-blocking layer, 436, 449
hole-injection layer, 436
hole-transporting layer, 436
holes, 436–437, 454, 461, 467
homogeneous catalysis, 337
homoleptic bis(phthalocyaninato)double-deckers, 169–171
host, 452, 458
host-guest chemistry, 281, 292
hybrid, 263–264
hydride transfer reaction, 325, 327
hydroamination/cyclization, 337–338
β-hydrogen elimination, 315, 326
hydrogenolysis reaction, 326
hydrolysis, 230–231, 249–251, 253, 257–259
hydroxide compound, 25
- imidazol, 153
imine, 174, 177–178, 181–182
immunoassays, 529–531
inner coordination sphere, 482–483, 492, 498, 514
intensity
 emission intensity, 499, 516
 luminescent intensity, 477, 480–481, 484, 486, 488
π–π interaction, 161, 163, 170–171, 185
internal quantum efficiency, 437, 441
intra-atomic transitions, 435
intramolecular energy transfer, 441, 449
ionic radius, 5
ising chain, 390
isolated pentagon rule (IPR)
 fused-pentagon, 283, 293–294
 non-IPR, 283, 293–294
isoprene polymerization, 342
isoxazolone, 44, 46, 57
- Jørgensen equation, 22
- lactide polymerization, 344
lactone polymerization, 344
lanthanide complex with
 alkyl complex, 319, 323–324, 326, 338–341
 allyl, 311–312, 343
 dialkyl, 317, 323, 326–327, 342
 dihydride, 326–327
 hydride, 325–329, 339, 341–342
 monoalkyl, 318, 323
 trialkyl, 314–317, 324
 triphenyl, 316
 tris(cyclopentadienyl), 310, 313–314
 tris(pentamethylcyclopentadienyl), 311–313, 334
lanthanide contraction, 2, 232
lanthanide coordination polymers, 535–536
laser scanning upconversion luminescence microscopy (LSUCLM), 562
leucine aminopeptidase, 540
lifetime, 9, 475, 501, 503–504, 507, 511, 513, 515
ligand, 475–499
 acyclic ligand, 476–480
 amino acid, 251, 254, 259, 264
 bridging, 229–230, 232–233, 235–236, 238–241, 243, 245, 250, 252, 254, 263–264
 bridging-chelating, 236, 240
 co-ligand, 490, 496, 499
 coordination mode, 231–233, 236, 241–243, 251–254
 degradation, 230
 diketonate, 251, 257, 259, 264
 doubly, 232, 236, 239, 252–253
 edge-bridging, 236
 fluorinated, 248
 halo, 233
 hydrido, 233
 hydroxo, 230, 233, 236, 241, 245, 249–253, 258, 261, 263
 macrocyclic ligand, 492–499
 monodentate, 232–233, 236, 241, 251, 254, 316, 332, 313, 336
 multidentat, 241–242, 251

ligand (*Continued*)

quadruply, 232, 252
 schiff base, 242–243, 251
 terminal, 233–234, 236, 239, 241, 243, 252, 258
 triply, 232, 236, 238, 252
 ligand field, 356–357, 360, 363–364, 392–393, 396–397
 low-lying excited state, 482, 497, 512
 low-work-function, 436
 luminance, 437–438, 442, 444, 448, 457, 452, 459, 464
 luminescence sensitization, 11
 luminescent chemosensors, 531–532
 luminous efficiency, 437, 459
 luminous yield, 448
 magnetic
 absorption, 380
 antiferromagnetic, 264
 dispersion, 380
 ferromagnetic, 264
 MRI contrast agent, 280–281, 295, 297
 orbital, 358, 360–361, 367
 ordering, 355–358, 360, 363, 367–369, 372–373, 375, 391, 396–397
 relaxation, 357, 378–379, 381, 388, 390, 394
 resonance imaging (MRI), 280–281, 295, 297, 116, 120, 407
 single-molecule, 264
 metal–cage interaction, 274, 276, 282, 284, 298–299
 metal–organic framework (MOF), 91–92, 107–110, 536
 metastable state, 9
 methyl methacrylate polymerization, 342–344
 molecular magnetism, 360, 370, 397
 monomeric phthalocyaninato complex, 171
 monomeric porphyrinato complexes, 166
 multiphoton luminescence probes, 556–557
N-heterocyclic carbene lanthanide complex, 320–322
N-heterocyclic carbene, 309, 320, 336
N-heterocyclic type ligands, 146
N-methylimidazole type ligands, 153–155
 nanoscale lanthanide-organic frameworks (NMOFs), 541
 1,8-naphthylridine type ligands, 152
 nitrate compound, 31
 nitrogen activation, 333–334
 non-radiative relaxation, 467
 octaethylporphyrin (OEP), 158–167
 olation, 250–271
 olefin polymerization, 339–340, 346
 oncology, 424
 one-electron reducing agent, 313, 333
 onset driving voltage, 448
 operating principles in OLEDs, 436
 orbach process, 381, 393
 orbital contribution, 360, 363–364, 396
 orbital moment, 356–357, 361, 363
 organic light emitting diodes (OLEDs), 435

organolanthanide π -complex
 reactivity, 312–314
 synthesis, 310–312
 oscillator, 475–476, 480, 482, 490, 498, 517
 outer coordination site, 489
 oxadiazole, 442, 448–449, 457
 oxalate compounds, 31
 oxidation of endohedral metallo-fullerenes
 chemical oxidation, 280, 282
 pendent arms, 532–534
 perchlorate compound, 23
 pH chemosensors, 532–534
 1,10-phenanthroline type ligands, 151–152
 phosphate compound, 29
 photoluminescence, 443, 456, 459, 461–463, 465–466
 photoluminescent efficiency, 443
 photophysical property, 490–491, 512–513, 517
 phthalocyaninato and porphyrinato double-decker complexes, 172
 phthalocyanine, 168–171
 platonic, 262
 polyaminocarboxylate, 484–486, 493
 polyaminopolycarboxylic acid, 91–92, 115–121
 polyaryloxide, 230, 242
 polycarboxylic acid, 106
 polymeric complex, 103–105, 123
 polymerization, control of, 95–99
 polynuclear lanthanide complex, 71–85
 polyoxometalate clusters, 194–208
 capping or supporting RE ions, with, 202
 large-sized clusters, 202–208
 rare earth ions in the center, with, 201–202
 RE/P₂W₁₇, 194–198
 RE/XM₁₁, 194
 sandwich type clusters, 198–201
 polyoxometalate complexes, 193–223
 polyoxometalate complexes, application of, 218–223
 catalysis, 221–223
 luminescence, 218–221
 magnetism, 221
 medicine, 223
 polyoxometalate complexes, extending structural of, 208–218
 Anderson anions as building units, 208–210
 decatungstate anions as building units, 210
 [H₂M₁₂O₄₂]¹⁰⁻ anions as building units, 210–211
 Keggin anions as building units, 211–212
 [Mn₄Si₂W₁₈O₆₈(H₂O)₂]¹²⁻ anions as building units, 216
 {Mo₃₆(NO)₄} as building units, 216
 monovacant Keggin anions as building units, 212–214
 monovacant Wells–Dawson anions as building units, 215
 [MV₁₃O₃₈]⁷⁻ and [MV₁₂O₃₈]¹²⁻ as building units, 217
 octamolybdate anions as building units, 210
 [P₈W₄₈O₁₈₄]⁴⁰⁻ anions as building units, 216–217
 Preyssler anions as building units, 216

- Silverton anions as building units, 214
Wells–Dawson anions as building units, 215
porphyrin, 498–499, 158–173
power efficiency, 438, 444, 452, 455, 460, 462, 465
process
 deactivation process, 475–476, 478, 482–483, 497
 double electron exchange process, 500
 energy transfer process, 493, 516–517
 radiationless deactivation process, 475, 517
proton relaxivity, 295–297
protonolysis reaction, 314
pyrazolone, 46, 56, 62, 72, 88–89
 electroluminescence, 458–459, 461–465
2-(2-pyridine)-benzimidazole ligands, 155–156
pyridine type ligands, 146

quadridentate triamidoamines, 145
quantum efficiency, 437, 440, 443–444, 459
quantum tunneling effect, 382, 392–394
quantum yield, 11, 477–479, 482–485, 487, 490, 492–493, 498, 500, 514
quencher, 475, 479–480, 485, 493, 496, 500, 502–503, 507, 512–513, 515
quinoline, 480–484

radical addition, 290–291
 radical coupling reaction, 290
Raman process, 381
receptor, 497–498
 macrocyclic receptor, 476, 492–499
recombination, 436–437, 440–441, 449, 457–460
reduction of endohedral metallo-fullerenes, 279–282, 286–287
 chemical reduction, 279–282, 286–287
relaxivity, 412
ring-opening polymerization, 344

sandwich type bis(porphyrinato), 159
Schiff base type ligands, 173–174, 178, 181
 Eu(Hsalen)(salen)-H₂O, 182–185
 H₂Salen type ligands, 180
selectivity, 498
sensitization, 443, 462
sensitizer, 475, 479–480, 482–484, 498, 500, 502, 511, 516
shield, 478–479, 481, 486, 499
silyl amide type ligands, 142–146
silylation, 287, 293
single-chain magnet, 381, 390, 392, 396
single-ion magnet, 390, 396–397
single-molecule magnet, 360, 381–387, 389, 394, 396
singlet oxygen (¹O₂), 554–556
small molecules chemosensors, 540–542
solvent, 475–476, 478–481, 492, 498–499, 514
 deuterated solvent, 475, 517
 water and alcohol, 475
spacer, 477, 485, 491, 493, 495, 500
specific interaction, 537
spectral terms, 8

spin delocalization, 360
spin polarization, 360
spin-lattice relaxation, 381
spin-orbit coupling, 356–357, 364, 367, 381, 385
spin-spin relaxation, 381
standard reduction potential, 12
steric hindrance, 96–98
sterically induced reactivity, 312
structure of endohedral metallo-fullerenes
 single crystallography, 276, 284, 288, 290–291, 298
 X-ray diffraction (XRD), 276, 288
structure–magneto correlation, 361
styrene polymerization, 341
sulfate compounds, 31
symmetry, 283, 287, 291, 293
synthesis of
 gel synthesis, 94
 hydro(solvo)thermal synthesis, 93
 rare earth-amino acid complex, 122
 rare earth-carboxylic acid complex, 92–94
 rare earth-polyaminopolycarboxylic acid complex, 115–116
synthetic strategy, 476, 493, 516–517

targeted imaging, 563–564
tautomerism, keto–enol, 41–42
template, 230, 254–255
terpyridine (tpy) type compounds, 149–151
tetraazatriphenylene, 547–549
tetrad effect of lanthanide elements, 21
tetrameric complex, 102–103
tetrapyrrole, 161–168
thermal evaporation, 436, 453, 455
thiocyanate of rare earth, 27–28
time-resolved luminescence imaging, 542
time-resolved luminescence microscopy (TRLM), 542–543
transmetalation, 316, 330
trimetallic nitride template (TNT), 277–279, 282, 284, 286, 288, 291, 296–297
triphenyl phosphine oxide, 449, 458, 461, 465
triphenylamine, 445, 459
triplet energy level, 443, 452, 460, 462, 467
triplet excited state, 441, 443, 462, 476–477, 483, 487, 497–498, 500, 512
turn-on voltage, 443, 449, 458

upconversion luminescence (UCL), 558–565
upconversion nanophosphors (UCNPs), 559–561

valence state, 14
volatile organic compounds, 541–542
volatility, 455

water-soluble derivative of fullerene, 280–281, 295–297
 yield, 275–281, 285, 287–288, 291–292, 299

zero field splitting, 382

@, 273–274, 276, 279, 283–285