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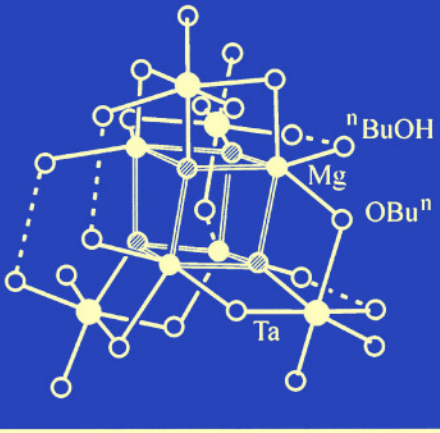

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SYMBOLS AND ABBREVIATIONS

Ac	MeCO	exp.	explosive
acac	Ac_2CH_2	gl.	glass
Am	amine	gr.	group
amor.	amorphous	grn.	green
antiferr	antiferro-magnetic	$h = [H_2O]:[M(OR)_n]$	
at.	atom	hc.	hydrocarbon.
ax.	axial	hex.	hexane
b.	boiling point	Hmpa	$(Me_2N)_3PO$
bipyr.	bipyramid	ins.	insoluble
bl.	blue	investig.	investigated
blk.	black	invol.	involatile
brn.	brown	isostr.	isostructural
bz.	benzene	liq.	liquid
cat.	cathode	m.	melting point
CN	coordinating number	magn.	magnetic
Cod	cyclooctadiene	Mössb.	Mössbauer sp.
colrl.	colorless	m-s	mass-spectra
compl.	complex	oct.	octahedron
conduct.	conductometry	or.	orange
cr.	crystalline	org.	organic
diamagn.	diamagnetic	paramagn.	paramagnetic
d	density	pentag.	pentagonal
dec.	decomposition	powd.	powder
Dig	diglyme	prop.	properties
Diox	dioxan	ref.	reference
Dipy	2,2’dipyridil	s.	soluble, ~tion
dist.	distorted	sld.	solid
Dme	$(MeOCH_2-)_2$	solv.	solvent
Dmfa	$HCONMe_2$	sp.	spectrum
Dmpe	$(Me_2PCH_2)_2$	stab.	stable
Dmso	Me_2SO	struc.	structure, ~al,
electr.	electronic	subl.	sublimation
En-	$(-CH_2NH_2)_2$	synth.	synthetic
equ.	equatorial	t	temperature, °C
eth.	Et_2O	tensim.	tensimetry

term.	terminal	vol.	volatile
tetrah.	tetrahedron	voltamet.	voltammetry
thd	tetramethylheptanedione	wh.	white
Tmeda	$(Me_2NCH_2)_2$	yel.	yellow
tol.	toluene	μ_{eff}	effective magnetic
trian.	triangle		moment, μ_B
trig.	trigonal	α	molecular complexity
unstab.	unstable	$\Delta H_{form.}$	enthalpy, cal/mol
v.	very	ε	dielectric constant
vac.	vacuum	μ	dipol moment, D
visc.	viscous	ψ	polyhedron one of which
vlt.	violet		vertexes is occupied by
			a pair of electrons

PREFACE

The study of the chemistry of metal alkoxides, which began more than 100 years ago, is now experiencing a renaissance connected with the broad application of these compounds as molecular precursors in the synthesis of materials of modern technology based on simple and complex oxides. The solution of this problem is occupying a wide circle of inorganic chemists, technologists specializing in fine synthesis in nonaqueous media, and those working on the production of films and coatings. The application of metal alkoxides in the first step of sol-gel technology (based on hydrolysis of alkoxides with subsequent dehydration of the hydrated oxides formed) can benefit from this monograph covering the modern literature devoted to all the steps of this process.

The information on chemistry of metal alkoxides has been reported in a number of reviews (devoted to the single groups of derivatives) and numerous original publications. The only other monograph — Metal Alkoxides by D. C. Bradley, R. C. Mehrotra and D. P. Gaur was published in 1978 (Academic Press, London) and, unfortunately, does not reflect modern findings.

The present book is devoted to the general questions of the chemistry of metal alkoxides — the synthetic routes to them (both laboratory and technology), physicochemical properties, structure, specific features of single groups of alkoxides, theoretical principles of their use for the preparation of simple and complex oxides by the sol-gel method, and major directions of the application of this method in the preparation of functional materials. Chapter 12 describes the derivatives of single elements of first throuth eighth Groups of the Periodic Table. The tables in this chapter contain the major data on the alkoxides, phenoxides, siloxides, derivatives of polyatomic alcohols, and phenols — their composition, structure, preparation techniques, and major physicochemical characteristics. Each table is accompainied by text that comments on it but is not a review in the classical sense of this word. These data allow this book to be used as a handbook permitting a quick and essentially complete acquaintance with the distinct compounds and the literature describing them.

The book is intended for chemists and technologists who specialize in the area of functional materials, and who apply the metal alkoxides in their practice. It also can be used as a textbook for students.

This book is written by a group of authors — Chapter 1 by N. Ya. Turova and M. I. Yanovskaya, Chapters 2 to 6 and 8 by N. Ya. Turova, Chapter 7 by V. G. Kessler, Chapter 9 and 10 by M. I. Yanovskaya, Chapter 11 by E. P. Turevskaya and Chapter 12 by E. P. Turevskaya, N. Ya. Turova, and V. G. Kessler. The general scientific editing of the book has been carried out by N. Ya. Turova and the English translation by V. G. Kessler.

The authors express their sincerest gratitude to their colleagues — professors L. G. Hubert-Pfalzgraf, K. G. Caulton, M. Veith, R. C. Mehrotra, W. E. Buhro, and G. Westin — who informed them about the publications of their works, Dr. A. I. Yanovsky for the continuous consultations on structural chemistry and tremendous help in the final editing of the text, Drs. D. E. Tchebukov and P. S. Berdonosov for assistance in the typing of the manuscript. The special thanks are directed to Dr. T. J. Leedham, the president of the Inorgtech Corp. (Mildenhall, Suffolk, UK) for sponsoring the writing of this book and to Professor B. A. Popovkin for the moral support of this work.

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Chapter 1

INTRODUCTION

1.1. Classification: General characteristic of the metal alkoxides

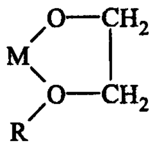
The $M(OR)_n$ derivatives are known now for almost all the elements of the Periodic Table (including the transuranium elements and Xenon). They are formal analogs of hydroxides but possess much higher thermal stability. Their properties are determined not only by the electronegativity of the metal atom but also by the nature of the radical — its ramification and the acidity of the corresponding alcohol, which provides their various properties. From this point of view they can be subdivided into the following groups of compounds:

- Derivatives of alkaline, alkaline earth metals and phenols, naphtols, antroles, *etc.* ($pK \geq 10$). These compounds are salts in their nature and, as the salts of strong bases and moderately weak acids, can exist in water solutions. They are soluble only in polar solvents (water, liquid ammonia), are prone to form adducts with phenols, water, *etc.*, have high thermal stability and cannot be transferred into the gas phase.
- Derivatives of nonmetals and alcohols with very low acidity ($pK = 15$–19). These are esters of inorganic acids, characterized by low melting and boiling points, solubility in alcohols and nonpolar solvents, and sensitivity even to the traces of water. They are usually monomeric or weakly aggregated. The representatives of this group are $B(OR)_3$, $P(OR)_3$ and $Se(OR)_4$.

- Metal alkoxides themselves — the derivatives of metal and aliphatic alcohols. The character of M-OR bonding in them is intermediate between phenoxides and esters. Their properties are varied, but almost all of them are sensitive to the action of water and, normally, aggregated in solution, gaseous, and solid phases.

Even for the alkaline metal alkoxides on transition from methoxides to t-butoxides it is possible to observe the transition from ionic compounds to more molecular, close to organic derivatives. Thus **M^IOMe** are soluble in alcohol and ammonia (but not hydrocarbons), have conductivity in solutions, crystallize giving polymeric structures analogous to LiOH (*anti*-PbO), and decompose without melting at temperatures >200°C [1644]. At the same time, **M^I-OBu^t** are soluble in hydrocarbons, ethers, and other nonpolar solvents; their crystal structures contain oligomeric molecules **(like cubane $[KOBu^t]_4$,** tetramers) and can sublime without decomposition [1728]. In the homologous series of alkoxides — derivatives of multivalent metals — the variation in properties is not so drastic, but nearly all the methoxides possess polymer structures (more stable than for the alkaline metals due to more covalent M–O bonding). They all are insoluble in organic solvents, decompose without melting, and cannot be transferred into a gas phase.

Special interest has recently been given to the metal 2-alkoxyethoxides, **$M(OC_2H_4OR)_n$** (R= Me, Et) — derivatives of the monoethers of ethyleneglycol. The presence of the second ether function in the molecule permits formation of chelate cycles:



and thus hinders the aggregation of the molecules. It results in much higher solubility of 2-methoxyethoxides compared to alkoxides and in higher volatility for them. In addition, the **$M(OC_2H_4OR)_n$** are a bit more stable to hydrolysis and oxidation. Especially stable **$MO_n \cdot xH_2O$** sols have been obtained from the water —$MeOC_2H_4OH$ systems.

The numerous reactions of metal alkoxides can be subdivided into three major groups: (1) complex formation with donor ligands or alkoxides of other metals; (2) partial or complete substitution for the OR-groups; and (3) various degradation reactions — such as oxidation and hydrolysis—leading to formation of oxoligands.

The numerous substitution reactions lay in the background of the application of metal alkoxides in inorganic and metal-organic synthesis (preparation of halides, hydrides, sulfides, carboxylates, alkyl derivatives, certain classes of coordination compounds, *etc.*). One advantage of their application is the formation of only alcohols as by-products:

$$M(OR)_n + nHX \rightarrow MX_n + nROH$$

The products of partial substitution for the OR-groups, i.e., alkoxocarboxylates, β-diketonates $M(OR)_mX_n$, where X= RCOO, acac, thd, *etc.*—the mixed-ligand complexes—usually are more soluble and stable than $M(OR)_n$, as their molecules contain the chelate cycles. Mehrotra *et al.* [223] have described a great number of such products (usually liquid or amorphous), in which individuality appeared sometimes questionable. During recent years, however, in connection with the application of these compounds to the synthesis of oxides, interest in them has increased, and a number of them have been isolated and structurally characterized (Chapter 7). Unfortunately, length restriction did not permit us to present a complete review of their chemistry in this book.

The solvates of alkoxides and the bimetallic complexes are described in Chapter 8, and oxocomplexes in Chapter 5. The products and mechanisms of hydrolysis for mono- and bimetallic alkoxides are considered in Chapters 9 and 10.

1.2. Main steps in the development of the chemistry of metal alkoxides

The first reports on the alcohol derivatives of potassium, sodium, boron, and silicon date from the 1840s, when Liebig for the first time observed the action of Na and K on ethanol. The term *alkoxides* was proposed by Kuhlmann [969] for the alkaline derivatives considered then as salts of alcohols as acids (in contrast to esters, where the alcohol acts as base). Next should be mentioned the works of Lamy [988], who in the 1860s prepared the homologous series of T1OR — along with other derivatives of this then recently discovered element and also those of Demarcay, who described $Ti(OEt)_4$. In the 1880s Berthelot and DeForcrand [575–580] studied the interaction of alkaline earth metals with alcohols to obtain the alkoxides and isolated a number of crystalline products, whose nature remains still unclear [1547,1644].

An outstanding input into the chemistry of metal alkoxides was made by the dissertation of V. E. Tishchenko, which was devoted to aluminium alkoxides. It was published in 1899 (unfortunately only in Russian) [1585] and—in contrast to his works on organic chemistry — is practically unknown by foreign chemists. A number of general synthetic approaches to metal alkoxides have been developed. The main regularities for the variation of the properties in the homologous series and ramification of the radical were found to determine the main directions of the thermal decomposition. He made also the proposal to use the $Al(OR)_3$ in ester condensation of aldehydes (Tishchenko reaction) (see also Chapter 12, Section 12.5).

For several decades after this, the metal alkoxides remained objects of interest only for organic chemists, who applied them for reduction of carbonyl compounds and as catalysts for disproportionation of aldehydes, condensation and polymerization. Among these works, of special interest is the work of Meerwein and Bersin [1101], who were the first to prepare the bimetallic alkoxides $M_nM'_m(OR)_p$ that were then called “Meerwein alkoxosalts” in analogy with much less stable hydroxosalts $M_nM'_m(OH)_p$.

The derivatives of the other new class — the alkoxide halides, $M(OR)_xHal_{n-x}$, which are more reactive than the alkoxides themselves — were first described by Meerwein and Schmidt for magnesium and aluminium [1103, 1098]. An important input into the development of synthetic and physicochemical methods in the investigation of metal alkoxides was made by an outstanding metalorganic chemist H. Gilman [855, 856], who studied the derivatives of uranium in Los Alamos during the Manhattan Project.

The most important step in the development of the modern chemistry of metal alkoxides is connected with the works of D. C. Bradley and the school that he started in 1950 [197, 198, 223]. His work has covered a very broad variety of chemical elements from Group III to Group VIII in the Periodic Table, including lanthanides and actinides. A variety of laboratory synthetic approaches have been developed. Preparation of a large number of homologues for each metal (including the derivatives of very ramified radicals) permitted Bradley to determine the structure of oligomeric alkoxides: the main principle was that metal atoms tried to achieve the highest coordination with the lowest possible molecular complexity. The data on molecular weights (taking into account the rule formulated) allowed him to formulate suppositions concerning the structures of many $[M(OR)_n]_m$ aggregates. This has stimulated the study of metal alkoxides using a variety of physicochemical techniques. The results of X-ray structure studies, carried out recently, urged the reconsideration of many concepts concerning not only structures but even the compositions of a number of alkoxides, to explain the particular features of behavior of these very unusual compounds (for details, see Chapter 4).

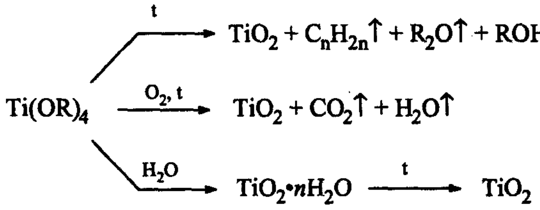
The present moment is characterized by a considerable interest of chemists and technologists in the metal alkoxides. It is connected in particular with the search for the precursors for synthesis of materials. Systematic studies of these classes of compounds are being carried out in the following laboratories — D. C. Bradley (Queen Mary and Westfield College, London, UK), R. C. Mehrotra (University of Radjastan, Jaipur, India), T. J. Boyle (Sandia National Laboratories, Albuquerque, USA), M. H. Chisholm (Ohio State University, Columbus, USA), K. G. Caulton and J. C. Huffamn (Indiana University, Bloomington, USA), D. L. Clark and D. M. Barnhart (Los Alamos National Laboratory, USA), G. B. Deacon (Monash University, Clyton, Australia), R.J.Errington (University of Newcastle, UK), W. J. Ewans (University of California, Irvine, USA), M. J. Hampden-Smith (University of New Mexico, Albuquerque, USA), W. A. Herrmann (Technische Universität, Munich, DBR), L. G. Hubert-Pfalzgraf (Universitê de Lyon 1, IRC, Villeurbanne, France), I. P. Rothwell (Purdue University, West Lafayette, Indiana, USA), C.Sanchez (Universitê P. et M. Curie, Paris, France), M. Veith (Universität des Saarlandes, Saarbrücken, FRG), G. Westin (Arrenius Laboratory, Stockholm University and Angstrom Laboratory, Uppsala University, Sweden).

In Chapter 12, devoted to the alkoxides of different metals, we try to reflect the activity of different groups that made the most important studies in this field.

For more than 30 years at Lomonosov Moscow State University, later at Karpov Institute of Physical Chemistry, and recently at the Swedish University of Agricultural Sciences, Uppsala (V. G. Kessler), the authors of this book have systematically studyied the synthesis and properties of homometallic alkoxides of Groups I–VIII of the Periodic Table, the bimetallic derivatives (alkoxoaluminates, -titanates, -zirconates, -niobates, -tantalates, -molybdates, -tungstates, -ferrates), and **$M(OR)_nX_m$ — alkoxocomplexes,** where X = Hal, O. The X-ray studies were carried out at the Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences by Yu. T. Struchkov, A. I. Yanovsky and Z. A. Starikova. Also studied were the synthesis conditions for the preparation of complex oxide materials — ferro- and piezoelectrics, HTSC, *etc*. The results of this work have laid the ground for the development of sol-gel technology in Russia.

1.3. Application of alkoxides in sol-gel processes

Over the last three decades an intensive development of the synthetic approaches to various oxide materials has been based on the application of metal alkoxides, **$M(OR)_n$**. In principle, a number of ways leading to the formation of oxides from metal alkoxides are possible — for example,



Both of the first two reactions (decomposition in plasma and oxidation) lead to high purity oxides, all their by-products being gases. If the initial alkoxides are volatile, they can be applied for the deposition from the gas phase (MOCVD). The broadest application was received, however, by the third reaction, that of the hydrolytic decomposition of the alkoxide of one or several metals in organic media, leading to formation of hydrated metal oxides, which are then subjected to dehydration. This principle is drawn from the sol-gel technology of inorganic materials, the alkoxides and the esters of inorganic acids being important raw materials in this technology (Fig. 1.1).

The successful application of the sol-gel route has been realized in the International technological practice of many branches of the industries—electronics, optics, construction of engines, nuclear energetics, chemical, and food industry equipment. Among these materials are ferro-, piezo-, and dielectrics, solid electrolytes, refractory materials, membranes, protective and decorative coatings, and also films with special optical and electrophysical properties, like hightemperature superconductors.

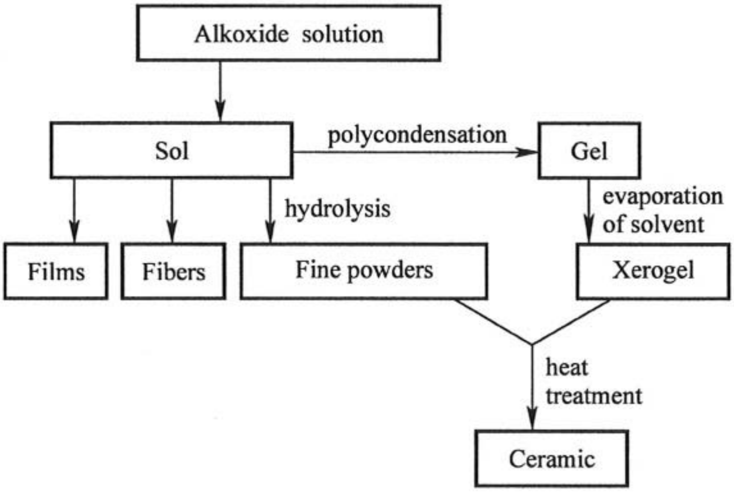


Fig. 1.1. Scheme of the sol-gel process

What are the applications of this technology? At its core lay the unique properties of metal alkoxides. First, the majority of the $M(OR)_n$ derivatives (with $n \leq 3$) can easily be subjected to deep purification by distillation or sublimation (below 200°C) or by recrystallization from organic solvents. Second, they easily undergo hydrolysis, forming hydrated oxides not containing any extra anions (in contrast to precipitation from the aqueous solutions of inorganic salts). These forms of $M_2O_n \cdot xH_2O$ are the least agglomerated and maximally hydrated (their structures do contain the minimal amounts M–O–M bridges), and therefore they easily form stable colloid systems — sols and gels — and have high reactivity (see Chapter 9). Their dehydration occurs at rather low temperatures, sometimes directly during the hydrolysis, and is accompanied by the formation of very small oxide particles ($\leq$100 Å) with well-developed surfaces, high chemical activity, and often amorphous or metastable phases that on subsequent thermal treatment are transformed into more stable forms. Varying the dehydration temperature it is possible to regulate the dispersion of the powders (and particle morphology), their phase composition, and their physical properties. Application of the solutions of alkoxides or the colloid solutions of the products of their hydrolysis (sols) permits gels, films, coatings, glasses, fibers, and so on to be prepared.

Application of alkoxides in the synthesis of complex oxides provides usually high homogeneity of the products, which gives it the advantage in comparison with precipitation from solutions of inorganic salts. In the latter case the formation of single $M_2O_n{\bullet}xH_2O$ occurs at different pH values, while the simultaneous presence of highly charged metal cations and such anions as SiO_4^{4-}, PO_4^{3-}, BO_3^{3-}, cannot be achieved at all. Low temperatures for the formation of oxide phases and the synthesis of ceramics (in comparison with the alternative technologies) hinders the loss of the more volatile components of the oxide composition and favors the preservation of the steichiometry.

* * *

For more than 50 years, the reaction of hydrolysis of metal alkoxides has been used for the preparation of oxide catalysts and adsorbents with highly developed surfaces, stable sols and gels of hydroxides, and the deposition of the optical coatings [629]. Before the World War II the State Optical Institute in Leningrad (Russia) developed and introduced into technological practices antireflective coatings of SiO_2, TiO_2, and complex compositions on their basis [1549]. In Germany the technology of SiO_2-TiO_2 coatings was developed by Schott Glasswerke Co. first for the production of automobile mirrors and then for a whole variety of antireflective coatings. Work continues quite intensively at present in the same company [485, 1513] and in many others. Application of different techniques of deposition (dipping, spinning, spraying), developed for optical coatings, permits films to be obtained with various functional properties: optical (with different reflective ability for different wave lengths), conductive transparent layers, opto- and acustoelectronic coatings, barrier, antistatic, decorative, protecting refractory, ferroelectric, HTSC, *etc.* It is already clear that the film deposition is a very promising direction in the application of metal alkoxides. This process demonstrates clearly the advantages of the sol-gel method connected with the simplicity of the necessary equipment, high purity of obtained materials, low temperatures of oxide phase formation, and exact conservation of the ratio of components given by solutions. At the same time the comparably high price of the raw materials (metal alkoxides), which has traditionally been regarded as a hindrance for their broad application, does not have any important role in this case due to very low amounts of solutions that are used in this process.

The other intensively developing direction in sol-gel technology is the preparation of fibers as precursors that are used for solutions of partially hydrolyzed alkoxides that form viscous gels. Pressing it via filiers at room temperature gives fibers that transform into glass fibers on further thermal treatment. The main compositions of the fibers are SiO_2, TiO_2, ZrO_2-TiO_2, ZrO_2, Al_2O_3 [1384, 1513]. The industrial production of fibers using sol-gel technology is carried out by, in particular, Japanese companies such as Asahi Glass Co. — SiO_2 [1242], and Sumimoto Chemical Co. — Al_2O_3 [767].

A traditional direction in sol-gel technology is the preparation of special glasses based on SiO_2, TiO_2, Al_2O_3, avoiding the melting step. Gel formed on aging of the hydrolyzed solution of the alkoxide is dried and subjected to thermal treatment. The major hindrance to formation of monoliths is cracking during the drying. It can be avoided via very slow step-by-step thermal treatment [1770, 1792], drying under hypercritical conditions (especially in the production of transparent warm-retaining fillings), and, finally, on addition into the initial solution of chemical additives, regulating the drying process (DCCA) [1717]. The latter technique has been used in the production of the SiO_2-based optical filters, doped by rare earth oxides.

The described applications of sol-gel processing deal mainly with the SiO_2-based materials, obtained from TEOS, $Si(OEt)_4$. In spite of that. Even now about 40% of patents in this technology are given for materials based on SiO_2. The range of compositions is continuously growing, the special place in the latter being occupied by the highly dispersed complex oxides — components for production of condensator, electrooptical, piezoelectric, and refractory ceramics. This direction in the sol-gel technology was started by the pioneering work of Mazdiyasni, performed in the late 1960s and early 1970s at Air Force Wright Aeronautical Laboratories, Ohio, USA [1084, 1083]. He has carried out the preparation of $BaTiO_3$, $SrTiO_3$, $Pb_{1-y}La_yZr_{1-x}Ti_xO_3$, being of main practical interest and demonstrated the great advantages in the application of alkoxides. Among them can be mentioned the high purity of the products, their chemical homogeneity, and their easy sintering.

Work in this area has been most successfully pursued in Japan. Synthesis of a large group of complex oxides — silicates, aluminates, stannates, germanates, and vanadates — was studied by Yamaguchi [1764]. The synthesis of ferroelectric oxides was systematically developed by Ozaki *et al.* [1245]. According to [58], alkoxides were used as precursors in the preparation of more than 100 varieties of monodisperse powders for the electronic ceramics. The Japanese have announced the industrial production of high purity monodisperse powders of $BaTiO_3$ for the preparation of multilayer thin film condensators and also the powders of mullite —$Al_6Si_2O_{13}$ — and cubic zirconia [1245]. According to Nomiya [1218], in 1978 to 1986 only in Japan were registered more than 800 patents on application of sol-gel technology in the synthesis of oxides (a drastic increase in their number started in 1980). Since 1981 the International Workshop on Glasses, Ceramics, Hybrids, and Nanocomposites from Gels, the International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites (1983 to 1991), and the Materials Research Society (MRS) Symposium on Better Ceramics Through Chemistry have been regularly held. Materials from these conferences are published in the Journal of Non-Crystal Solids and the Journal of Sol-Gel Science and Technology. Physicochemical principles of different processes of sol-gel technology were considered in the book by C. J. Brinker and G. W. Scherer [243]). Its application aspects were treated in two collected series of articles edited by L. Klein [1513].

In conclusion, we would like to mention that, in addition to this new direction, a large consumer of metal alkoxides (initially aluminium and titanium) is by tradition the technology of materials, where the alkoxides are used for hydrophobization and for cross-linking of the polyhydroxocompounds, epoxides and polyester resins, and organosilicon polymers. The products of the partial hydrolysis and pyrolysis of alkoxides — polyorganometalloxanes — are applied as components of the thermally stable coatings [48].

Concerning the other areas of application for metal alkoxides, see Chapter 12.

Chapter 2

GENERAL SYNTHETIC APPROACHES

Synthesis of metal alkoxides has been studied for more than a century by different researchers, who have proposed a large variety of synthetic techniques aimed at preparation of different distinct derivatives. In the 1950s in the course of the systematic studies Bradley suggested a few general techniques [196]. In the present review we would like to differentiate the methods that had technological applications and those that are mostly used in laboratory practice.

All metal alkoxides are sensitive to moisture. They decompose even in the presence of traces of water in solvents or in the atmosphere the products of their partial decomposition usually contain oxo-groups. When operating with the alkoxides in general and especially with those of alkaline or alkaline earth metals it is necessary to avoid the presence of even the traces of oxygen as the peroxides formed on oxidation decompose giving water and other undesirable products. Therefore, all operations with alkoxides are to be performed in an inert atmosphere of nitrogen or argon, dried over P_2O_5, zeolite, or other moisture absorbents; only anhydrous solvents should be used (some considerations concerning the drying of alcohols are discussed below).

2.1. Reactions of metals with alcohols (method 1)

$$M + nROH \longrightarrow M(OR)_n + n/2\, H_2\uparrow$$

This method may be used only in the case of the most active metals, with the values of the standard electrode potential in the approximate range of **$-3.0 \div -2.3$** V (alkaline and alkaline-earth metals and Mg). These metals usually react readily with the first representatives of the homological series of alcohols or with phenols; however, to bring the reaction to completion it is important to dissolve the alkoxides obtained, which is why a considerable excess of alcohols usually is used together with heating of the reaction mixture. Alkoxides usually crystallize in the form of solvates, such as **$LiOEt \cdot 2EtOH$, $NaOPr^i \cdot 3{}^iPrOH$, $KOMe \cdot 3MeOH$, $Mg(OMe)_2 \cdot 3.5MeOH$, $Ca(OEt)_2 \cdot 4EtOH$, $Ba(OEt)_2 \cdot 4EtOH$, $KOPh \cdot 3PhOH$, $NaOPh \cdot H_2O$** (Tables 12.1 and 12.2). High temperatures of their desolvation (sometimes close to the temperature of pyrolysis of **$M(OR)_n$**) determine the necessity of direct synthesis of nonsolvated alkoxides (which are far more reactive and find applications, for instance, as catalysts). One of such methods involves the reaction of metal with the stoichiometric amount of alcohol in an inert solvent such as xylene or dioxane. The solvated alkoxide first formed in the process reacts with the new portion of metal while the nonsolvated alkoxide precipitates [567].

One of the modem methods is associated with the application of pyrophoric metals formed, for examle, as a result of low-temperature gas phase codeposition with toluene vapor (MVS-metal vapor synthesis) [757].

Liquid ammonia may aso be used as a solvent in reactions of metals with alcohols, such as

$$Na + NH_{3\,(liq.)} \xrightarrow{-e} [Na(NH_3)_6]^+ \xrightarrow[-NH_3]{+ROH} NaOR\downarrow + 1/2H_2\uparrow$$

This reaction is especially important for the synthesis of the derivatives of higher unsaturated and polyatomic alcohols [1644, 313].

Reactions of metals with alcohols may frequently be accelerated by amalgamation with mercury or its salts:

$$2M + Hg^{2+} \longrightarrow M/Hg + M^{n+}$$

On the other hand, application of alkali metal amalgam permits the slowing down of the reaction of metals with alcohols, which is used in the industrial production of alkali metals alkoxides. Production of NaOR by Mathieson Alkali Works is based, for instance, on the reaction of sodium amalgam (formed as a result of the electrolysis of aqueous NaCl solution with the mercury cathode) with alcohol; **$NaOR \cdot nROH$** is isolated from the solutions. Na residue in the amalgam is hydrolyzed, the obtained mixture is returned to the electrolyzer, and the evaluated heat is used for initiation of the reaction of the amalgam with alcohol [1644].

I_2, Br_2, $MHal_n$, $M(OR)_n$ may also speed up the reaction; good results were obtained when two reagents were introduced simultaneously, such as **$HgCl_2$ + I_2 or $HgCl_2$ + $Hg(OAc)_2$.** The following metal alkoxides were synthesized in this way: **$Be(OEt)_2$ [1645], $Al(OR)_3$ [$Al(OPr^i)_3$** and **$Al(OBu^s)_3$** are produced by this method commercially] [1301], **$M(OR)_3$** (M = Y, La, Ln) [1084, 251, 466]. The mechanism of this activation lies in formation in the solutions of oxonium complexes **$Hal_2 \bullet nROH$,** which readily react with the metal to form **$MHal_n(OR)_m$.** The value of the electrode potential **M^{n+}/M-solid** is not changed; however, overvoltage is removed. The overvoltage is caused by the existence of a layer of oxide on the surface of metals. Even the addition of catalyst does not eliminate this layer completely. Therefore, the dissolution of metal occurs in a nonuniform manner, leaving a fine powder of oxides or suboxides of metals when reactions are completed. In those cases when common catalysts are inefficient, Caulton and his coworkers have successfully used activation of Ba by short time bubbling of **NH_3** in solutions of ROH in THF **($R=Ph_3C$, Ph_3Si). $Ba(NH_2)_2$** formed under these conditions supposedly acts as a proton carrier [497, 305].

It is noteworthy that solubility of the formed metal alkoxide is in many cases even more important for the reaction than the values of the metal standard electrode potentials or the mobility of protons of the alcohol. The following examples illustrate this statement. Despite higher acidity of MeOH in comparison with EtOH (pK = 15.5 and 16, respectively), the insoluble **$Ca(OMe)_2$** is formed very slowly in comparison with the soluble derivatives **$Ca(OEt)_2$** or **$Mg(OMe)_2$** (both latter compounds crystallize from solutions as solvates) [1646]. Aluminum readily reacts with **^iPrOH** with the formation of the highly soluble **$Al(OPr^i)_3$** even in the absence of the catalyst **(pK ROH = 18, E^0 Al^{3+}/Al_{sld} = −1.66 V).** On the other hand, polymeric **$Al(OMe)_3$** and **$Al(OEt)_3$** are formed only on prolonged refluxing of the metal with alcohols in xylene (140°C) in the presence of **$HgCl_2$** and **I_2** [1301].

Binding of the polymeric alkoxide in a soluble complex allows metals to react with alcohols even for the elements with standard potentials close to zero, such as

$$Cu + mROH + nL + O_2 \longrightarrow Cu(OR)_2 \cdot nL \cdot mROH$$

(R = Me, Et; L= En, Dipy, Phen) [936]

Due to high solubility and stability of 2-methoxyethoxide derivatives, high-purity aluminium and lanthanides readily react with 2-methoxyethanol without any catalyst.

2.2. Anodic oxidation of metals (method 2)

Direct interaction of metals with alcohols may be efficiently performed only for the most active metals; therefore, it seemed promising to use the anodic oxidation for synthesis of the derivatives of less active metals. The first attempt in this direction was made by Szilard in 1906: he performed electrolysis of NaOMe solutions in MeOH with Cu or Pb anodes [1552]. For many years, however, this idea did not receive the appropriate attention; it was not until 1970 that Monsanto Chemical Co. disclosed the electrochemical synthesis of Si, Ge, Ti, Zr, and Ta alkoxides by anodic dissolution in alcohols in the presence of electroconductive additives (NH_4Cl or R_4NCl) [1599]. In 1974 Lehmkuhl and his coworkers elaborated on a continuous process of synthesis of insoluble $M(OR)_2$ (M = Fe, Co, Ni; R = Me, Et, ^nBu, ^tBu) in alcohols with $[Bu_4N]Br$ or NaBr as additives [1005]. In the early 1980s we proposed and introduced into laboratory practice a series of electrochemical techniques for synthesis of the following metal alkoxides: $M(OR)_n$, M = Sc, Y, La, Ln, Ti, Zr, Hf, Nb, Ta, Ni, Cr(III); R = Et, Pr^i, C_2H_4OMe; $MO(OR)_4$, M = Mo, W; R = Me, Et, ^iPr, OC_2H_4OMe as well as methoxyethoxides $M(OC_2H_4OMe)_n$, M = Be, Cu, Fe(III), Co,Ni, Cr(III); $[Bu_4N]Br$ or LiCl were used as additives [1478, 953, 968,1637, 1367, 1652, 1614, 906]. Recently, synthesis of the following insoluble derivatives also has been reported: $Ni(OR)_2$ [1410], $U(OEt)_4$ [1701], $Cu(OR)_2$, [R = Me, C_2H_4OMe, C_5H_{11}, Ph] [97], $Sn(OMe)_2$ [828], $Cd(OR)_2$ [R=Me, Et, Pr, Bu, Ph] [98], $Re_4O_2(OMe)_{16}$ [906].

The character of the processes that take place on anodic dissolution is dependent on the nature of metal. Those that have high enough negative potentials to dissolve directly in alcohols (lanthanides, for example) need only some additional anodic potential to overcome the overvoltage. The electric current yields (i.e., the ratio of the amount of alkoxide formed and that calculated theoretically taking into account the electric charge that passed through the solution) are in this case much higher than 100% [1478, 953]. For the less active metals the nature of of the process is much more complex (an overvoltage problem appears to be of importance for many of those cases, as the dissolution of metals is often incomplete and precipitation of fine powders of metal or lower oxides can be observed). Lehmkuhl has supposed that for the late transition metals, such as Fe, Co, and Ni, the oxidation of the conductive additive takes place [1005]. Halide radicals that are released attack the surface of electrode and form a solvated metal halide. The latter is transported to the cathode and reduced to an alkoxide, which is usually insoluble in this case. The same kind of transformation occurs presumably in the electrochemical synthesis of the heavy main group alkoxides. Precipitating alkoxides in this case are often contaminated with alkoxide halides. It has recently been reported that the presence of amines (Dipy, Phen) in the electrolyte permits to avoid halide contamination and accelerates the dissolution of Cd and Cu due to the formation of stable insoluble complexes with metal alkoxides or phenoxides [97, 1062].

When the anodic dissolution of niobium was investigated there was observed the reaction, leading to formation of metal alkoxides already in the anodic process [911, 1676]. The cathodic reactions are limited to partial reduction of the alkoxides formed (it is usually a monoelectronic process — that is Ti(IV) is reduced to Ti(III), Nb(V) to Nb(IV), Mo and W(VI) to M(V) [908], Fe(III) to Fe(II) [1005]). Reduction is accelerated at higher concentrations of $M(OR)_n$ or on heating of the solutions. It is often associated with the color changes in solutions. Thus, in the course of the electrochemical synthesis of niobium alkoxides the solutions turned brown due to formation of $Nb(OR)_4$ [911, 1676]. Oxidation of the low-valent derivatives thus formed by oxygen, present in the solvents or in atmosphere, gives oxoalkoxides that contaminate the final product. It has been also noticed that the electrochemical destruction of the conducting additives can play a considerable role:

$$MX + ROH \longrightarrow MOR + ½H_2 + ½X_2$$

The appearance of the alkali alkoxide can lead to formation of bimetallic alkoxides or bimetallic alkoxide halides as impurities. For example, lithium oxoalkoxocomplexes were isolated as side products of the anodic dissolution of Mo and W when LiCl was used as conductive additive [908].

The electrochemical technique can be used also for direct synthesis of bimetallic alkoxides. For instance, the anodic dissolution of rhenium in the methanol-based electrolyte that already contained $\mathbf{MoO(OMe)_4}$, permitted to prepare with a good yield (60%) a bimetallic complex $\mathbf{Re^{V}Mo^{VI}O_2(OMe)_7}$, with a single Re–Mo bond [904]. Application of the same procedure permitted the preparation of complex alkoxide solutions with controlled composition for sol-gel processing of ferroelectric films [1777].

It should be mentioned that by changing the conditions of electrochemical synthesis — such as nature of the alcohol, the purity of the metal used as anode, the nature and concentration of the conductive additive, the voltage (usually 30 — 110 V DC is applied), the temperature, and even the construction of the cell — one can significantly effect the process of the anodic dissolution or even change its mechanism. As it has already been mentioned, the electrochemical dissolution of iron in alifatic alcohols gives insoluble iron (II) alkoxides [1005], while in 2-methoxyethanol a soluble iron (III) complex is obtained [1514]. Another example is provided by tantalum dissolution in isopropanol: while high-purity metal is rapidly dissolved anodically [1639], the one containing impurities is passivated. Therefore, it is quite clear that each synthesis requires careful study, optimization of parameters of electrochemical synthesis, and isolation and purification of final products.

An important advantage of the electrochemical technique lies in its simplicity because metals are much easier to handle than metal halides and are always commercially available; the consumption of the solvents is also much smaller than for conventional techniques [1639, 1612]. The electrochemical method allows the creation of a highly efficient, low-waste continuous process for commercial production of metal alkoxides [948].

2.3. Reactions of metal oxides or hydroxides with alcohols (method 3)

$$\mathbf{M^{I}OH + ROH \leftrightarrow M^{I}OR + H_2O}$$
$$\mathbf{M^{II}O + 2ROH \leftrightarrow M^{II}(OR)_2 + H_2O}$$

Both reactions are used for the commercial production of alkaline and alkaline-earth alkoxides from very cheap raw materials. As far as the metal alkoxides thus formed are soluble in alcohols, both reactions are reversible. Thus, application of these methods is expedient in the case of alcohols with the boiling temperature higher than 100°C (water is distilled off). When low-boiling alcohols are used the reaction time increases greatly, water is eliminated in the form of an azeotrope with benzene. Sometimes hydrophilic agents **(e.g., CaC_2)** are added; metal alkoxides may be also precipitated by addition of acetone (NaOEt) [1273, 1644].

This method is especially important for synthesis of thallium (I) alkoxides, such as for the most frequently used TlOEt:

$$\mathbf{TlOH + EtOH \leftrightarrow TlOEt + H_2O}$$
$$\mathbf{2Tl + EtOH + \tfrac{1}{2}O_2 \longrightarrow TlOEt + TlOH}$$

In this case isolation of metal alkoxide from water does not require any special measures: liquid TlOEt is accumulated in the bottom of the flask in a 95% mixture with EtOH, while TlOH and water comprise the upper layer [1625]. Alkaline metals react in analogous way with alcohols that do not mix with water. For instance, reaction of KOH with **Et_2CHOH** (pentanol-3) at 120°C also results in the formation of two layers; the upper (alcoholic) layer contains 40 wt% of KOR and 2 wt% of KOH while the lower (aqueous) layer contains 54 wt% of KOH [1277].

Alcoholysis of metal oxides may also be used for the synthesis of multivalent metal alkoxides; nevertheless, application of this method is restricted to "covalent" oxides with low values of lattice activation energies. Usually these are derivatives of M in the higher oxidation states, and their interaction with alcohols is complicated by oxidation-reduction processes — for example,

$$V_2O_5 + 6ROH \longrightarrow 2VO(OR)_3 + 3H_2O\uparrow \quad \text{(azeotrope with benzene)}$$
$$R = Et\text{–}C_5H_{11}{}^i\text{; or. liq., b.p. 108-155/2 [1313, 1238]}$$
$$CrO_3 + 2{}^tBuOH \rightarrow \underset{\text{yel. liq.}}{CrO_2(OBu^t)_2} + \underset{\text{red liq.}}{Cr_2O_5(OBu^t)_2} + \underset{\text{(in the upper layer)}}{Cr_3O_8(OBu^t)} + H_2O \quad [131]$$
$$MoO_3 + 3\underset{\text{b.p.>180°C}}{[MeCH(OH)]_2} \rightarrow (MeCHO)_2MoO_2\bullet 2R(OH)_2 + H_2O\uparrow \quad [154]$$
$$Re_2O_7 + 2\,{}^tBuOH \rightarrow ReO_3(OBu^t) + \text{“}HReO_4\text{”} \quad [1358]$$
$$Os^{VIII}O_4 + \underset{\text{b.p. >197°C}}{(\text{-}CH_2OH)_2} \rightarrow Os^{VI}O[(\text{-}CH_2O)_2]_2 + H_2O\uparrow + \ldots \quad [406]$$
$$\begin{array}{c} H_2XeO_4 + {}^tBuOH \rightarrow XeO_2(OH)(OBu^t) + H_2O \\ \downarrow KOBu^t \\ K[XeO_3(OBu^t)]\bullet{}^tBuOH \quad [839] \end{array}$$

Application of metal hydroxides is especially fruitful for the preparation of metal phenolates as the latter are exceptionally stable to hydrolysis. Reactions can be performed in alcohols, benzene, water or melted phenols [1644].

In conclusion, it should be mentioned that the reactions discussed in the present section are very important for drying of alcohols. The application of sodium alkoxides, which has been employed in old techniques, can hardly be recommended because the equilibrium of the reaction

$$\mathrm{NaOEt + H_2O \leftrightarrow NaOH + EtOH}$$

is shifted to the left. The equilibrium constant of the reaction

$$\mathrm{EtOH + OH^- \leftrightarrow EtO^- + H_2O}$$

at 25°C is equal to 0.68 [290, 1186], which means that in the 0.1 M solution of NaOH in 99% EtOH, 96% of Na is present in the form of NaOEt. There are unfortunately no available thermodynamic data concerning the equilibria of alkaline-earth metals with water; however, refluxing over $\mathrm{Ca(OR)_2}$ or $\mathrm{Mg(OR)_2}$ allows the minimizing of the traces of water in alcohols [155]. Presumably, low solubility of the hydrolysis products $\mathrm{MO_x(OR)_{2-2x}}$ ensures the shift of the equilibrium toward the formation of alcohols. Therefore, we would like to give some practical recommendations concerning the methods of drying of alcohols. Alcohols are usually dried by the most readily available metal alkoxides Mg, Ca, Al. These alkoxides are previously synthesized by reactions of metals with **anhydrous** alcohols and introduced into the alcohol that is to be dried **(H_2O content < 1%);** refluxing of the reaction mixture for 4 to 6 hours is performed; then alcohol is distilled off with a deflegmator. 5–8 g of Mg or Al or ~ 20 g of Ca is necessary for drying of 11 of alcohol. $\mathrm{Mg(OMe)_2{\cdot}3.5MeOH}$ is convenient for drying of MeOH, $\mathrm{Ca(OEt)_2{\cdot}4EtOH}$ (or $\mathrm{Mg[Al(OEt)_4]_2}$) for EtOH; $\mathrm{Al(OR)_3}$ for BuOH and $\mathrm{{}^iPrOH}$. In the two latter cases it is also useful to reflux the alcohols thus obtained with zeolites NaA (with the pore size < 5Å). The content of H_2O in alcohols thus prepared is usually $\leq 0.02\%$ (determined by Fischer technique).

2.4. Alcoholysis of MX_n (method 4)

$$\mathrm{MX_n} + n\mathrm{ROH} \longrightarrow \mathrm{M(OR)_n} + n\mathrm{HX}$$
$$\mathrm{X = H, Alk, C{\equiv}C, {\equiv}N, NH_2, NR_2, N(SiR_3)_2, SH...}$$

The main idea of these techniques lies in the interaction of the "active" hydrogen atom of the alcohols with the "anions" of metal hydrides, alkyls, acetylides, nitrides, amides, dialkylamides, bis(trialkylsilyl)amides, sulfides, etc., with formation of compounds where an H atom is bonded by a strong covalent bond (usually gaseous HX). Alkaline hydrides of the most active metals (K, Rb, Cs) are used to slow down the reaction of metal with alcohol; sometimes it is necessary simply to avoid explosion.

On the other hand, to accelerate alcoholysis of NaH and KH in solutions of benzene or THF [2.2.1] – [2.2.2] – cryptands are used (which bind alkaline metal into a rather stable chelate complex) [1004]. Quite stable, volatile perfluorotert-butoxides were first obtained in reactions of LiH or NaH with $(CF_3)_3COH$; they distill at atmospheric pressure at 218 and 232°C, respectively [467] (the application of metals would presumably lead in this case to condensation of Wurtz type). Li and Na hydrides are used as cheaper than metal raw materials for production of the corresponding metal alkoxides. In particular it has been suggested that the equipment used in production of MH could be cleaned from its residue by the mixture of EtOH and the aromatic hydrocarbon (40 to 60% by volume). After hydrogen evolution is completed the solvent is eliminated under vacuum at $\leq 90°C$; the residue is MOEt with the content of the main product > 98% [342].

Alcoholysis of amides was first reported for the preparation of alkaline alkoxides. The reaction was carried out in liquid ammonia solutions and was aimed at the obtaining of the derivatives of aromatic alcohols:

$$MNH_2 + PhCH_2OH \longrightarrow MOCH_2Ph + NH_3 \quad [1740].$$

The individual dialkylamides were first applied for the synthesis of metal alkoxides by Gilman *et al.* who used them for the preparation of $U(OR)_4$ [856]. The universal character of this method was demonstarted later by Bradley and Thomas [196], who reported the synthesis of $Cr(OBu^t)_4$, $V(OR)_4$, $Sn(OR)_4$, and $Nb(OBu^t)_5$ using this route. The advantage of this technique lies in almost quantitative yields. It also can be applied in the preparation of the derivatives of any alcohols including $M(OR^t)_n$. Formation of only gaseous side products (i.e., HNR_2) that can be easily removed by the evacuation can be considered to be another advantage of the technique. However, in some cases the formation of stable complexes of alkoxides with the amines to be removed was nevertheless observed (as, for instance, in case of $W_2(OSiMe_3)_6(HNMe_2)_2$ [16]).

The other problem in the application of this route originates from the necessity of synthesis of the initial amides (which are not commercially available) and the complicated procedure of their separation from LiCl. The alkylamide group is a strong σ- and especially π-donor, and it can act both to stabilize the higher oxidation states and to reduce the derivatives of highly electronegative metals (thus $W(NMe_2)_6$ synthesized from WCl_6 is always contaminated with $W_2(NMe_2)_6$ [207]). The high extent of additional π-bonding that is observed for the electronegative elements in higher oxidation states makes them even inert to alcoholysis by ROH, which are extremely weak acids. For example, $W(NMe_2)_6$ at ambient temperature is almost stable to the action of ^tBuOH [207].

To overcome these difficulties the application ofbis-(trialkylsilyl)-amides was recently recommended [770]. The latter ligands are much weaker π-donors and, therefore, are easier hydrolizable and higher thermally stable. Due to highly ramified radicals, attached to the nitrogen atom of the amide, they are usually monomeric and highly volatile and thus can be efficiently purified by distillation.

Alcoholysis of bis-(trimethylsilyl)-amides provides a very advantageous route to the synthesis of alkoxides of early transition (Cr(II), Mn(II) [770]) and heavy main group metals (Zn [649], Cd [183], Pb [1074, 1254], Bi [649, 1069]). Unfortunately, the derivatives of late transition elements, in particular Co and Ni, cannot be obtained using this route because of poor stability even of the corresponding silylamides [265]. Also known are some examples of only partial substitution of the ligand on alcoholysis; for example, the interaction of $Y[N(SiMe_3)_2]_3$ with Ar_2Bu^tSiOH gives at the first step $Y(OR)[N(SiMe_3)_2]_2$ [1464]. However, the main obstacle that limits the application of this route only to the laboratory practice is the comparably high price of the initial reagents for the synthesis of bis-(trimethylsilyl)-amides — $LiN(SiMe_3)_2$ and $HN(SiMe_3)_2$.

We would like to mention alcoholysis of MR_n (accompanied by evolution of hydrocarbons). However, metal alkyls are practically unavailable; therefore, they are used for the synthesis of metal alkoxides very rarely. Only a few examples are known: CuOMe [413], $Mn(OPr^i)_2$ [1306], $V(OBu^t)_4$ [1338], $Cr(OR)_2$ [350]. On the other hand, alcoholysis of metal alkyls is frequently performed to obtain alkoxoalkyls $MR'_m(OR)_{n-m}$ — catalysts in polymerization processes [400, 401]. The latter are often quite stable to further alcoholysis and cannot be transferred to metal alkoxides (recently, however, a contribution has reported the preparation of $Mg(OR)_2$ [$R=Pr^i$, Bu^t, $CHMe(C_6H_{13})$] by action of alcohols on $MgEt_2$ [1582]).

In contrast to all the above mentioned MX_n the chloride atoms in the molecules of covalent chlorides can be replaced only on the action of phenols. In the case of sterically hindered alcohols such as $2,6\text{-}R_2C_6H_3OH$ the alcoholysis often yields only phenoxide chlorides such as $TiCl(OC_6H_3Ph_2\text{-}2.6)_2$ [749], and $Ta_2OCl_3(OC_6H_3Pr^i_2\text{-}2.6)_5$ [389].

2.5. Metathesis reactions of MX_n with alkaline alkoxides or ammonia (method 5)

$$MHal_n + nM^IOR \longrightarrow M(OR)_n + nM^IHal$$

This method hitherto has been the most commonly used for the synthesis of metal alkoxides; the reaction is usually carried out in alcohols. That is why at first some considerations concerning interaction of metal halogenides with alcohols should be made. It has been emphasized by Tishchenko [1585] that dissolution of $ZnCl_2$ in alcohols is accompanied by vigorous reaction leading to $ZnCl_n(OR)_{2-n}$, accompanied by evolution of HCl, and followed by further reaction:

$$ROH + HCl \longrightarrow RCl + H_2O$$

This reaction is catalyzed by $ZnCl_n(OR)_{2-n}$. Metal halogenides being strong Lewis acids demonstrate pronounced tendency to solvolysis, which increases in the series primary < secondary < tertiary. Indeed, interaction of $ZrCl_4$ with EtOH or $SiCl_4$ with *t*-BuOH results in the formation of $MO_2{\bullet}nH_2O$ [223]. The following examples illustrate the dependence of the rate of the reaction on the valency of metal (the ionic character of M-Cl bond) and the pK of alcohol:

$$VCl_3 + ROH \longrightarrow VCl_3{\bullet}nROH \quad (R = Me, Et, Pr^i)$$
$$VCl_4 + ROH \longrightarrow VOCl_2{\bullet}nROH, \; n = 3,4 \; [1634]$$
$$VOCl_3 + EtOH \xrightarrow[{[CCl_4]}]{} VOCl_2(OEt) \xrightarrow[EtOH]{} VOCl(OEt)_2$$

$$\underset{pK=10}{VOCl_3 + PhOH} \longrightarrow VOCl(OPh)_2$$

$$VOCl_3 + \underset{pK=8}{4\text{-}ClC_6H_4OH} \longrightarrow VO(OC_6H_4Cl\text{-}4)_3 \quad [607]$$

Because reactions are accompanied by the formation of oxochlorides (the derivatives of the most acidic phenols being the only exception) with partial substitution of chlorine atoms by alkoxide groups, they should be avoided in synthesis of metal alkoxides.

Alkoxylation of $MHal_n$ is performed by KOR, NaOR, or LiOR or by ammonia in solution in alcohol (formally *ammonium alkoxide*). Reaction with NaOR is accompanied by formation of NaCl, which is almost completely insoluble in organic solvents and is, therefore, used in the synthesis of soluble metal alkoxides. One of the first examples of application of such reactions has not lost its importance as a method of synthesis to this day:

$$TiCl_4 + 4NaOR \xrightarrow{ROH} Ti(OR)_4 + 4NaCl\downarrow$$

For many years attempts were made to improve this method: different authors suggested changing the techniques of introductihg the components, separating the products, lowering of the reaction temperature, and so on. In all the cases the yield of the alkoxide did not exceed 70% [473, 560]. We succeeded in making considerable improvements in the yields of $M(OR)_n$ (M = Ge, Ti, In, La, Ln, Bi, V, Nb, W, Fe) in these reactions by complete elimination of alcoholysis reactions: metal halogenides were very slowly introduced either without solvent or in the form of solution or suspension in an inert organic solvent (ether, hydrocarbon, alkyl halide) in reaction with the solution of NaOR in alcohol [953, 968, 1613, 1648, 1652].

The process is complicated by the formation of bimetallic complexes $NaM_n(OR)_p$ or $NaM_n(OR)_pCl_q$, which may be decomposed by prolonged refluxing or stirring of the reaction mixture after the addition of the reagents is complete. In the case of $Ti(OR)_4$, due to the low stability of alkoxotitanates reaction can be successfully accomplished; however, the attempt to synthesize $Zr(OR)_4$ by this reaction failed: complexes $NaZr_2(OR)_9$ are quite stable and may even be distilled in vacuum without decomposition [115]. Alkoxochlorides and especially $M(OMe)_nCl_m$, which are formed in this reaction, are also usually very stable. YCl_3 and $NdCl_3$ react with 3 moles of NaOR to give $Y_3(OBu^t)_8Cl{\bullet}2THF$ and $Nd_6(OPr^i)_{17}Cl$, while $LaCl_3$ in the same conditions yields $La_3(OBu^t)_9{\bullet}2THF$ [553, 41]. Syntheses of $U(OEt)_5$ and $U(OEt)_6$ are the rare examples of reactions of fluorides with NaOR [699, 19].

To synthesize insoluble polymeric metal alkoxides (primarily methoxides) LiOR is usually used, such as

$$UCl_4 + 4LiOMe \xrightarrow{MeOH} U(OMe)_4\downarrow + 4LiCl \ [856]$$

$$MCl_2 + 2LiOMe \xrightarrow{MeOH} M(OMe)_2\downarrow + 2LiCl$$
$$M = Cr, Mn, Co, Ni, Cu \quad [6]$$

Solubility of LiCl in MeOH, EtOH, and ^nBuOH is 30.4, 19.6, and 13.9%, respectively. That is why after refluxing of the reaction mixture and washing off the precipitate with alcohol, alkoxides free from LiCl are obtained. However, this reaction in many cases is also complicated by formation of bimetallic complexes. Formation of stable intermediate complexes is especially characteristic when LiOR is applied for alkoxylation. Thus $Li_4Y_4O(OBu^t)_{12}Cl_2$ was isolated in reaction of YCl_3 with 2 mols of $LiOBu^t$ (i.e., on lack of OR-ligands) [553].

Thus, in accordance with the data of [1367], the synthesis of $Ni(OR)_2$ suggested by Mehrotra [99] leads, in fact, to $Li_nNi(OR)_{1.8+n}Cl_{0.2}$ (R = Me, Et). In the synthesis of metal alkoxides highly soluble in hydrocarbons (with branched or chelated radicals) both LiOR or NaOR may be used. The product is usually extracted by hexane, Et_2O, or other low-boiling solvents, such as

$$BiCl_3 + 3NaOC_2H_4OMe \xrightarrow{THF;\ 2h} Bi(OC_2H_4OMe)_3 + 3NaCl\downarrow$$

$$BiBr_3 + 3NaOBu^t \xrightarrow{THF;\ 24h} Bi(OBu^t)_3 + 3NaBr\downarrow \ [1069]$$

$$CuCl + LiOCHBu^t_2 \xrightarrow{Et_2O;\ 48h} CuOCHBu^t_2 + LiCl\downarrow \ [167]$$

Ammonia in alcohols is used for alkoxylation much more frequently than the alkaline alkoxides. This method, which was first patented by Nelles in 1939 [560], remains hitherto the main technological process for the production of titanium alkoxides:

$TiCl_4 + 4ROH + 4NH_3 \rightarrow Ti(OR)_4 + 4NH_4Cl\downarrow$
$R = Me, Et, Bu^n, Bu^i, C_5H_{11}{}^n, C_5H_{11}{}^i, C_6H_{13}{}^n, C_8H_{18}{}^n$ [1547]

Chloride may be also bound by $HCONH_2$ or $HCONMe_2$: NH_4Cl is soluble in amides (and nitriles), while titanium alkoxides remain in the bottom layer. However, reactions with gaseous NH_3 in an alcohol-benzene (toluene, cyclohexane, CCl_4) mixture are by far the most economic. The latter are added in approximately 90% concentration to decrease the solubility of NH_4Cl in alcohols (which comprises 3.3% in MeOH, 1.5% in EtOH). Higher concentration of hydrocarbons results in very fine precipitates, that cannot be filtered off. It has already been mentioned above that pronounced solvolysis of $MHal_n$ in ^tBuOH does not allow the performance of synthesis of $Ti(OR^t)_4$ under the above conditions. To overcome this obstacle, $TiCl_4$ is introduced in reaction with alcohols in the alkaline medium in the form of $TiCl_4{\bullet}8NH_3$ (which crystallizes on the bubbling of NH_3 through the solution of $TiCl_4$ in benzene or cyclohexane). On refluxing of this complex with ROH ($R = Bu^t, Am^t, CH_2{=}CH{-}CH_2, Et$) $Ti(OR)_4$ were obtained with high yields [560,1547].

The use of NH_3 instead of M^IOR allows the formation of bimetallic complexes to be overcome; thus by this method $Zr(OR)_4$ and $Hf(OR)_4$ were first synthesized [196]. Alcohol derivatives of different elements (such as Si, Ge, V, Nb, Ta, Sb, Mo, W, U, Fe, and Re) were also prepared using this route. Sometimes instead of NH_3 the tertiary amines were used:

$2ReOCl_4 + 8MeOH + 8R_3N \rightarrow [O{=}Re(OMe)_3]_2O + 8[R_3NH]Cl$ [519]

Application of this method is limited by high stability (and presumably low solubility in alcohols) of the complexes of chlorides with ammonia, such as $LnCl_3{\bullet}3NH_3$. Interaction of $MHal_n$ with "ammonium alkoxides" cannot lead to compounds with higher basicity, such as $Th(OR)_4$ (its alcohol solution is alkaline). Such alkoxides are synthesized by reaction of $ThCl_4$ with NaOR.

In one of the variants of this reaction Bradley suggested using pyridinium halogenmetallates instead of $MHal_4$:

$$(PyH)_2ZrCl_6 + 6NH_3 + 4ROH \rightarrow Zr(OR)_4 + 6NH_4Cl\downarrow + 2Py$$

This allows the exclusion alcoholysis of the strong Lewis acid; the precursor, which is much more stable than the chloride, is synthesized by reaction:

$$ZrOCl_2{\bullet}8H_2O + 4HCl + 2Py \xrightarrow{EtOH} [PyH]_2ZrCl_6 + 9H_2O \text{ [829]}$$

This method is the only possible way for synthesis of $Ce(OR)_4$ and $Pu(OR)_4$ from the halogenide precursors, since the corresponding $MHal_4$ has not been described [196].

* * *

This section concludes with a discussion of the reactions of metal halogenides with other alkoxylating agents (besides M^1OR) and the reactions of the salts MX_n with alkaline alkoxides, used in the synthesis of $M(OR)_n$. In this connection the synthesis of Mo and W alkoxides and akoxohalogenides of ortho-series, using alkylalkoxoorthosilicates or B, Nb, P alkoxides, are described:

$$MoF_6 + Me_nSi(OMe)_{4-n} \longrightarrow MoF_x(OMe)_{6-x} + nMeF$$

$$WCl_6 + Me_3Si(OMe) \rightarrow WCl_3(OMe)_3 \rightarrow WCl_2(OMe)_4 \xrightarrow{2NaOMe} W(OMe)_6$$

$$WF_6 + B(OMe)_3 \longrightarrow WF_5(OMe) + BF_3 + MeF \quad \text{[705, 1714]}$$

For complete substitution of fluoride ligands in such complexes, application of $Mg(OR)_2$ was recently proposed (exploiting the much lower solubility of MgF_2 in comparison with MF) [262].

Among metal salts other than $MHal_n$, metal carboxylates (and especially acetates) are sometimes used in the synthesis of metal alkoxides. Their advantage in reactions with M^1OR lies in considerably lower stability of intermediates — metal alkoxoacetates in comparison with metal alkoxohalogenides.

Indeed, reactions

$$M(OAc)_2 + 2NaOMe \xrightarrow{MeOH} M(OMe)_2\downarrow + 2NaOAc\ (M = Zn, Cd, Hg)$$

$$M(OAc)_2 + 2LiOR \xrightarrow{EtOH} M(OEt)_2\downarrow + 2LiOAc\ \ (M = Cd, Hg)$$

can be performed due to precipitation of polymeric alkoxides [1623]; whereas in the synthesis of $Pb(OR)_2$ it is NaOAc, which is insoluble in alcohols:

$$Pb(OAc)_2\downarrow + 2NaOR \xrightarrow{ROH} Pb(OR)_2 + 2NaOAc\downarrow;\ R = Pr^i, Bu^n\ \ [1627]$$

$$Pb(OAc)_2\downarrow + 2NaOBu^t \xrightarrow{PhMe} Pb_4O(OBu^t)_6 + Bu^t_2O + 2NaOAc\downarrow\ \ [1254]$$

Application of halogenides under the same conditions results in $MHal_n(OR)_{2-n}$, which does not decompose in excess of M^1OR or under refluxing. The patent [833] describes the general method of preparation of the stable metal alkoxide solutions (which are used in technology); it comprises a heterogeneous reaction of Zn, Cd, Y, Ln, In, Pb, Sn, Zr, Sb, Bi and Mn carboxylates in alcohol solutions with NH_3 or amines with subsequent purification by ionic exchange.

The use of complex cerium nitrate (IV) (which is more accessible in comparison with $(PyH)_2CeCl_6$) in the synthesis of $Ce(OR)_4$ proved quite fruitful:

$$(NH_4)_2Ce(NO_3)_6 + [NH_3 + ROH + NaOR] \xrightarrow{ROH} Ce(OR)_4 + NH_4NO_3 + NaNO_3$$
$$(R = Me, Et, Pr^i, C_2H_4)\ [670]$$

2.6. Reactions of alcohol interchange or transesterification (method 6)

$$M(OR)_n + nR'OH \longrightarrow M(OR')_n + nROH$$
$$M(OR)_n + nR''COOR' \longrightarrow M(OR')_n + nR''COOR$$

This method is especially important for the preparation of homologues, which are hardly accessible by other techniques. According to the data of ^1H NMR spectroscopy, the first step of the reaction lies in addition of the free alcohol (and presumably destruction of the existing $[M(OR)_n]_m$ oligomers) [196]. There may be two ways to shift the equilibrium in the desired direction: distillation of the alcohol with lower boiling point (usually as an azeotrope with benzene) or precipitation of the newly formed alkoxide. Tishchenko was the first to use this method for the synthesis of insoluble aluminium alkoxides — derivatives of methyl, allyl alcohols, and glycol (which do not react with Al-amalgam) from $Al(OPr^i)_3$. Reactions are performed under mild conditions; there are no side reactions, associated with the presence of $MHal_n$ and HC1. The use of benzene as a reaction medium allows the amount of the introduced R'OH (for the synthesis of $M(OR)_m(OR')_{n-m}$ to be controlled. In some cases the stoichiometric amount of R'OH is sufficient for synthesis of $M(OR)_n$ — for instance, in the case of preparation of 2-methoxyethoxides). Under these conditions it is also possible to lower the reaction temperature, which is especially important in the case of application of the high-boiling alcohols.

Bradley and Mehrotra demonstrated that high-boiling alcohols may be substituted by low-boiling alcohols; however, in this case considerable excess of R'OH is necessary along with repeated treatment (with complete evacuation of the solvent) [196]. This reaction is, in fact, used for synthesis of all methoxides (because of their polymeric character and minimal boiling temperature of MeOH in comparison with other alcohols) and for the derivatives of unstable alcohols, which in other cases may undergo decomposition. For instance, trimethylsilanolates $M(OSiMe_3)_n$, the formal analogues of *t*-butoxides, may be obtained only in this way (usually from ethoxides or isopropoxides). Substitution of OR groups in the polymeric alkoxides is especially difficult to perform. Thus refluxing of $Zn(OMe)_2$ for 120 to 130 hours with fractionation leads to $Zn(OR)_n(OMe)_{2-n}$, where R = Et, Bu^t [223]. However, it proved possible to obtain $Be(OMe)_2$ and $Cd(OEt)_2$ by refluxing of the insoluble $Be(OEt)_2$ and $Cd(OMe)_2$ for a few hours [1645, 1623]. Substitution by OR groups with branched radicals (especially tertiary) is nearly never complete, presumably because of the high stability of the partially substituted alkoxides, such as

$$2Al(OPr^i)_3 + 4{}^tROH \longrightarrow [Al(OR^t)_2(OPr^i)]_2 + 4{}^iPrOH \quad (R^t = Bu, C_5H_{11})$$
$$Zr(OEt)_4 + 3{}^tBuOH \longrightarrow Zr(OBu^t)_3(OEt)$$
$$Ta(OMe)_5 + 4ROH \longrightarrow Ta(OR)_4(OMe) + 4MeOH \quad (R = Pr^i, Bu^t)$$
$$2Mg[Al(OEt)_4]_2 + 6{}^tBuOH \longrightarrow Mg[Al(OBu^t)_3(OEt)]_2 \quad [223]$$

Apart from alcohols, esters are also used as alkoxylating agents for $M(OR)_n$. If the boiling points of the introduced and eliminated alcohols are the same (e.g., ^{i}**PrOH** and ^{t}**BuOH,** b.p. 82.4°C), application of **AcOBu**^{t} allows t-butoxides to be obtainied by distilling off the low-boiling ester:

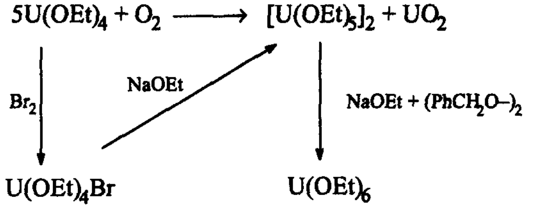
$$Zr(OPr^{i})_4 + \underset{\text{b.p.98°C}}{4AcOBu^{t}} \longrightarrow Zr(OBu^{t})_4 + \underset{\text{b.p.80.8°C (azeotrope with }(C_6H_{12}{}^{c})\text{)}}{4AcOPr^{i}}$$

In many cases application of esters in contrast to alcohols results in complete substitution of OR-groups, which (according to Bradley) is due to the stronger coordination of the carbonyl oxygen in comparison with the alkoxide oxygen on the first step of the reaction [196]. Application of esters in the synthesis of trialkylsilanolates is expedient due to their high stability in comparison with R_3SiOH, which readily undergoes polymerization and oxidation:

$$Ti(OR)_4 + 4AcOSiR_3 \longrightarrow Ti(OSiR_3)_4 + 4AcOPr^{i} \qquad [235]$$

2.7. Redox reactions of metal alkoxides: Oxidation of organometallic compounds (method 7)

Only a few of rather numerous reactions of oxidation of alkoxides by oxygen, peroxides, halogens, and other compounds may be used for synthesis of $M(OR)_n$ (with considerable yields). These reactions are known for uranium alkoxides [197, 856], such as



Alkoxides of Mo and W with the metal-metal bonds are readily oxidized to M(VI) alkoxides:

$$Mo_2(OR)_6 + 2O_2 \longrightarrow 2MoO_2(OR)_2 + 2RO\bullet \ (R{=}Pr^{i}, Bu^{t})$$
$$Mo_2(OR)_8 + O_2 \longrightarrow 2MoO(OR)_4 \ (R = Pr^{i}, C_5H_{11}{}^{neo}; Bu^{t}, \text{conc.}{>}0.25\ M/l)$$
$$W_2(OR)_6 + O_2 \longrightarrow W_2O_3(OR)_6 \quad [356, 357, 370]$$

Oxidation of $Cr(OR)_3$ or $Cr(C_6H_6)_2$ (e.g., by *t*-butylperoxide) is the only way to synthesize $Cr(OR^{t})_4$ — one of the unique compounds of Cr(IV); it is quite stable to hydrolysis and oxidation, presumably because of high stability of the tetrahedral molecules with the central atoms completely hindered by tertiary radical. On the other hand, primary and secondary ROH reduce $Cr(OR)_4$ to $Cr(OR)_3$ [197, 696, 960]. Such original oxidants as TlOAr and $Hg(C_6F_5)_2$ were used for transformation of metallic ytterbium into Yb(III) and Yb(II) phenoxides [465, 466]:

$$2Yb + 3Hg(C_6F_5)_2 + 3ArOH = 2Yb(OAr)_3 + 3Hg + 6C_6F_5H$$
$$(Ar = C_6H_3Ph_2\text{-}2.6)$$
$$Yb + 2TlOAr + 3THF = [Yb(OAr)_2(THF)_3] + 2Tl$$
$$(Ar = C_6H_2Bu^t_2\text{-}2.6\text{-}Me\text{-}4)$$

Reduction reactions are primarily characteristic of Cr, Mo, and W(VI) compounds. The UV-irradiation of the solutions of $(NH_4)_2CrO_4$ or $C_6H_6Cr(CO)_3$ in alcohols results in $Cr(OR)_3$ [248, 769]. Reaction of pinacol $[(CF_3)_2C{-}OH]_2$ with aqueous solutions of K, Cs, or Et_4N chromates leads to alkoxochromates (V) $MCrO(RO_2)_2$, which are stable to hydrolysis due to chelating of the ligand [1750]. For W aryloxides reduction of very stable $W(OAr)_6$ by K (in the presence ofReneu nickel) to $W(OPh)_5$ and $W(OC_6H_4Me\text{-}4)_5$ is of practical interest [600]. $Ti(OR)_3$ ($R = Et, Pr, Bu^n$) were obtained by reduction of $Ti(OR)_4$ by Na in solutions in alcohols (i.e., by hydrogen *in statu nascendi*) or by K in ether [560], while the action of ytterbium amalgam on $Yb(OAr)_3THF_2$ produced $Yb(OAr)_2THF_3$ ($Ar = C_6H_3Ph_2\text{-}2.6$) [461].

Recently, $Ce_4^{3.75+}O(OPr^i)_{13}(^iPrOH)$ was obtained by irradiation of $Ce(OPr^i)_4{\bullet}^iPrOH$ solutions in $({-}CH_2OMe)_2$ and ^iPrOH by the visible light [1803]. Partial reduction of alkoxides occurs in the course of electrolysis of metal alkoxides (see above). Oxoalkoxoniobates $NbO(OR)_3$ (R = Me, Et, Bu), the products of oxidation of the $Nb(OR)_4$, were isolated in the course of electrolysis performed with Nb anode and Pt cathode [911]. Although the reduction products are highly unstable (they cannot be used for synthesis of oxides) their formation in electrochemical synthesis should be taken into consideration because their subsequent oxidation by O_2 (or even its traces) leads to oxoalkoxides.

Butlerov and Francland in the XIX century made an attempt to synthesize alkoxides by oxidation of MR_n. However, the oxidation is a quite complicated process, which first led to peroxides [241]:

$$ZnR_2 + O_2 \longrightarrow Zn(OOR)_2$$

Metal alkoxide is formed as one of the products in this complicated process (its formation is usually registered by the presence of alcohols in the products obtained after the hydrolysis of the reaction mixture) [241].

* * *

Application of metal alkoxides in preparation of oxide materials assumes their high purity, which satisfies the requirements for modern electronic materials. Nevertheless, there are only few works that consider the question of purification of metal alkoxides and that give the characteristics of their purity [522]. Future studies of the syntheses of metal alkoxides should pay special attention to the problems of their purification.

Chapter 3

PHYSICOCHEMICAL PROPERTIES OF ALKOXIDES: REGULARITIES IN THE HOMOLOGOUS SERIES

High donor activity of the oxygen atom in the OR-groups allows the possible formation of M–O(R)–M bridging, binding the monomeric alkoxide units into oligo-or polymeric structures. Therefore, the major factor determining all the physicochemical characteristics of $M(OR)_n$ is their molecular complexity. The latter decreases usually in the homologous series from methoxides to ethoxides and then from the derivatives of *n*-radicals to ramified primary, secondary, and ternary groups. The highest possible ramification for R^t causes serious difficulties in the formation of donor-acceptor bonds, providing the lowest molecular complexities for $M(OR^t)_n$ and making them most soluble in nonpolar solvents and often volatile. The ionic component in the M-O bonding decreases in the same series.

Let us take the LiOR series as an example. The methoxide and ethoxide crystallize from solutions in alcohols as $LiOR \cdot 2ROH$ solvates, demonstrating good solubility in alcohols (LiOMe, 12.0; LiOEt, 16.4% at 20°C) [1643]. Thensolutions have good conductivity; for the $3 \cdot 10^{-3}$ M solutions of LiOMe $\lambda = 92$; LiOEt, 40; $LiOPr^n$, 20[112, 852].Desolvation of $LiOR \cdot 2ROH$ occurs at 28 and 55°C under solvent and over 40 and 110°C for solids with elimination of gaseous ROH for R = Me and Et, respectively. As can be seen in Fig. 3.1, the desolvation is associated with the change in the sign of the dissolution enthalpy, ΔH: the process is endothermic for $LiOR \cdot 2ROH$ and exothermic for LiOR.

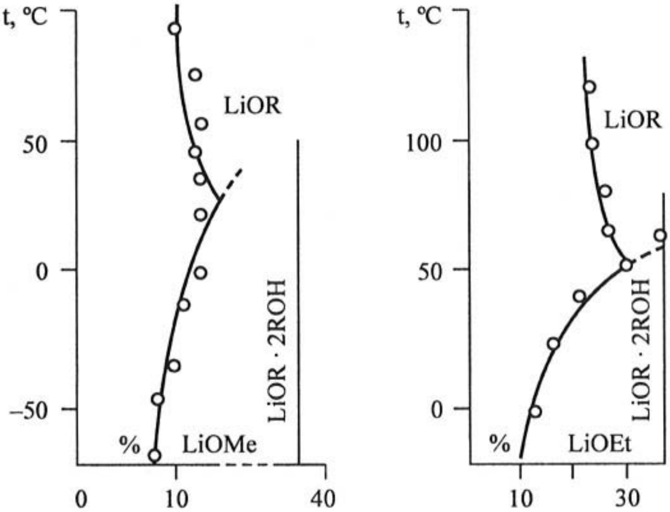


Fig. 3.1. Solubility (mass %) in the LiOR–ROH (R = Me, Et) systems [1643]

This situation can be explained by the difference in the structure of the solid phases. LiOMe has a polymer structure analogous to that of LiOH (see Section 4.8.2), the lattice of solvate contains molecules, 6 alcohol molecules are incorporated into the core of the **$[LiOMe \cdot 2MeOH]_4$** tetramer, while other 2 are connected with it only by hydrogen bonds (see Fig. 4.6) [1521]. Thermolysis of both LiOR occurs at ~320°C, but while the methoxide cannot be transformed into the gas phase, the ethoxide sublimes easily at **150°C/10^{-2} mm,** and **$LiOPr^i$** at **100°C/5•10^{-2} mm.** The latter derivative is in contrast to both methoxide and ethoxide soluble in hydrocarbons — benzene, cyclohexane, and so on. **$LiOBu^t$** sublimes easily at **110°C/10^{-1} mm;** its mass-spectrum reveals the fragments of hexameric molecules. The molecular complexity of **$LiOPr^i$** in solution varies between 3 and 11 according to different authors and is equal to 6 for **$LiOBu^t$.** The chemical shift for methyl protons in the **^1H NMR** spectrum of **$LiOBu^t$** is higher than for **^tBuOH,** which indicates the higher covalence of the Li–O bond even in comparison with the O–H one [1489]. The *tert*-butoxide, perfectly soluble in hydrocarbons, ethers, and so on, is practically insoluble in the parent alcohol (1.3%). While its structure remains unknown, it is possible to suppose that its hexanuclear molecules are built up in the same manner as in

$[NaOBu^t]_6$ [675] or in the $[Me_3C–C(=CH_2)OLi]_6$ enolate [1748], where there have been found the hexagonal prisms with alternating metal and oxygen atoms in the vertices (see also Section 12.1).

In all the homologous series of $M(OR)_n$ ($n>1$) a special place is occupied by the methoxides possessing usually polymeric structures. They are often insoluble in organic solvents, decompose without melting on heating, and are not volatile. The difference between $M(OMe)_n$ and other homologues is often visual even in the color. Thus, $Ni(OMe)_2$ with the octahedral coordination of metal is yellowish green, while other $Ni(OR)_2$ ($R = Et, Pr^n, Pr^i$) containing tetrahedrally coordinated Ni atoms are violet [1367,1005]. The violet color of the polymeric $Cr(OMe)_2$ distinguishes it from the other $Cr(OR^n)_2$, which have an orange color [6, 770].

The polymeric structures are sometimes observed even for other homologues with n-structure, especially ethoxides and n-propoxides. In the series of oligomeric $M(OR)_n$ one can observe the regularly decreasing m.p., density — the parameters connected directly with the regularity of the structure, density of molecular packing, and so on. B.p., ΔH of evaporation increase in the same series in connection with the increasing molecular weights and also with the effect on entanglement of the long hydrocarbon chains, reflected directly in the increasing viscosity in the series of, for example, monomeric $Ge(OR)_4$ (Fig. 3.2).

The refraction coefficient in the $Ge(OR)_4$ and $Ti(OR)_4$ homologous series varies in different directions, while the molecular refraction (MR_D) increases as usual with the increase in the molecular weight. The influence of the ramification of R on the boiling point can be illustrated comparing the isomeric series of Ti, Zr, Nb, Ta [225, 237, 205], and Al amyloxides [1107, 91]. In Fig. 3.3 it can be seen that in the series of the primary alkoxides the boiling points are decreasing with the ramification of R for the same value of molecular complexity (4 for $Al(OR)_3$, ~1 for $Ti(OR)_4$). It is very interesting that the b.p. for $M(OC_5H_{11}{}^{neo})_n$ appears in all the series to be as low as for $M(OC_5H_{11}{}^t)_n$ (in case of $Al(OR)_3$ the molecular complexity is ~2 for both isomers). For $M(OR^s)_n$ the boiling points are very close for all three isomers and decrease sharply on transition to $M(OR^t)_n$, while practically no changes are observed for the molecular complexities (being 1 for Ta, Nb, Ti -derivatives and 2 for Al and Zr). The boiling point therefore turns out to be a parameter more sensitive to ramification than the molecular complexity.

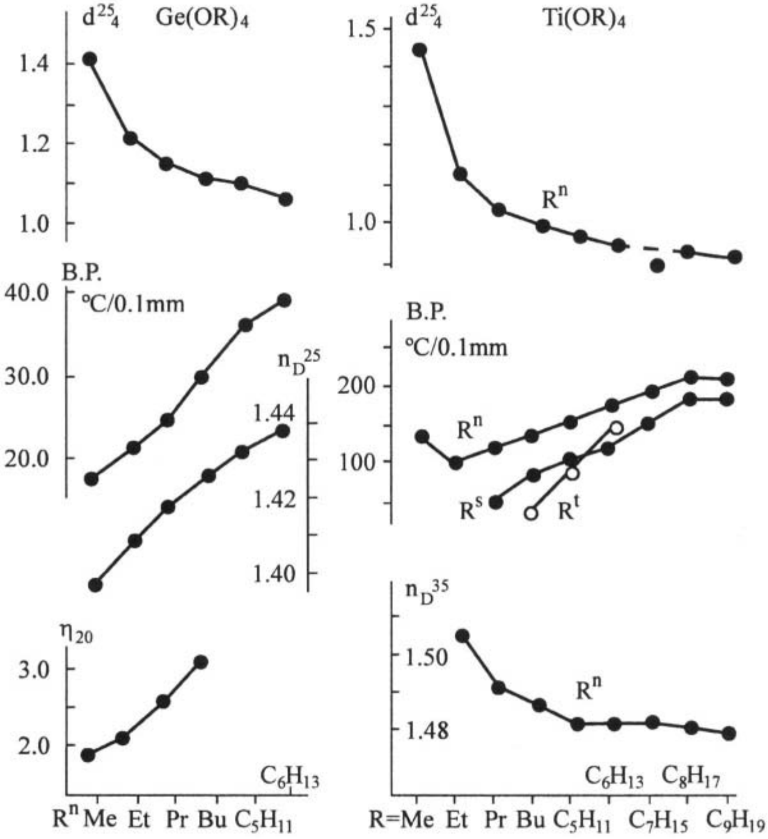


Fig. 3.2 Variations of density (d), boiling points (B.P.), refractory index (n_D), and viscosity (η) in the homologous series $Ge(OR)_4$ and $Ti(OR)_4$ [223, 560, 857, 222, 1759].

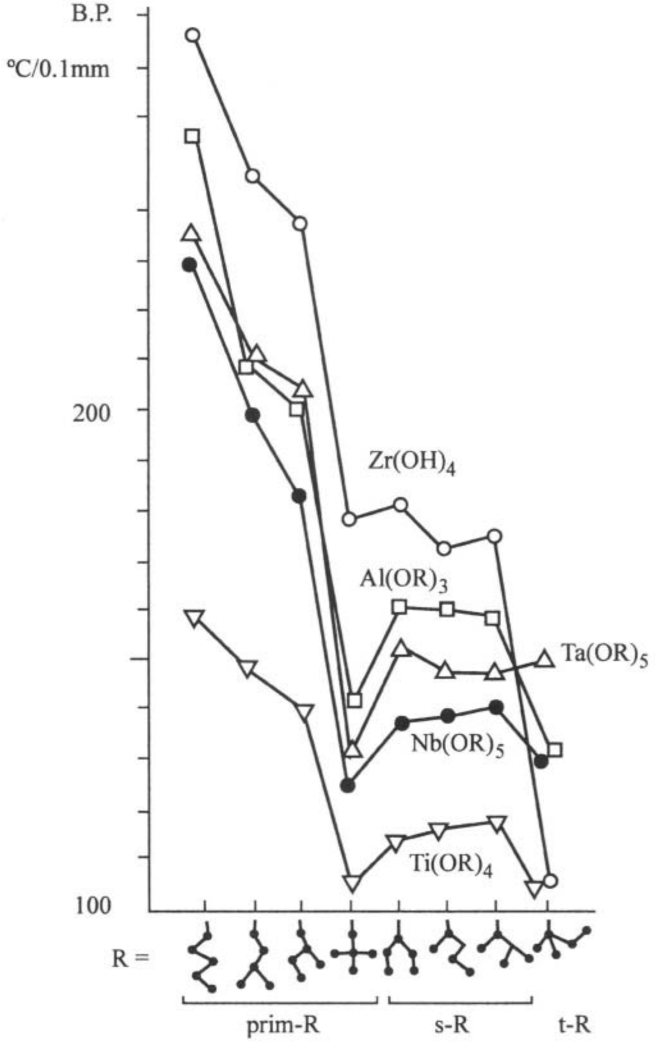


Fig. 3.3. Variations of boiling points in the series of isomeric amyloxides with ramification of R [223].

General considerations lead then to the following conclusion: the increase in the ramification of the radical should promote the solubility in organic solvents, especially the nonpolar ones, while the numeric data on this topic are quite rare and often contradictory in literature. For reasons for this situation see, Chapter 6.

The state of the alkoxides in the gas phase appears important in connection with their purification. The mass-spectra of the volatile species indicate the existence of aggregates, whose size is usually corresponds to that established for the solid phase by the X-ray single crystal studies [952, 1655]. It is, however, important to take into consideration the fact that the distillation is in some cases accompanied by ether elimination reaction and formation of oxoalkoxides:

$$\mathbf{M(OR)_n \longrightarrow MO_x(OR)_{n-2x} + R_2O}$$

[968, 1639, 1612, 1655].

A special case is represented by the $\mathbf{MO(OR)_4}$, M = Mo, W oxoalkoxides, which in analogy with the corresponding oxide halides undergo disproportionation in the gas phase:

$$\mathbf{MO(OR)_4 \longrightarrow M(OR)_6 + MO_2(OR)_2}$$

Therefore, in spite of the identical microanalysis data for the initial product and the destilled one, the X-ray powder diffraction indicates the presence of the admixture phases in the latter [950, 968]. Details of the physicochemical characteristics of different derivatives are provided in Chapter 12. They are also described in the review part of the book by Bradley *et al.* [223].

Chapter 4

CRYSTAL AND MOLECULAR STRUCTURES OF METAL ALKOXIDES

High donor activity of the oxygen atom in the alkoxide group causes the formation of rather stable M-O(R)-M bridges, combining the alkoxide units into various oligo- and polymeric structures.* For more than 100 years the size of the aggregates and their probable structures could be deduced only from the data on their molecular weights (obtained by cryo- and ebullioscopic measurements). The structures of the mono- and dimeric molecules could be deduced practically unambiguously (the cyclic $M(\mu\text{-}OR)_2M$ units, where two metal atoms are connected via two bridges, being usually present in the structures of dimers). Sidgwick [1482] as early as 1930 predicted the cubane-like structure of $[TlOR]_4$ (later confirmed by the single crystal X-ray study of $[TlOMe]_4$ [439], $[TlOSiPh_3]_4$ [714]; see Fig. 4.6) using the data on molecular weight and parachore of the ethoxide.

In 1950s and 1960s Bradley developed the "structure theory" for metal alkoxides, based on the principle that metal atoms should achieve maximal coordination at minimal molecular complexity of the aggregate, $[M(OR)_n]_m$.

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* The orthoesters of nonmetals $E(OR)_n$, E = B, Si, P, C – in contrast to metal alkoxides – are monomeric, the stabilization of their molecules being achieved via the increase in multiplicity of E-O bonds due to $p_\pi\text{-}d_\pi$ interaction of the filled orbitals of O-atoms and vacant orbitals of the E atoms.

This theory permitted the predict of the structures of a number of oligomeric aggregates and in particular of such an important product as **$[Al(OPr^i)_3]_4$** [198, 199] (see Fig. 4.8).

Experimental studies of the structures of metal alkoxides started more than 40 years ago. The very first study of this kind was made at Moscow State University in 1957 by Struchkov and Lobanova and was devoted to the investigation of **$W(OPh)_6$** [1358]. During the last 20 years work in the field of structural studies of metal alkoxides and phenoxides has been intensified. At present more than 1000 structures of the derivatives containing exclusively OAlk- and OAr- functional groups have been described. We consider them in relation to their molecular complexity beginning with the monomers and finishing with polymers.*

4.1. Mononuclear complexes

The compounds of this group are formed only in two cases:

- If the donor ability of the oxygen atom of the OR-group is hindered sterically (in case of sterically hindered ligands) or functionally — due to the presence of other donor groups in the alkoxide ligands, permitting chelation, or via coordination of other donor ligands such as solvating molecules; or
- If the oxidation number of the central atom is equal to its coordination number.

The intensification of studies of the derivatives of sterically hindered ligands such as **OCR_3 [where R = Ph, Bu^t (tritox)],$OCHBu_2^t$(ditox), $OSiR_3$,** 2,6- or 2,4,6- substituted phenoxides **$R_nC_6H_{5-n}O$ (where R= Me, Pr^i, Bu^t, Ph)** is caused by the search for new soluble and volatile alkoxides required for the synthesis of inorganic materials. The application of such compounds is justified in the cases when the derivatives with sterically less demanding radicals are polymeric, not volatile, and soluble in the best case only in polar solvents. The most considerable efforts have recently been made in synthesis and structural characterization of the derivatives of alkaline, alkaline earth, and rare earth metals — precursors of ferro- and piezoelectric materials, high temperature superconductors, and so on.

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*The accumulated data on structures belonging to different structure types are available on request from the author via e-mail at natalie@inorg.chem.msu.ru.

The coordinatin numbers (CNs) ofthe metal atoms in the monomeric molecules are quite varied (from 2 to 8) and are usually minimal ones for the metal in question. Thus the atoms of lanthanides have very unusual for them CNs of 3, 4, and 5, Al has 3 and 4 Cr(II) and Cr(III) have 4, U has 4, Mn has 4 and so on. This fact explains the formation of the monomeric molecules instead of polymers that are usually formed for these elements in the lower oxidation states. As the examples can be taken the 2,6-substituted phenoxides of V(II) and V(III), Re(III), Nb(II), Cr(II), Mo(IV), Co(I), Yb(II), $Cr(OSiBu^t_3)_2$, and so on. (see Chapter 12). It is supposedly the matching of the sizes of both central atom and ligands that permits the existence ofmonomeric tetrahedral $Cr(OR)_4$ molecules, where $R = Bu^t, C_5H_{11}^{neo}$ being stable not only in the solid phase but even in the gas phase [167, 1573]. It is well known that the +4 oxidation state is not characteristic ofchromium and these are polymeric $[Cr(OR)_3]$ and monomeric $CrO_2(OR)_2$ that are formed with less bulky radicals. In the monomeric $[Be(OC_6H_2Bu^t_3\text{-}2,4,6)_2(Et_2O)]$ molecule the steric hindrance introduced by the ligands favors the triangular coordination of Be-atoms [1372].

The bulky and branched radicals in the monomeric molecules are known in some cases to stabilize the ortho-forms of alkoxides — $M(OR)_n$. Thus $M(OBu^t)_4$, M = Zr, Hf are monomers stable in both gas and the solid phases, while the derivatives of less branched alcohols form when desolvated (even partially) the oligomeric oxocomplexes, like $Hf_3O(OEt)_{10}(EtOH)_2$ [1520]. The alkoxide ligands possessing π-acceptor properties (like phenoxides) can also favor the formation of the ortho-forms via stablilization of the molecules against the ether elimination reaction. Thus, while the alkoxides of $W(OR)_6$ series are easily forming monooxoderivatives $WO(OR)_4$ on heating, the phenoxides of tungsten in all oxidation states (for example, $[W^{IV}(OC_6H_3Ph_2\text{-}2,6)_2Cl_2(PR_3)]$ or $[W^V(OC_6H_3Ph_2\text{-}2,6)_2Cl_3(THF)]$ [897]) are stable to heating to reasonable temperatures. The total shielding of the central atom in $W(OPh)_6$, where the phenyl rings are arranged as propeller blades covering the W atom, explains the unique stability of this compound to hydrolysis [1538]. Examples of stabilization of the monomers via chelation include $[Mo[\eta^2\text{-}O(CMe_2)_2O]_3]\bullet CH_2Cl_2$ [284] and $[Mn([\eta^2\text{-}2,5\text{-}Bu^t_2C_6H_2O_2\text{-}1,4)_2]_4$ [1037].

The coordination numbers ofthe metal atoms in the monomeric molecules can in some cases be increased by coordination ofadditional ligands. Thus the coordination oftwo THF molecules by the tetrahedral $[TiCl_2(OC_6H_3Ph_2\text{-}2,6)_2]$

gives the product that has an octahedral structure [480, 876]. The trigonal pyramidal $Ce(OC_6H_3Bu_2^t\text{-}2,6)_3$ molecule is converted into trigonal bipyramidal complex via solvation with two Bu^tNC molecules [1528].

Some characteristic features of the alkoxide structures can be identified for the monomers:

- The presence of solvating ROH-molecules gives rise to the hydrogen bonding leading usually for the formation of network aggregates. According to the common rules we do not consider such aggregates in the determination of the molecular complexity.
- The compounds containing phenoxide ligands are often stabilized by intra-and even intermolecular $M\text{-}\eta\text{-}Ar$ bond formation, which is most characteristic of Ln, Nb and so on. Thus the agostic Yb...Me (3.42 Å) interaction in the $[Yb(OC_6H_2Bu^t\text{-}2,6\text{-}Me\text{-}4)_2THF_3]$ molecule or Yb-C (2.98 Å) bond formation in $[Yb(OC_6H_3Ph_2\text{-}2,6)_3]$ leads to chelation [465, 466]. A great number of studies of such derivatives have been reported by Rothwell *et al.* [1371]. These derivatives are not considered in this book because of the presence of M–C bonds in their structures.
- The presence of fluorine atoms in the alkyl residue is known to increase the volatility of alkoxides. The data of X-ray single crystal studies indicate unambiguously the presence of the secondary intramolecular M...F interaction, which is especially pronounced in case of alkali and alkaline earth, lanthanides, and some other metals. The coordination sphere of M becomes then saturated by the F atoms, which thus preclude the formation of OR-bridges [732]. The literature describes many dimeric alkoxide structures (for example, $[Mg(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2]_2$ [288], $[Ln(OAlk^t)_3]_2$ [548], $[U(OBu^t)_5]_2$[527]), which have monomeric fluorinated analogs — $[Mg[OC_6H_2(CF_3)_3\text{-}2,4,6]_2THF_3]$ [1361], $[Ln[OCMe(CF_3)_2]_3THF_3]$ [208, 209], $[U[OC(CF_3)_3]_4(OEt)(EtOH)]$ [527].

A parameter, which is of special importance for the description of $M(OR)_n$ in addition to the coordination polyhedron of the central atom and the M-O bond lengths, is the M-O-C bond angle. Bradley [198] was the first to emphasize the role of unshared electron pairs at the oxygen atoms that can be involved into interaction with the vacant *d*-orbitals of the transition metal. Thus in the molecules containing maingroup metals such as Bi, Sn, Ge, Te, and Al. the values of these angles usually do not exceed 120 to 130°, while in those of the derivative of transition metals (represented mainly by phenoxides) they achieve 170 to 180°. Tesh [1572] has pointed out that this increase can be caused in addition to the electronic effects by the sterical hindrance (the individual input of these factors can hardly be distinguished). This fact can be illustrated by the structures of phenoxides of some maingroup metals such as $M(OC_6H_2X_3\text{-}2,4,6)_n$, where M = Mg, Ca, Sr, Al, where in contrast to the alkoxides of the same elements the M-O-C angles are 170 to 180°[495, 723, 757, 1361, 1572].

4.2. Binuclear complexes

The majority of alkoxide aggregates are dimers containing a four-member $[M_2(OR)_2]$ cycle. The stability of this fragment is apparently so high that the dimerization occurs for the vast majority of monomeric molecules containing only one OR-group along with other ligands (this is of special importance for the OMe-group, which is the smallest among the alkoxide ligands). Below are considered some examples of dimeric molecules (arranged with the increasing CN of the central atoms).

ψ-trigonal coordination for both metal atoms is observed in the molecule of indium(I) phenoxide, $[:In(\mu\text{-}OC_6H_2Me_3\text{-}2,4,6)_2In:]$, where the terminal ligands are absent [1434] and $[LiOCBu^t_3]_2$ [128]. Monosolvates of lithium alkoxides or phenoxides and those of copper(I) alkoxides (see Sections 12.1 and 12.2) with bulky ligands of $[MOR(L)]_2$ type ($R = CBu^t_3$, $SiPh_3$, Bu^t, $C_6H_3X_2$-2,6) form dimeric molecules with trigonal planar coordination of the metal atoms $L\text{-}M(\text{-}OR)_2M\text{-}L$. The same structure is observed for $[Mg(OC_6H_3Bu^t_2\text{-}2,6)_2]_2$ [288],$[Co(OCPh_3)_2]_2$[1484] and other $[M(OR)_2]_2$ molecules. Tetrahedral coordination of both central atoms is observed for $[MOR(L)_2]_2$, $[M(OR)_2L]_2$, and $[M(OR)_3]_2$.They can be exemplified by $[NaOC_6H_2(CF_3)_3\text{-}2,4,6\ (THF)_2]_2$ [246], $[Co(OSiPh_3)_2THF]_2$ [1484], $[Al(OBu^t)_3]_2$ [391],and $[La(OCPh_3)_3]_2$ [548].

Dimers containing two pentacoordinated atoms are the molecules of the $[M(OR)_nL_{4-n}]_2$ type — $[LiOPh]_2(18\text{-crown-}6)$ [1184] (n=1), $[Cu(OPh)_2En]_2(PhOH)_2$ [289] (n = 2),$[Nd(OCHPr^i_2)_3L]_2$ [105], $[VO(OC_5H_9^c)_3]_2$[752](n = 3), $[Ti(OC_5H_{11}^{neo})_4]_2$ [186, 191](n = 4). Let us consider in particular the structure of the $[Ti(OPh)_2Cl_2]_2$ dimer, where the Ti-Ti distance is 3.27 Å (compared with 3.33 Å in the compact metal) and the Ti-O one is 1.74 Å; the red color of the complex being caused by the delocalization of electrons in the [PhOTi] fragment [1719].

The most widespread dimers are those of 2 octahedra — $[M(OR)_nL_{5-n}]_2$. Let us consider such structures of 2 centrosymmetric $[Nb(OR)_5]_2$ molecules, R =Me, Pr^i [1304, 1782] and the $[M(OR)_4(ROH)]_2$ solvates (Fig. 4.1 *a*, *b*). In the $[Nb(OR)_5]_2$ the lengths of the bridging Nb-O bonds is 2.13–2.14, and the terminal ones are 1.89–1.91 Å. These values are approximately 0.17 Å smaller than the sums of the covalent radii, which indicates a considerable role of the p_π-d_π-interaction.

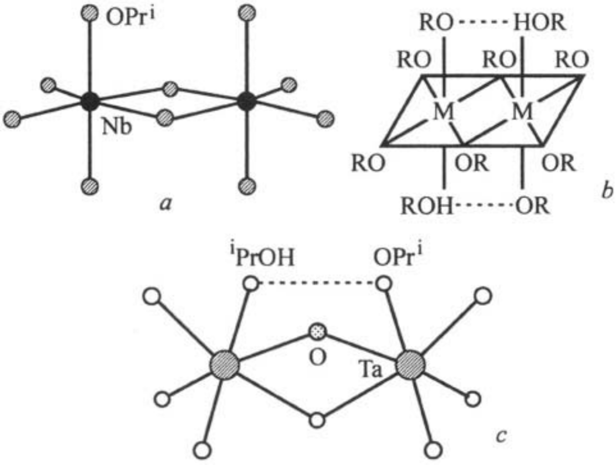

Fig. 4.1. The metal-oxygen core in structures of $[Nb(OR)_5]_2$(R = Me, Pr^i) [1304, 1782] (a); $[M(OR)_4(ROH)]_2$. M = Ce, Sn, Zr, Hf [702, 1350, 1589, 1665] (b); $[Ta_2O(OPr^i)_8(Pr^iOH)]$ [1639] (c).

This can be even more clearly seen in the Nb–O–C valent angles: they are equal to 121 to 123° for the bridging groups, while their average for the terminal ones is 145°. In general it can be pointed out that the values of these angles decrease with the increase in coordination of the ligands: the largest angles are observed for the terminal ligands (achieving for some derivatives of Mg, Ba, Ln, Cr, and U nearly 180° — i.e., *sp*-hybridization of the oxygen atoms). It should be also mentioned that this parameter is in many cases more sensitive to the molecular geometry than even the C–C bond length. The $[Nb(OR)_5]_2$ dimers are partially destroyed on dissolution.

The molecules of the solvates at the same time demonstrate much higher stability. Thus an attempt at desolvation of $[Zr(OPr^i)_4(Pr^iOH)]_2$ leads to its decomposition with formation of the oxocomplexes like $M_3O(OR)_{10}$, while the crystalline solvates are partially recuperated on the action of the excess of ^iPrOH on the latter [1612]. In the structures of $[M(OPr^i)_4(Pr^iOH)]_2$, where M = Ce, Sn, Zr, or Hf [702,1350, 1589,1665], the molecules of alcohols are situated on different sides of the equatorial plane and form the intramolecular hydrogen bonds with the neighboring OR-group (O...O 2.77 Å). The resulting angles between the *trans*-axial become reduced to 161 (M=Zr) and 155°(M=Ce). The ^1H **NMR** indicates that the structure is preserved in solution and the protons are migrating between all the OR-groups in solution. The same structural type is observed for many solvates, particularly, $[SnCl_n(OR)_{4-n}(ROH)]_2$ [1350, 1496, 1531, 1721], $[TiCl_3(OPr)(^iPrOH)]_2$ [624], $[ThI_2(OPr^i)_2(Pr^iOH)]_2$-*cis* [108], $[Ti(OPh)_4(PhOH)]_2$ [1550], $[WCl_2(OR)_2(ROH)]_2$-*cis* **(R= Me, Et,** Pr^i**)** [43,417], $[UI_2(OPr^i)_2(Pr^iOH)]_2$-*cis*$]_2$ [1669]. All of them exist unchanged in solutions and do not loose the solvating alcohol molecules below the pyrolysis temperatures.

In the molecule of $[Ta_2O(OPr^i)_8(Pr^iOH)]$ the formation of only one rather strong hydrogen bond leads to the mutual approach of the corresponding alkoxide groups (O...OH 2.52 Å) and elongation of the distance between the OR-groups situated at the other side of the equatorial plane (Fig. 4.1 *c*) [1639].

Let us consider the structure of the planar $[M_2O_2]$ cycle present in the molecules of nearly all binuclear alkoxides and phenoxides. In the vast majority of structures the M-O-M bond angle is 107 to 112° independently of the nature of the alkyl group, the metal, or its coordination polyhedron. Taking into account that for the bridging groups the value of the M-O-C bond angles lays usually in the 120 to 130° interval, the sum of the valent angles at **μ-O** approaches 360°, and the hybridization approaches sp^2. For the derivatives of smaller metal atoms such as Li, Cu, Be, and Al the angles at the oxygen atoms in the cycle become decreased to 80–100°. Even smaller angles are observed for the complexes, where the formation of strong M-M bonds takes place: for example, in $[Mo(OPr^i)_4]_2$ it is 76, and in $[MoCl_2(OPh)_3]_2$ it is 90° (the Mo=Mo and Mo–Mo bond lengths are 2.52 and 2.69 Å respectively) [350, 870].

Much less common are dimers, where the metal coordination polyhedra share a common face. As examples can be taken $[(Bu^tSiO)Ba(\mu\text{-}OSiBu^t_3)_3Ba(THF)]$ built up of 2 tetrahedra [497] or bimetallic *t*-butoxides

$[:Sn(\mu\text{-}OBu^t)_3M:]$, M = In, Tl, consisting of two **ψ-tetrahedra** [1693, 1685] (Fig. 4.2 *a*).

In the asymmetric **$[THF(Ph_3CO)Ba(\mu\text{-}OCPh_3)_3Ba(THF)_2]$** molecule the connected elements are trigonal bipyramids [497], while in that of **$[U_2(\mu\text{-}OBu^t)_3(OBu^t)_6]$** they are the octahedra around U(IV) and U(V) atoms [419]. In the **$[Re^{VI}_2O_2(\mu\text{-}O)(\mu\text{-}OMe)_2(OMe)_4]$**dimer the metal atoms are connected by a Re-Re bond (2.56 Å) in addition to 3 alkoxobridges [519].

In the molecule of the **$[K(OC_6H_2(CF_3)_3\text{-}2,4,6)(THF)_3]_2$** complex the 2 distorted octahedra share 4 vertexes — 2 OAr and 2 THF ones (along with the extra connection via K...F interaction) [246].

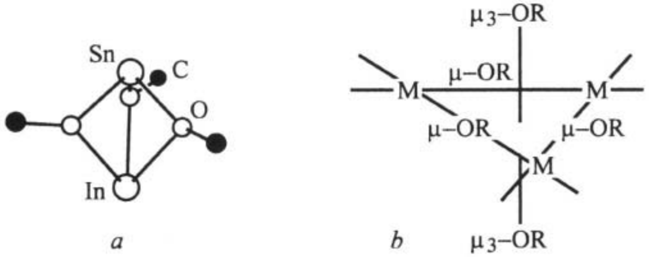

Fig. 4.2. The metal-oxygen core in structure of $[Sn(\mu\text{-}OBu^t)_3M]$, M = In, Tl, [1693, 1685](a); triangle$[M_3(\mu_3\text{-}X)_2(\mu\text{-}OR)_3]$ (b).

The dimeric molecules ofphenoxides have also a number of specific features worth to be noted. The number of bridging units there can be increased via **$M\text{-}\eta^n\text{-}Ar$**, where n = 1–6, bond formation. This phenomenon can be traced in the case of **$[MLa(OC_6H_3Pr^i_2\text{-}2,6)_4]$** bimetallic phenoxides. In the molecule of **$[(THF)Li(\mu\text{-}OAr)_2La(OAr)_2(THF)]$** the metal atoms are connected only by 2 OAr-bridges. In the molecule of **$[(THF)_2Na(\mu\text{-}OAr)_2La(OAr)_2THF]$** the Na atom (which already possesses *d*-orbitals) forms an extra bond with the **C_1-atom** of the **μ-OAr-group** in addition to 4 bonds in the tetrahedron [383]. In the **$[MLa(OAr)_4]_\infty$** complexes the K atoms are connected by 16 bonds **$M\text{–}Ar\text{–}(\eta^6)_2$, $(\eta^2)_2$**, and the Cs atoms by 12 bonds **$(\eta^3)_4$**, which leads to the formation of a continuous one-dimensional polymer chain, where no bridging via O-atoms occurs [381, 383]. The analogous features are observed for the dimeric **$[Ln(OAr)_3]_2$** molecules, where Ln = La, Nd, Sm, Er [283,105]. The literature describes numerous examples of phenoxides of Nb, U, and so on, where both kinds of bridging — via **μ-OAr-groups** and **$M\text{-}\eta^n\text{-}Ar$-groups** — are present.

A specific class of dimeric alkoxides is represented by the cluster derivatives of Mo and W in lower oxidation states studied during the 2 last decades by Chisholm *et al.* The derivatives of Mo (II) and (III) as well as W(III) with bulky or ramified radicals (*sec-*, *tert-*, ***neo*-R**, $C_6H_3R_2$-2,6) form ethane-like molecules with multiple M-M bonds. In contrast to the abovementioned aggregates, they do not contain any bridging groups, for example, $(RO)_3Mo{\equiv}Mo(OR)_3$,where $R = CH_2Bu^t$. The length of a metal-metal bond is a good indicator for determinating its multiplicity: for a quadruple M ≣ M bond in $[M_2]^{4+}$ it is 2.13-2.15, for a triple M≡M — 2.2-2.3, double M=M—2.5 and single M–M — 2.7 Å. These are quadruple and triple bonds ($\sigma^2\pi^4$ and $\sigma^2\pi^4\delta^2$ configurations for the metal-metal bonding orbitals) that can exist without any supporting bridging ligands [345]. The diffuse **$d\pi$-orbitals** being involved in bonding, the triple **Mo≡Mo** bonds turn out to be much more stable than the **W≡W** ones (no alkoxides with quadruple tungsten-tungsten bonds have ever been mentioned in the literature). **W≡W** dimers have a strong trend to dimerize and form butterflytetramers and can often be stabilized by the addition of extra N- and especially P-donor ligands [347]. The length of the metal-metal bond is very sensitive to the nature of the additional ligands (which can affect its multiplicity). Thus the presence ofthe bridging OR and other ligands results in the elongation of the M-M bond. Thus on transfer from the “pure” metal cluster $Mo_2(OC_5H_{11}{}^{neo})_6$ to $(Pr^iO)_3Mo(\mu\text{-}OPr^i)_2Mo(OPr^i)_3$ the Mo–Mo distance increases from 2.22 to 2.53 Å, which corresponds to the replacement ofa triple bond with a double one. The addition of 2 strong electron-acceptor NO molecules as terminal ligands to the molecule of $[Mo(OPr^i)_3]_2$ leads to the complete breakdown of the Mo-Mo bonds. The dimeric molecule thus formed exists only due to the presence of two μ-OPr^i bridges; the distance between Mo atoms is increased to 3.33 Å (see also Section 12.18).

4.3. Trinuclear complexes

The majority of the compounds that are part of this group belong to the 3 following types: triangular molecules, linear chains, and nonlinear chains. The molecules of the first type **$[M_3]$-triangles** are built up of 3 $[MO_n]$ polyhedra (most often of octahedra), bound by the common vertexes in the equatorial plane. In addition, both above and below the plane of the triangle are placed 2 tridentate ligands (Fig. 4.2 *b*).

In the majority of triangular structures both μ_3-groups are the alkoxide ones — for example, in $[NaTh_2(\mu_3\text{-}OBu^t)_2(OBu^t)_7]$ [387]. There are, however, many examples where one of them is an oxogroup — for example, $[Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OMe)(OPr^i)_9]$ [454], $[Zr_3(\mu_3\text{-}O)(\mu_3\text{-}OBu^t)(OBu^t)_9]$ [1520], $[Mo_2W(\mu_3\text{-}O)(\mu_3\text{-}OPr^i)(OPr^i)_9]$[356], or μ_3-Hal — $[Y_3(\mu_3\text{-}Cl)(\mu_3\text{-}OBu^t)(OBu^t)_7THF_2]$ [553]. Quite unusual are molecules with only one μ_3-group -$[Sn_3(\mu_3\text{-}O)(OBu^i)_{10}({}^iBuOH)_2]$ [1350] and $[BiTi_2(\mu_3\text{-}O)(OPr^i)_9]$ [1258]. The presence of 4 bridging groups — 2 μ_3- and 2 μ-, — causes naturally a rather strong distortion of the octahedron. This conclusion can be illustrated by the structures of compounds quite different in composition and containing not only octahedra but even tetrahedra or 5-vertex polyhedra $[MO_n]$ — $[La_3(\mu_3\text{-}OBu^t)_2(\mu\text{-}OBu^t)_3(OBu^t)_4(Bu^tOH)_2]$ [209], $[KBa_2(\mu_3\text{-}OSiPh_3)_2(\mu\text{-}OSiPh_3)_3(Dme)_2]$ [398], $[Y_3(\mu_3\text{-}Cl)(\mu_3\text{-}OBu^t)(\mu\text{-}OBu^t)_3(OBu^t)_4(THF)_2]$ [553], $[Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OMe)(\mu\text{-}OPr^i)_3(OPr^i)_6]$ [454], and $[CdIM^{IV}{}_2(\mu_3\text{-}OPr^i)_2(\mu\text{-}Pr^i)_3(OPr^i)_4]$ (M^{IV} = Sn, Ti, Zr, Hf) [1688]. All these molecules are built around $[M_3(\mu_3\text{-}X)_2]$ trigonal bipyramids, contracted in apical direction: the $(\mu_3\text{-}X)\text{-}M\text{-}(\mu_3\text{-}X)$ angles are 64–75°, $M\text{-}(\mu_3\text{-}X)\text{-}M$ angles are 92–97°, $(\mu_3\text{-}X)\text{-}M\text{-}(\mu\text{-}O)$ 70-80°, $(\mu\text{-}O)\text{-}M\text{-}(\mu\text{-}O)$ angles are ~140°, $(\mu\text{-}O)\text{-}M\text{-}(t\text{-}O)$ angles are ~105°, and the (t-O)-M-(t-O) angles are 85–105°.

The derivatives of Mo, W, and Re belonging to this type contain the cluster $[M_3]$ units, such as $[Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_6]$, R = Pr^i, $C_5H_{11}{}^{neo}$, Mo=Mo 2.53 Å. [357], but also known are the molecules, where the μ_3-groups are absent and the bonding in the triangle is due to doubly bridging groups and M-M bonds as in $[W_3(\mu\text{-}O)_2(OBu^t)_8]$ (2 W–W 2.93 and 1 W=W 2.45 Å) [348], $[Re_3(\mu\text{-}OPr^i)_3(OPr^i)_6]$ [762].

The linear trinuclear molecules can be formed on the condition that the central metal atom has no terminal ligands and its polyhedron shares an edge or a face with those of the peripheral metal atoms. This type is exemplified by $Be[(\mu\text{-}OBu^t)_2BeCl]_2$ [137], $Mn[(\mu\text{-}OCHBu^t{}_2)_2Mn(OCHBu^t{}_2)]_2$ [1185], $M^{II}[(\mu\text{-}OBu^t)_2Al(OBu^t)_2]_2$, M^{II} = Mg, Ni [1691], $Mg[(\mu\text{-}OC_6H_4Me\text{-}2)_2Li(Tmeda)]_2$ [727], $Be[(\mu\text{-}OPr^i)_2Ta(OPr^i)_4]_2$[1561] (Fig. 4.3 *a*) structures with tetrahedrally coordinated central metal atoms (the $[M_2O_2]$ cycles being situated in perpendicular planes). In the molecule of $[Na(Tmeda)]_2Cr(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_4$ [518], where the central atom has a square planar coordination, the $[M_2O_2]$ cycles lay in the same plane.

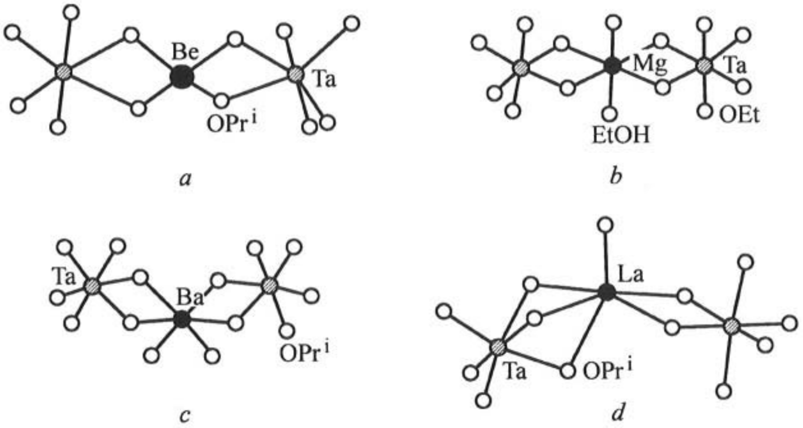

Fig. 4.3. The metal-oxygen core in structures of $Be[(\mu\text{-}OPr^i)_2Ta(OPr^i)_4]_2$ (*a*); $[Mg(EtOH)_2][(\mu\text{-}OEt)_2Ta(OEt)_4]_2$ [1561] (*b*); $(Pr^iOH)_2M^{II}[(\mu\text{-}OPr^i)_2M^V(OPr^i)_4]_2$, M^{II} = Ba, Sr; M^V = Nb, Ta (*c*); $[LaM^V_2(OPr^i)_{13}]$, M^V = Nb, Ta [334, 1562, 1622] (*d*).

The linear trinuclear molecules can also be formed in the case of the presence in the central octahedron of 2 terminal ligands in *trans*-configuration because both $[M_2O_2]$ cycles are arranged in the equatorial plane in this case.

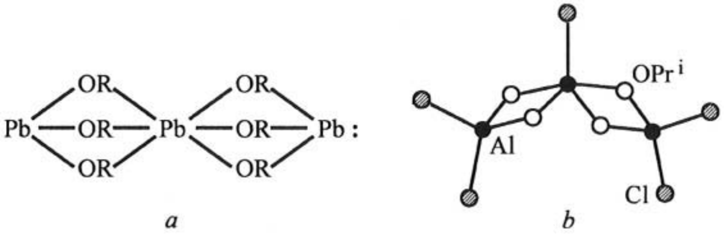

Fig. 4.4. The metal-oxygen core in structures of $[Pb(\mu\text{-}OBu^t)_2]_3$ [649] (*a*); $ClAl[(\mu\text{-}OPr^i)_2AlCl_2]_2$ [1781] (*b*).

Examples include $[UO_2][(\mu\text{-}O)(\mu\text{-}OBu^t)U(OBu^t)_4]_2$ [277] and $[Mg(EtOH)_2][(\mu\text{-}OEt)_2Ta(OEt)_4]_2$ (Fig. 4.3 *b*) [1561], $Cl_2Sn[(\mu\text{-}OC_6H_4Me\text{-}4)_2SnCl_3]_2$ [849].

The third possibility of linear arrangement of the 3 metal atoms observed in $[Pb(\mu\text{-}OBu^t)_2]_3$ (Fig. 4.4 *a*) [649], $Zr\{[\mu\text{-}OCH(CF_3)_2]_3Tl\}_2$ [1389], $[:M^{IV}(\mu\text{-}OBu^t)_3M^{II}(\mu\text{-}OBu^t)_3M^{IV}:]$, where M^{IV} = Ge, Sn, Pb, M^{II} = Mg, Ca, Sr, Cd, Pb

[1681], and $\{W[(\mu\text{-}OPh)_3NaTHF_3]_2\}^+[OPh]^-$ [453] cation is due to the sharing of the parallel opposite 2 $(\mu\text{-}OR)_3$ faces by the central octahedron and the peripheric ligands. In the $Ba[(\mu\text{-}OBu^t)_3Zr(OBu^t)_2]_2$ molecule, the considerable trigonal distortion of the central octahedron results in Zr–Ba–Zr ~150° [1689].

Less represented is the group containing molecules with *cis*-configuration of the groups of the central octahedron. It includes $Mg(^iPrOH)_2[(\mu\text{-}OPr^i)_2Al(OPr^i)_2]_2$ [1402], $MgTHF_2[(\mu\text{-}OPh)_2Al(OPh)_2]_2$ [1104], $SnI_2[(\mu\text{-}OPr^i)_2Ti(OPr^i)_3]_2$ [1691], $(Pr^iO)_2Hf[(\mu\text{-}OPr^i)_2Al(OPr^i)_2]_2$ [1608], $(Pr^iOH)_2M^{II}[(\mu\text{-}OPr^i)_2M^V(OPr^i)_4]_2$, M^{II} = Ba, Sr; M^V = Nb, Ta [1622, 1562] (Fig. 4.3 *c*). The angular configuration is characteristic also of the asymmetric $[LaM^V_2(OPr^i)_{13}]$, M^V = Nb, Ta molecules [1622, 334], where the central octahedron is sharing with the peripheric ones a face and an edge (Fig. 4.3 *d*). The central atom polyhedron in $ClAl[(\mu\text{-}OPr^i)_2AlCl_2]_2$ [1781] is a trigonal bipyramid and the shared edges are therefore not parallel (Fig. 4.4 *b*).

The structure of the $[M_2O_2]$ cycles in the chain-like trimers is in general analogous to that in the molecules of dimeric alkoxides.

4.4. Tetranuclear complexes

This class of compounds displays a large variety of structural types, which can be generalized as follows:

- Tetrahedral molecules;
- "Butterfly" with an open tetrahedron (1 M–M bond is missing) or a cluster molecule built up of 2 $[M_3]$ triangular fragments with one common edge, laying in different planes;
- Cubane-like molecules with $[M_4(\mu_3\text{-}O)_4]$ core ($[M_4]$ tetrahedron with 4 μ_3-centered planes);
- Planar $[M_4]$ rhombs with 2 μ_3-X- and 4 μ-ligands ("$Ti_4(OMe)_{16}$ -type");
- Planar $[M_4]$ cycles, where the metal atoms are connected by bidentate bridges (OR, O, Hal, *etc.*) or M–M bonds;
- An octahedron sharing ages with 3 tetrahedra ("$Al_4(OPr^i)_{12}$-type");
- Linear and non-linear chains with μ-OR -groups.

4.4.1. Tetrahedra

The regular tetrahedron exists supposedly only in the $[Pb_4(\mu_4\text{-}O)(\mu\text{-}OSiPh)_6]$ molecule, where in addition to the central μ_4-O ligand are present only the 6 **μ-OR-groups** placed over the edges of tetrahedron (Fig. 4.5 a) [608]. Some distortion should be present in the molecule of **$[NaBi_3(\mu_4\text{-}O)(\mu\text{-}OC_6F_5)_6(OC_6F_5)_2THF]$** due to its heterometallic nature and different terminal ligands being present [1742].

The absence of one or several **μ-OR-groups** in the structures of **$[Al_4(\mu_4\text{-}O)(\mu\text{-}OR)_5X_5(ROH)]$, X = $(OPr^i)Cl_4$** [1657], **CH_2CF_3 [1396], OBu^t** [1492], **$[Pb_3Zr(\mu_4\text{-}O)(\mu_3\text{-}OBu^t)(\mu\text{-}OBu^t)_5(OBu^t)_2]$** [1565], **$[Ce^{3.75+}{}_4(\mu_4\text{-}O)(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_4(OPr^i)_7(Pr^iOH)]$** [1803], and so on, molecules permits them to be considered as “butterfly” tetramers, where the “wings” are bound by an additional tetradentate oxogroup and, in the structures of solvates, also by a rather short hydrogen bond between 2 terminal groups (OR and ROH).

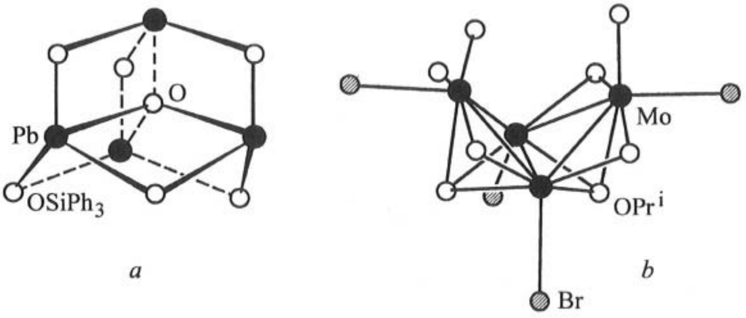

Fig. 4.5. The metal-oxygen core in structures of $[Pb_4(\mu_4\text{-}O)(\mu\text{-}OSiPh)_6]$ [608] (*a*); $[Mo_4(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_4(OPr^i)_2Br_4]$ [346] (*b*).

Among the distorted **$[M_4]$** tetrahedra with 4 edges missing it is necessary to mention the “Chinese lamp” (2 trigonal **$[M_2X_4]$** prisms with perpendicular axes and a common **$[X_4]$** plane). Its pure form was discovered in only one case, that of **$[Mo^{III}{}_4(\mu\text{-}F)_4(OBu^t)_8]$** [365]. In the distorted **$[W^{III}{}_4(\mu\text{-}O)(\mu\text{-}OPr^i)_2(OPr^i)_7Cl]$** tetrahedron the **$\mu_4$-O-group** is absent and the molecule exists due to **μ-O, μ-OR,** and 6 W-W bonds (2.47–2.96 Å) [362]. Tetrahedral cluster containing a tetradentate OAr-group has been observed in only one structure, that of **$[Me_4N]^+[Na_2La_2THF_5(\mu_4\text{-}OAr)(\mu_3\text{-}OAr)_2(\mu\text{-}OAr)_4(OAr)_2]^-\bullet THF$, Ar = $C_6H_4Me\text{-}4$** [548].

4.4.2. Butterfly

Butterfly is a **$[M_4X_{12}]$** cluster molecule built up of 2 **$[M_3]$** triangles with a common edge lying in different planes. This type of structure was discovered by Chisholm for the derivatives of trivalent Mo and W with ramified radicals such as **$[M_4(\mu\text{-}OCH_2R)_4(OCH_2R)_8]$, R = Pr^i, $C_5H_9{}^c$, $C_6H_{11}{}^c$** [354]. They contain usually M-M bonds with multiplicity varying between 1 and 3. The metal atoms placed at the ends of the "butterfly wings" are coordinating 1, 2 or 3 terminal OR or Hal ligands; the atoms forming the "body of the butterfly" are connected with 1 or 2 or even none of those. The edges of the **$[M_3]$-triangles** are supported by one or 2 bidentate OR-bridges. In some cases the outer side of one or both triangles bears also the **μ_3-OR-groups,** which permits these molecules to be considered as those of **$Ti_4(OMe)_{16}$** type (see Section 4.4.5), contracted along the **M_1-M_1** axis. The examples are provided by **$[Mo_4(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_4(OPr^i)_2Br_4]$** with 5 Mo=Mo bonds (2.48-2.51 Å) [346] (Fig. 4.5 *b*). A very asymmetric molecule of **$[Mo_4{}^{III}(\mu\text{-}H)_3(\mu\text{-}OBu^t)_3(OBu^t)_4(Me_2NH)]$** bears **3 μ-H-groups** along one of the edges of 1 triangle and **2μ-OR** along 1 of those of the other triangle and 1 **μ-OR** along its other edge [365]. In the structure of **$[Mo_4(\mu_4\text{-}H)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_4]^-$** anion, where **R= $C_5H_{11}{}^{neo}$,** there is present even a hydride ligand bound to all the 4 Mo atoms [271]. The complexes **$[(KPy)_2M_2(\mu\text{-}OCH_2Bu^t)_8]$,** where M=Mo, W are the only examples of heterometallic butterflies; the M=M bonds are present naturally only in the "body" of the butterfly [271]. The quantum-chemical aspects of the description of this type of structures are discussed in [346, 271] (see also Section 12.18).

4.4.3. Cubane-like molecules

Molecules possessing **$[M_4(\mu_3\text{-}O)_4]$** core can be considered as **$[M_4]$-tetrahedra** with all the 4 faces capped by **μ_3-OR-groups.** The molecules of this type are characteristic of alkaline metal alkoxides (with branched radicals) and those of T1(I) (Fig. 4.6 *a*)(see also Section. 12.1 and 12.6). The **$[M_4(\mu_3\text{-}OR)_4(OR)_n(ROH)_{12\text{-}n}]$** cubanes are present in the molecules of solvates such as **$Mg(OMe)_2$•3.5MeOH,** magnesium methoxochloride [1524,165], and **$Ba(OBu^t)_2$ •2^{t}BuOH [174].** The **$[LiOMe$•$2MeOH]_4$** molecule is a distorted cubane with two square **$[Li_2(\mu\text{-}OR)(\mu\text{-}ROH)]$** faces, and 4 **$[Li_2(\mu\text{-}OR)_2(\mu\text{-}ROH)]$** pentagons, the hydrogen bonds inside the latter leading to formation of a closo-polyhedron [1521] (Fig. 4.6 *b*). Among the derivatives of transition metals the cubanes are characteristic of pyrocatechinates — $[Co(\eta^2\text{-}3,5\text{-}Bu^t_2C_6H_2O_2\text{-}1,2)]_4 \cdot 5.5THF$ [1235], $[M_4(1,2\text{-}O_2C_6H_2Bu^t_2\text{-}3,5)_4Py_6]$, M = Mn, Fe [1475].

The molecules of this type display quite high stability, many of them being observed in the gas phase. Like dimers, they are common for heteroleptic complexes, containing at least one OR-group per metal atom and are especially common for methoxides. Examples include the numerous complexes of Zn, Mn, Fe, Co, Ni, and so on containing μ_3-OMe along with acac, OAr, OC_6H_4CHO, $[M(CO)_n]$, and other ligands [1771, 276]. Methanolysis of ZnR_2 and CdR_2 leads to cubane-like $[RM(\mu_3\text{-}OMe)]_4$ molecules, containing tetrahedrally coordinated metal atoms M [1468,1220]. On further treatment they are transformed into $Me_6Zn_7(OMe)_8$ dicubanes—pairs of $[Me_4Zn_4(OMe)_4]$ cubes with a common vertex an octahedrally coordinated Zn atom [1812].

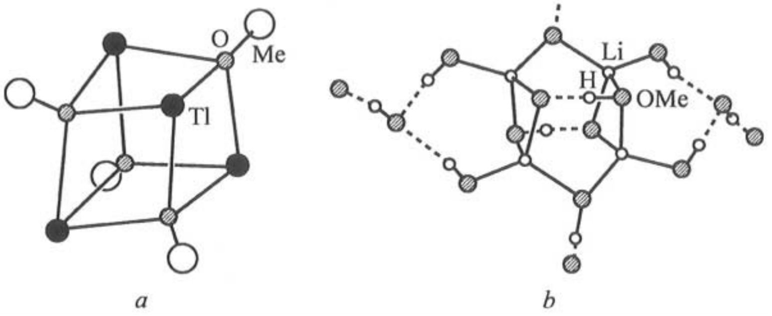

Fig. 4.6. The metal-oxygen core in structures of $[Tl(\mu_3\text{-}OMe)]_4$ [439] (a); $[LiOMe \cdot 2MeOH]_4$ [1521] (b).

The same kind of $[M_4O_4]$-cube distortion (analogous to that in the $[M_2O_2]$ cycles) is observed for all the structures of this kind: the bond angles at the oxygen atoms turn to be bigger than 90, and those at the metal atoms are smaller than 90. The minimal deviations are observed for the derivatives of alkaline metals (the symmetry of the tetramer itself is T_d). According to ^1H NMR data the rotation of the Bu^t radicals, which are situated on the volume diagonals of the $[M(\mu_3\text{-}OBu^t)]_4$ cube, is not frozen over –20°C, while the thermal motion of the Me-groups remains noticeable even below –50°C [352,1728].

4.4.4. Planar $[M_4]$-rhombs with 2 μ_3- and 4 μ-ligands ("$Ti_4(OR)_{16}$-type").

This most widespread type of tetrameric structures is a rhombus of 4 metal atoms, where 4 edges are supported by μ-OR ligands and where both triangles are capped by **μ_3-ligands** lying on different sides of the rhombus plane — that is, 4 **$[MO_n]$** polyhedra sharing common edges. In such molecules there are present 2 types of metal atoms, one connected with 2 **μ_3-groups** and of the other one with only one of them (in Fig. 4.7 a they are designated as **M^1** and **M^2**). The number of terminal groups in them is rather much varied—from 0 in **$[M_2Sn_2(\mu_3\text{-}OBu^t)_2(\mu\text{-}OBu^t)_4]$, M = Li, Na** [1692] to 14 in **$[(UO_2)_2U_2(\mu_3\text{-}O)_2(\mu\text{-}OPh)_4(OPh)_6THF_4]$** (CN = 7 for U atoms) [1813]. The majority of these molecules are, however, built up of the octahedra, the structure of **$[Ti_4(\mu_3\text{-}OMe)_2(\mu\text{-}OMe)_4(OMe)_{10}]$** being the first one of this kind determined by an X-ray study. In this centrosymmetric molecule one can clearly trace the correspondence between the structural function of the ligand and the Ti–O bond lengths and Ti–O–C bond angles. These parameters vary in the term-, **μ-, μ_3-OR** row in the ranges 1.78–2.08, 1.96–2.08 and 2.13–2.20 Å,140–161, 117–126 and 100-106° [1759]. The shortest ones turn to be the terminal bonds situated in *trans*-position to the **μ_3-OR** groups (1.75 and 1.82 Å).

In addition to **$[Ti_4(OMe)_{16}]$** this structural type is also observed for the homometallic derivatives with branched and bulky radicals — **$[Mg_4(OC_2H_4OMe)_6Dme_2]^{2+}$ [1380], $[Sr_4(OPh)_8(PhOH)_2THF_6]$ [496], $[Ba_4(OC_5H_9{}^{neo})_8({}^{neo}C_5H_9OH)_6Py_2]$ [191] , $[(MoO_2)_4[MeC(CH_2O)_3]_2(OEt)_2]$ [1752], $[Ti_4(MeC(CH_2O)_3)_2(OPr^i)_{10}]$ [193].**

Oxo- (hydroxo-) ligands occupy most often the **μ_3-positions,** like in **$[Bi_4(\mu_3\text{-}O)_2(OBu^t)_8]$** [1405], **$[(MoO)_4(\mu_3\text{-}O)_2(OEt)_4Cl_4(EtOH)_2]$** [1014], **$[Ba_2Zr_2(\mu_3\text{-}OH)_2(OPr^i)_{10}({}^iPrOH)_6]$** [1689], and **$(VOCl)_2[VO(\mu_3\text{-}OH)_2]_2[CMe_2(CH_2O)_2]_4$** [425].

It should be mentioned that in the structures of bimetallic alkoxides the **M^1** position is occupied in the majority of cases by an alkaline or alkaline earth metal atom (often coordinating the solvating molecules), while the **M^2** is occupied by an atom of electronegative transition metal. That is true for **$Li_2Ti_2(OR)_{10}$, R = Pr^i, $C_5H_{11}{}^{neo}$** [187, 703], **$[Li_2Nb_2(OCH_2SiMe_3)_{12}]$** [652], **$[Mg_2(MoO_2)_2(OMe)_{10}(MeOH)_4]$** [52], **$[Na(EtOH)_2]_2(WO)_2(OEt)_{10}$** [1638]. At the same time, in the molecules of **$Li_2Hf_2(OPr^i)_{10}$** [1690], **$[Li_2(MO)_2(OEt)_8(EtOH)_2]$, M = Nb, Ta** [1622, 1561], **$Na_3La_2(OC_6H_4Me\text{-}4)_9{\bullet}THF_2Dme_6$** [548], and many others the inverse arrangement is observed. In this sense of the special interest is the **$[Mg_nTi_{4-n}(OEt)_{16-2n}(EtOH)_{2n}]$** complex with the statistic distribution of Mg and Ti between **M^1** and **M^2** positions, unusual for the molecular structures of metal alkoxides [1773].

It is to be pointed out that the packing of the metal atoms in the discussed structure type is rather less dense than in the cubane-like structures (where all the 4 bridges are μ_3-ones), and therefore their stability is usually lower than that of the latter ones. The planar rhombs with 2 μ_3- and 4 μ-OR groups do not exist in the gas phase and usually dissociate giving trimers in solution [198]. Even cluster molecules such as $[W(OEt)_4]_4$ give monomers in gas (while their molecular complexity in solution is 4) [364]. The same relationship is actually observed for many inorganic tetramers — for example, the cubane-like molecules of $[TeCl_4]_4$ turn to be more stable than tellurium(IV) bromide or iodide the structure analogs of $[Ti(OMe)_4]_4$.

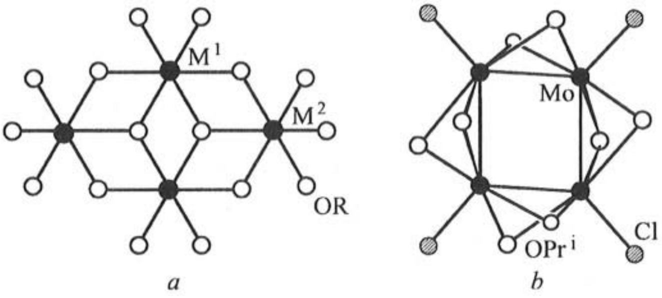

Fig. 4.7. The metal-oxygen core in structures of $[Ti_4(OMe)_{16}]$ [1759] (*a*); $[Mo_4(\mu\text{-}OPr^i)_8Cl_4]$ [347] (*b*).

The structures of $[BaTi(OPh)_6Dmfa_2]_2$ [456], $[K_2Zr_2(OBu^t)_{10}]$ [1564] molecules and $[(NaDme)_2(LaTHF)_2(OC_6H_4Me)_9]^-$ and $[(NaTHF_2)(NaTHF)(LaTHF)_2(OC_6H_4Me\text{-}4)_9]^-$ [548] anions can be considered as derived from that of $[Ti_4(OR)_{16}]$ — the first of them containing 4, the second one 3 μ_3-OR, and the third one 1 μ_4-OR and 2 μ_3-OR. The polyhedra turn then out to be joined not via edges but via faces. The pairs of metal polyhedra are then sharing not edges but faces.

4.4.5. Planar [M4] cycles with μ-ligands or M-M bonds

This group includes in particular the square planar molecules of $[CuOR]_4$, R = Bu^t, $SiPh_3$, $C_6H_3Ph_2$-2,6 (analogs of $[Cu_4O_4]^{4-}$ oxocuprates), where the Cu atoms have linear coordination, the vertexes of the squares being occupied by the oxygen atoms [676, 1094, 1027]. In the cluster molecules of Mo, W, and

Re alkoxides, the vertexes of the tetragon are occupied by the metal atoms, the R, OR, O, Hal, and so on groups being the bridging ones — $[Mo_4(\mu\text{-}OPr^i)_8Cl_4]$ (Fig. 4.7. *b*) [347], $[Re_4O_4(\mu\text{-}O)_2(\mu\text{-}OMe)_4(OMe)_8]$ [906].

A special notice is to be made for the $\{BaCu[OCMe(CF_3)_2]_3THF\}_2$ structure, where the groups being tridentate in the $[Ti_4(OMe)_{16}]$ molecules, turn bidentate and connect only Ba atoms [173] (Fig. 4.8 *a*).

4.4.6. An octahedron coupled to 3 tetrahedra(“$Al_4(OPr^i)_{12}$-type”)

The structure of the tetrameric molecule of aluminium isopropoxide containing the metal atoms with 2 types of coordination — octahedral and tetrahedral — has been predicted by Bradley and then confirmed by the NMR data. The X-ray single crystal study has shown that the central and the three peripheric aluminium atoms are situated in the same plane perpendicular to the main trigonal axis, which goes through the central atom. The 3 $[Al_2O_2]$ 4-member cycles are situated in the mutually perpendicular planes [1642, 574] (Fig. 4.8 *b*).

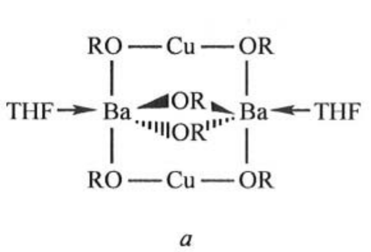

Fig. 4.8. The metal-oxygen core in structures of $\{BaCu[OCMe(CF_3)_2]_3(THF)\}_2$ [173] (a); $Al_4(OPr^i)_{12}$[1642] (b).

The analogous structure of the metal-oxygen core was discovered for $Er[Al(OPr^i)_4]_3$ [1744] and also $V[(\mu\text{-}OPh)_2Li(\eta^2\text{-}Dme)]_3$ [1746] and $Y[(\mu\text{-}OCH(CF_3)_2)_2NaTHF]_3$ (with peripheric $[NaO_2F_5]$ groups) [996]. The molecules of this kind have apparently high stability and are present not only in the solid phase but also in the gas phase.

4.4.7. Four-member chains

Four-member chains turn out to be linear, as has already been mentioned for the trinuclear molecules in the cases, for the tetrahedrally — $Cu_4(\mu\text{-}OBu^t)_6[OC(CF_3)_3]_2$ [1321], $[M_2Sn_2(\mu\text{-}OBu^t)_6(OBu^t)_2]$, M = Mg, Cr, Mn, Co, Ni [1683] or square planar $-[Li(THF)_2Cr(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_3]_2$[518]) coordination of the 2 central atoms. If the latter are octahedrally coordinated, the linearity can be achieved when they share common faces — $[(RO)_3W(\mu\text{-}OR)_2(\mu\text{-}H)W(OR)(\mu\text{-}OR)\text{-}]_2$, $R = Pr^i$ [17]. In the $[(RO)_2PyTh(\mu\text{-}OR)_2Th(\mu\text{-}OR)]_2$ [106] and $[(RO)_2Al(\mu\text{-}OR)_2Er(ROH)(OR)(\mu\text{-}OR)]_2$, $R= Pr^i$ [962] molecules the chains are zigzag formed because of the *cis*-coordination of the terminal groups in the central octahedra.

* * *

Molecules containing more than 4 metal atoms are very often conglomerates of smaller stable fragments described above. There do exist, however, a number of highly symmetric (often closo-) aggregates containing 5, 6, or 9 nuclei.

4.5. Pentanuclear complexes

Pentanuclear complexes are represented by 2 major structural types: closo-"clusters" with a μ_5-O-ligand in the center (heteroleptic complexes) and by combinations of 2 $[M_2M']$ triangular aggregates, having 1 common metal atom (heterometallic ones as this M' "central" metal atom should have higher coordination number and be rather electropositive to permit the existence of such an aggregate).

The molecules containing $[M_5O]$ groups are described as tetragonal pyramids or trigonal bipyramids. The structures of $[Ln_5(\mu_5\text{-}O)(\mu_3\text{-}OPr^i)_4(\mu\text{-}OPr^i)_4(OPr^i)_5]$ derivatives of Sc, Y, Er, Yb, $[Y_4Pr]$, In [208, 783, 1309, 1607, 1734] belong to the first type (Fig. 4.9 *a*), and those containing the $[Sm_4Ti]$ [444], $[(Tb_{0.9}Eu_{0.1})_4Ti]$ [1179] groups, and the $[Nd_5(\mu_5\text{-}O)(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_6(OPr^i)_5(^iPrOH)_2]$ solvate [726] to the second.

Except for the isopropoxides this structural type includes $[Ba_5H(\mu_5\text{-}O)(OPh)_9THF_8]$ [303], $[Ba_5(\mu_5\text{-}OH)(OR)_9THF_5(H_2O)]$, $R = CH(CF_3)_9$, $C_6H_3Bu^t_2\text{-}3,5$ [1702, 1150], $[Li(MgTHF)_4(\mu_5\text{-}O)(\mu\text{-}OC_6H_3Me\text{-}2)_7]$ [727], and $[Li_2Sn_3(\mu_5\text{-}O)(OR)_6]\cdot 2ROH$, $R = CMe_2C_6H_4$ [1506].

The $[Na_3La_2(OC_6H_4Me\text{-}4)_9THF_5]$ trigonal bipyramid [548] does not contain any pentadentate ligand, while in the $[Sr_5(\mu_4\text{-}O)(OC_5H_9{}^{neo})_8({}^{neo}C_5H_9OH)THF_4]$ tetragonal pyramid the oxogroup is placed in the center of the basal plane and is tetradentate [191].

The aggregates of this type are very stable: they are present in solutions and in the gas phase and display low reactivity, in particular, toward the complex formation with the alkoxides of other metals (see Chapter 8).

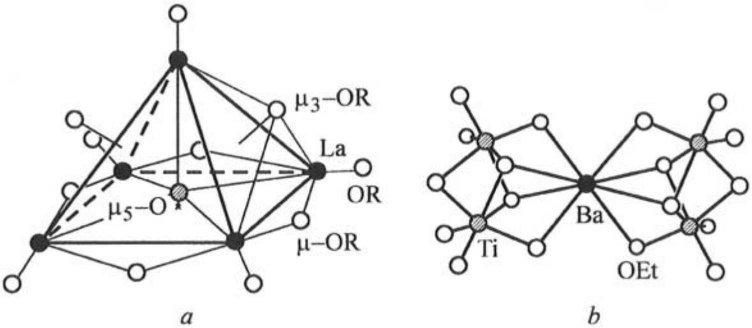

Fig. 4.9. The metal-oxygen core in the structures of $[Ln_5(\mu_5\text{-}O)(OPr^i)_{13}]$ [208, 783, 1309, 1607, 1734] (*a*); $M^{II}[M^{IV}_2(OR)_9]_2$, M^{II} = Ca, Ba, Sr, M^{IV} = Ti, Zr, R = Et, Pr^i [125, 970, 1611, 1662] (*b*).

A combination of 2 triangles with a common vertex is known only for heterometallic complexes. These are, for example, the very stable $M^{II}[M^{IV}(OR)_9]_2$, M^{II} = Ca, Ba, Sr, M^{IV} = Ti, Zr, R = Et, Pr^i. The central 8-coordinated atom in these molecules coordinates 2 $[M^{IV}_2(OR)_9]$ groups (of 2 octahedra sharing a common face) via 2 μ_3- and 2 μ-OR-ligands (Fig. 4.9 *b*) [125, 970, 1611, 1662]. In the $NaBi_4(\mu_3\text{-}O)_2(\mu\text{-}OC_6F_5)_7(OC_6F_5)_2]$ molecule, the $[NaBi_2]$ triangles are centered by μ_3-O-groups [1742], while in the structure of $[Mg_2Al_3(OPr^i)_{13}]$ the $[Mg_2Al_2(OR)_5]$ cycle is situated between 2 tetrahedrally coordinated Al atoms [1104].

$Mo^V_2Mo^{VI}Ta_2O_8(OPr^i)_{10}$ provides the first example of a molecule, where all the 5 metal atoms are involved in a nonplanar cycle (incorporating a Mo=Mo bond in addition to μ-O and μ-OR ones) [847].

4.6. Hexanuclear complexes

The majority of the complexes studied belong to one of the 2 most widespread structural types:

- $[M_6]$ octahedra or trigonal prisms (containing μ_6-O or not centered by any atom); or

- Pairs of triangles connected via μ_4-O, $(\mu\text{-X})_2$ groups, and so on. Much more rarely observed are pairs of cubes with a common plane, and so on. and also tetramers of the $[Ti_4(OR)_{16}]$ type with 2 additional $[M(OR)_n]$-groups or zigzag chains.

4.6.1. $[M_6]$ octahedra and trigonal prisms

These prisms containing a $(\mu_6\text{-O})$ in the center have been observed for both homo- and heterometallic alkoxides. Examples include $[Mo_6(\mu_6\text{-O})(\mu\text{-OEt})_{12}(OEt)_6]\cdot 4.8H_2O$ [763],$[Ba_6(\mu_6\text{-O})(OC_2H_4OMe)_{10}(MeOC_2H_4OH)_4]$ [304]. In the first case the 12 $(\mu\text{-OR})$-groups are situated on the edges of the octahedron, while in the second the 8 $(\mu_3\text{-OR})$ ones are capping the faces of it. The bimetallic molecules contain usually a *trans*-$[M_2M'_4(\mu_6\text{-O})(\mu_3\text{-OR})_8]$ cluster such as $[Na_2Gd_4(\mu_6\text{-O})(\mu_3\text{-OBu}^t)_8(OBu^t)_4]$ [1441], and $[K_4Zr_2(\mu_6\text{-O})(\mu_3\text{-OPr}^i)_8(OPr^i)_2]$ [1666], $[K_4Sb_2(\mu_6\text{-O})(OBu^t)_8]$ [1696].

The same group includes the $[Fe_6(\mu_6\text{-O})(OMe)_{18}]^{2-}$, $[Fe_6(\mu_6\text{-O})[MeC(OCH_2)_3]_6]^{2-}$ anions (Fig. 4.10 *a*) [724] and numerous vanadium oxoalkoxides described by Zubieta *et al.* possessing a highly symmetric structure of $[W_6O_{19}]^{2-}$ type [337, 913] (see also Section 12.15).

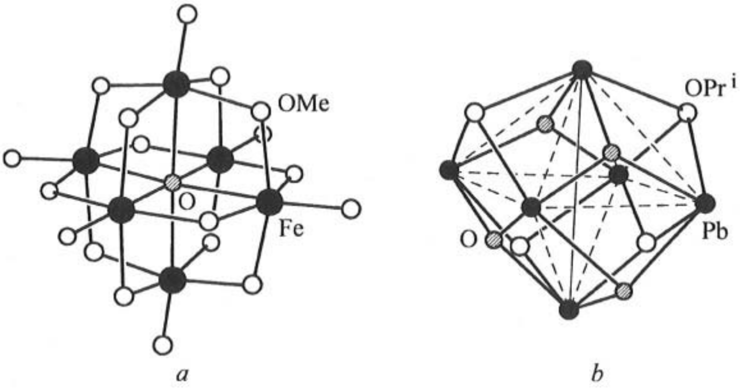

Fig. 4.10. The metal-oxygen core in structures of $[Fe_6(\mu_6\text{-O})(OMe)_{18}]^{2-}$[724] (*a*); $[Pb_6(\mu_3\text{-O})_4(\mu_3\text{-OPr}^i)_4]$ [1786] (*b*).

Among the octahedral clusters not containing a hexadentate oxoligand one can note $[M_6(\mu_3\text{-O})_4(\mu_3\text{-OR})_4]$, M = Sn, Pb, R = Me, Pr^i with alternating O and OR ligands capping the faces of octahedron [492, 710,1401,1786], which are the structural analogs of the hydroxides of the same metals (Fig. 4.10 b), and also bimetallic *trans*-$[(NaL)_4Cr_2(\mu_3\text{-}OR)_8]$, R = Pr^i, Ph, $C_6H_3Me_2$-2,6, L = THF, Py[518] and $[La_2(MoO)_4(\mu_4\text{-}O)_4(\mu\text{-}OPr^i)_8(OPr^i)_6]$ [909].

Significantly less represented are the trigonal pyramidal molecules containing a hexadentate ligand in the center, tridentate ones on the bases, and bidentate ones along the 9 edges of the cluster $[Nd_6(\mu_6\text{-}Cl)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_9(OR)_6]$, R = Pr^i [41]). In the molecule of $[Mo_6(\mu_6\text{-}O)(\mu\text{-}OEt)_{12}(OEt)_6]\bullet 4.8H_2O$ the bidentate groups are situated also along 3 diagonals of the side faces [763]. The molecules of Li and Na alkoxides with branched radicals such as $[Li(\mu_3\text{-}OR)]_6$, R = CMe_2Ph, $CMe(CHCH_2CH_2)^c{}_2$, $C(=CH_2)CMe_3$, Ph(THF) [352, 656, 1748, 810], and also $[Na(\mu_3\text{-}OBu^t)]_6$(in the structure of $[Na(\mu_3\text{-}OBu^t)]_6[NaOBu^t]_9$) [675, 452] contain the uncentered $[M_6]$ prisms.

4.6.2. Aggregates of two $[M_3]$triangles

These belong to one of the 3 known types. The first one is represented by the $[Gd_3(OC_2H_4OMe)_8]_2(\mu_4\text{-}O)$ molecule, containing two triangles situated in the perpendicular planes and connected by a tetradentate oxoligand [446]. A big group is formed by the molecules, where the vertices of 2 triangles are connected by a pair of bridging groups, forming a $[M^{II}{}_2(\mu\text{-}X)_2]$, X = OR, Hal cycle. This group includes bimetallic complexes like $[MgTi_2(\mu_3\text{-}OEt)_2Cl(OEt)_8]_2(\mu\text{-}Cl)]_2$ [1061], $[M^{II}M^{IV}{}_2(\mu_3\text{-}OR)_2(OR)_7]_2(\mu\text{-}X)_2$, M^{II} = Ba, Cd, Sn; M^{IV} = Ti, Zr, Hf; X = OPr^i, Cl, I [1508, 1662, 1688, 1691], $[PbZr_2(\mu_3\text{-}OR)(OR)_8]_2(\mu\text{-}OR)_2$ [1565], $[PrAl_2(\mu\text{-}OR)_4(OR)_4(ROH)]_2(\mu\text{-}Cl)_2$ [1598], R = Pr^i, *etc.* (Fig. 4.11 *a*).

The third possibility is provided by the connection of different triangles via μ-OEt-groups like in $[Hf_3(\mu_3\text{-}O)(OEt)_8(EtOH)]_2[(\mu\text{-}OEt)_2]_2$[1520] (Fig. 4.11 *b*) or μ-oxogroups like in $[Na({}^iPrOH)(MoO_2)(MoO)(\mu_3\text{-}OPr^i)_2(OPr^i)_3(\mu\text{-}O)]_2$ [1638], $[(MoO_2)Ta_2(\mu_3\text{-}OMe)(OMe)_8(\mu\text{-}O)]_2$ [847],$[IZnTa_2(\mu_3\text{-}O)(OPr^i)_7(\mu\text{-}O)]_2$ [180].

4.6.3. Aggregates of 2 cubane-like tetramers with a common face

These are known for only one homometallic alkoxide — $[Ca_6(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_4(OEt)_4]\bullet 14EtOH$ (common $[Ca_2(\mu_4\text{-}O)_2]$ face) [1653] (Fig. 4.11 *c*) and heterometallic alkoxide — $[Li_5Sm(\mu_4\text{-}OBu^t)_2(\mu_3\text{-}OBu^t)_4(OBu^t)_2]$ (common $[Li_2(\mu_4\text{-}O)_2]$ face) [1441].

4.6.4. Aggregates of 2 $[M_4]$ tetrahedra with a common $[M_2]$ edge

These have been found only in the structure of the $[Fe_6(\mu_4\text{-}O)_2(\mu\text{-}OMe)_8(OMe)_4[N(C_2H_4NH_2)_3]_2]^{2+}$ cation, containing the $[Fe_2(\mu_4\text{-}O)_2]$ fragment in its center [1188].

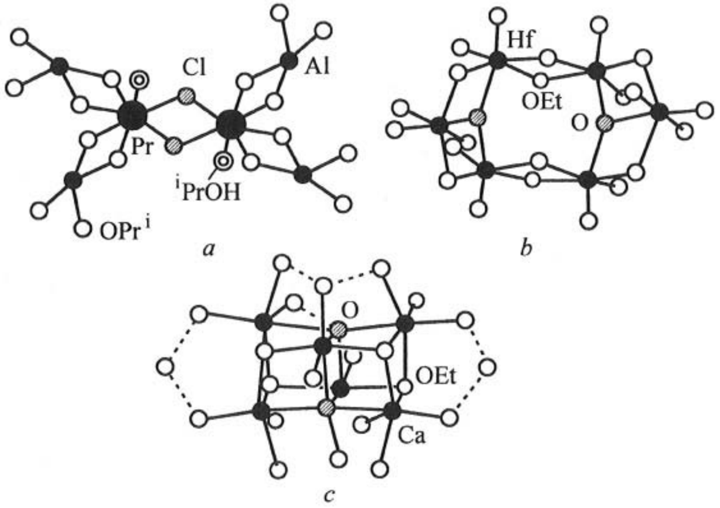

Fig. 4.11. The metal-oxygen core in structures of $[PrAl_2(OPr^i)_8(Pr^iOH)]_2(\mu\text{-}Cl)]_2$ [1598] (*a*); $[Hf_3O(OEt)_{10}(EtOH)]_2$ [1520] (*b*); $[Ca_6O_2(OEt)_8]\cdot 14EtOH$ [1653] (*c*).

4.6.5. $[Ti_4(OMe)_{16}]$-type core with 2 additional $[M(OR)_n]$-groups

This is demonstrated by the molecules of $[Ba_6(OPh)_{12}[(\text{-}CHNMe)_2]_4$ [304] and also by a whole series of bimetallic complexes such as $[Er_2Ti_4(\mu_4\text{-}O)_2(OEt)_{18}(EtOH)_2]$ [1735], $[M^{II}{}_2Sb_4(\mu_3\text{-}OEt)_2(\mu\text{-}OEt)_8(OEt)_6]$, $M^{II} = Mg, Mn, Ni$ [140], $[(NaTHF)_2Bi_4(\mu_3\text{-}O)_2(\mu\text{-}OC_6F_5)_{10}]$ [1742] $[Na_2V_4(\mu_3\text{-}OMe)_2(ArO_2)_4(OArOH)_2(MeOH)_8]$, $Ar(OH)_2 = Bu^t{}_2C_6H_4(OH)_2\text{-}1,2$ [1034], and $[Li(WO_2)(OC_2H_4OMe)_3Li(MeOC_2H_4OH)_2]_2{}^{2+}$ [902].

4.6.6. Hexanuclear chains

These are always nonlinear. They are represented by one homometallic zigzag chain complex— $[(MoO)_3(\mu\text{-}O)_2(OPr^i)_6]_2$ [357] — and by a number of heterometallic ones, such as $[Pb_2Zr(OPr^i)_8]_2$ [1565], $[M^V(MoO)_2(\mu\text{-}O)_2(OPr^i)_7]_2$, $M^V = Nb, Ta$ [847].

4.7. Oligomeric alkoxides containing more than 6 nuclei

Oligomeric alkoxides containing more than 6 nuclei nearly always incorporate oxogroups and are represented by the following structural types

- Closo-polyhedra;
- Condensed structures related to the inorganic isopolyanions;
- Pairs of clusters connected via the central $[M_2(\mu_2\text{-}X)_2]$ group;

- Cycles; and
- Fragments of a planar polymer layer.

4.7.1. Closo-polyhedra ("cluster" structures with or without a centering polydentate group).

The highest symmetry in the considered group is demonstrated apparently by the complexes containing 9 metal atoms. These are, first the $[Na(\mu_3\text{-}OBu^t)]_9$ molecule (in the structure of $[Na(OBu^t)]_6[NaOBu^t]_9)$ a doubly truncated hexagonal bipyramid with alternating Na and μ_3-OR -groups [675]. The second molecular type is represented by $[Na_8Ln(\mu_9\text{-}X)(\mu_4\text{-}OBu^t)(\mu_3\text{-}OBu^t)_8(OBu^t)]$, Ln = Eu, Y -square antiprism $[Na_8]$ with a [Ln(OR)] -cap centered by a nonadentate X = Cl or OH ligand [553].

Molecules containing cubane-like cores in their structures are represented by 2 types. To the first one belongs $[Li_4Ti_4(\mu_5\text{-}O)_2(\mu_3\text{-}O)_2(OPr^i)_{12}]$, built up of 2 $[Li_2Ti_2O_3(OR)]$ cubes sharing a common $[Ti_2(\mu_5\text{-}O)_2]$ face, connected also by the outer $[TiO(OR)_4]$ groups [970].

The second is formed by the molecules of $[Mg_4Ta_4O_4(OBu^n)_{20}(^nBuOH)_4]$ (Fig. 4.12 *a*), $[Sr_4Ta_4O_4(OMe)_{20}(MeOH)_{10}]$, $[Ba_4M_4O_4(OEt)_{20}(EtOH)_6]$, M = Nb, Ta and $[Ba_4Ti_4O_4(OPr^i)_{16}(^iPrOH)_{3.5}]$, which central core is a $[M^{II}_4(\mu_4\text{-}O)_4]$-cube. The M^{II} atoms are connected to $[M^nO(OR)_5]$ octahedra via oxoligands and 2 or more μ_2-OR-groups [1522, 1622, 1787]. The coordination of M^{II} is completed by solvating alcohol molecules. In spite of the different nature and even valence of M^n and R, these compounds have almost analogous structures. The only difference is based on different orientation of the $[MO(OR)_5]$ octahedra in relation to the cubane-like core: they can be situated along the continued edges (Mg–Ta), face diagonals (Ba–Nb), or volume diagonals (Ba–Ti). It is reasonable to suppose that the described structure can be observed even for other oxoalkoxides with M^{II}: M^n = 1:1 ratio. The Mg-Ta complex is the first example of a structurally characterized *n*-butoxide. The formation of the cubane-like core permits the effect of entanglement of the hydrocarbon chains, to be overcome, usually preventing the crystallization of n-butoxides.

A number of examples represent a structural type, where the 8 faces of the central octahedral $[M_6]$ core are capped by alternating μ_3-OR and octahedral $[(\mu_4\text{-}O)M'(OR)_5]$ groups. Among those are $[Pb_6Nb_4O_4(OEt)_{24}]$ [1253], $[Sr_6Ti_4O_4(OPr^i)_{20}]$ [1519], and $[Ni_6Sb_4O_4(OEt)_{16}(EtOH)_4]$ [140].

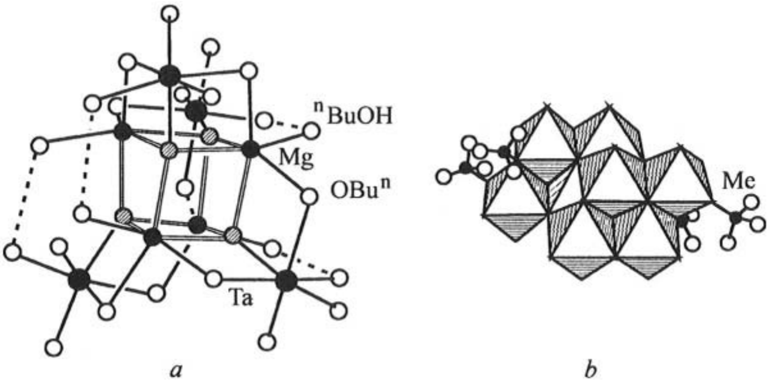

Fig. 4.12. The metal-oxygen core in structures of $[Mg_4Ta_4O_4(OBu^n)_{20}(^nBuOH)_4]$ [1522] (*a*); $[Mo_8O_{24}(OMe)_4]^{4-}$ [1087] (*b*).

As a tetrahedral analog of the preceding structure type one can consider the $[Ba_4Cu_6(\mu_4\text{-}O)(\mu\text{-}OCEt_3)_{12}]$ molecule, where the edges of the central $[(\mu_4\text{-}O)Ba_4]$ tetrahedron are capped by 6 linear $[Cu(\mu\text{-}OR)_2]$ groups [1321].

4.7.2. Condensed structures related to inorganic isopolyanions

This type is represented by a considerable number of oxoalkoxo complexes containing more than 6 metal atoms, where the oxogroups usually (with the exclusion of the doubly bonded terminal oxoatoms) are bridging (bi- to hexadentate ones) and the OR-groups are terminal or bidentate bridging. Among the known structures include two groups: (1) a dense packing of octahedra sharing common edges and vertices analogous to $[V_{10}O_{28}]$ and $[Mo_8O_{26}]$; and (2) skeleton molecules, where the pairs or triades of octahedra are connected via shared vertices directly or via single octahedra.

The first type is represented by oxoalkoxomolybdates (VI) and (V, VI) and -alkoxovanadates (V), (IV) and (IV, V), studied by Zubieta *et al.* [914, 913, 1018, 1039] (see Sections 12.15 and 12.18). The centrosymmetric $[(MoO_2)_6(MoO)_2(\mu_4\text{-}O)_2(\mu_3\text{-}O)_4(\mu\text{-}O)_4(\mu\text{-}OMe)_2(OMe)_2]^{4-}$ anion (Fig. 4.12 *b*) can be considered as an analog of metamolybdate $[Mo_8O_{26}]^{4-}$ [1087]. The surface of the $[V_{10}O_n]$ groups is covered by the residues of various polyols — $EtC(CH_2O)_3$, and so on.

The second type includes $M_8O_{10}(OEt)_{20}$, M = Nb, and Ta oxoethoxides (Fig. 4.14 *b*) [219, 911, 1617], $[LiTa_9O_{13}(\mu\text{-}OEt)_6(OEt)_{20}(EtOH)]$ [1519] (Fig.

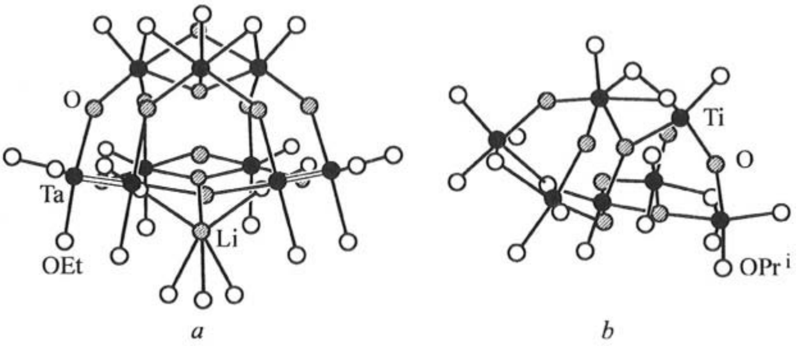

Fig. 4.13. The metal-oxygen core in structures of: $[LiTa_9O_{13}(\mu\text{-}OEt)_6(OEt)_{20}(EtOH)]$ [1519] (*a*); $[Ta_7O_9(OPr^i)_{17}]$ [1639] (*b*).

4.13 *a*). The $[Ta_7(\mu_3\text{-}O)_3(\mu\text{-}O)_6(OPr^i)_{17}]$ molecule (obtained on hydrolysis of $Ta(OPr^i)_5$) consists of 2 $[Ta_4]$ tetrahedra with a common vertex, connected also by one μ_3-O and 2 μ-OR groups (Fig. 4.13 *b*). An unusual feature of this molecule is the presence in it of pairs of octahedra sharing common faces [1639].

Of special interest are the titanium oxoalkoxides recently studied by Klemperer *et al.* [291, 454, 457] and Mosset [1177], of which many do not have analogs among the inorganic systems. The molecule of $Ti_7O_4(OEt)_{20}$ — the primary hydrolysis product of titanium ethoxide (see Chapter•. 5) — can formally be considered as derived from the structures of the $[Ti_4(OR)_{16}]$ tetramer and $Ti(OR)_2[(\mu\text{-}OR)_2Ti(OR)_3]_2$ trimer (existing in solution). The molecule contains a $[Ti(\mu_4\text{-}O)(\mu\text{-}O)]_2Ti]$ linear chain and the 2 $[Ti(\mu_3\text{-}O)(\mu\text{-}O)Ti]$ groups, situated above and below it with their centers in front of each other but shifted from the center of the trinuclear unit [457, 1414, 1719] (Fig. 4.14 *a*). The analogous principles lay in the background of construction of the bigger molecules like $[Ti_8O_6(OCH_2Ph)_{20}]\cdot Et_2O$, $[Ti_{10}O_8(OEt)_{24}]\cdot PhMe$, $[Ti_{18}O_{28}(OBu^t)_{16}(^tBuOH)]$, where the parallel chains of pairs or triades of octahedra are connected with each other via μ_4-, μ_3-O and μ-OR-groups. The $[Ti_{16}O_{16}(OEt)_{32}]$ molecule contains 2 perpendicularly placed blocks of 8 octahedra, where each of them contains a layer of 6 octahedra with NiAs-type structure and 1 octahedron below and 1 above the layer [1177] (see also Section 12.11).

A special group is composed by "spherical" molecules such as $[Zr_{13}O_8(OMe)_{36}]$ [1173] (Fig. 4.14 *b*) and $Zr_3Mo_8O_{24}(OPr^i)_{12}(^iPrOH)_4$ [901], in

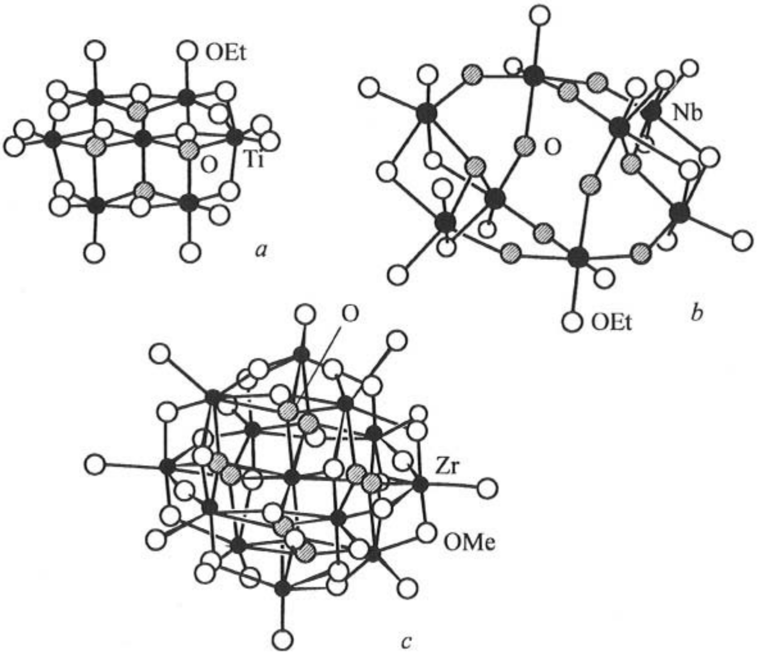

Fig. 4.14. The metal-oxygen core in structures of $[Ti_7O_4(OEt)_{20}]$ [457, 1414, 1719] (*a*); $Nb_8O_{10}(OEt)_{20}$ [219, 911] (*b*); $Zr_{13}O_8(OMe)_{36}$ [1173] (*c*).

the center of which are situated the 8-coordinated zirconium atoms, their surface being covered by the OR-groups. Of the same kind are the $[Ba_4Ti_{13}O_{18}(OC_2H_4OMe)_{24}]$ molecules with one central tetrahedron and 12 peripheric octahedra for Ti (a structural analog of the known Keggin structure of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$) [293], and $[Mn_8Sb_4(\mu_5\text{-}O)_4(\mu_3\text{-}OEt)_4(\mu\text{-}OEt)_{16}]$ ones possessing S_4 symmetry and containing 2 Mn-octahedra in the center [140].

4.7.3. Pairs of clusters connected via the central $[M_2(\mu_2\text{-}X)_2]$ unit

These can be considered as derived from the structural type discussed in Section 4.6.2, described for hexanuclear complexes. The central unit in this case is connecting usually 2 tetranuclear complexes. This group includes $[(LiTHF)_3Cr(\mu\text{-}OPh)_5]_2$ (2 $[Li_3Cr(OR)_4]$ and the $[Cr_2(OR)_2]$ unit) [5182], $[W_4O_2(OPr^i)_8]_2$ (2 $[W_4]$ tetrahedra and the $[W_2(\mu\text{-}OR)_2]$ unit) [368]. The most interesting appear the trimetallic isopropoxides, $\{[M^{IV}_2(OR)_9]M^{II}(OR)_2Cd(\mu\text{-}OR)\}_2$ M^{IV} = Sn, Ti, Zr; Hf; M^{II} = Ba, Sr, Ca, described by Veith [1687, 1686, 1691]. In the latter, 2 triangles, for example, $[Ti_2(OR)_9]Ba$, are connected by a linear $[(\mu\text{-}OR)_2Cd(\mu\text{-}OR)_2Cd(\mu\text{-}OR)_2]$ unit.

In the molecules of Al and Fe oxoethoxides, $[M_5O_2(OEt)_{11}]_2$, five-member rings are connected via the $[M_2(\mu_3\text{-}O)_2]$ unit [1785,1365] (see Fig. 6.4)*. The $[Li(OH)_2(\mu\text{-}OH)_2]$ cycle is situated in the center of the 16-nuclear molecule of $[Li_8(OH)_3(OBu^t)_5]_2$ obtained by microhydrolysis of $LiOBu^t$ [986]. In the molecule of $[Li_4Y_4(\mu_4\text{-}O)(OBu^t)_{12}Cl_2]_2$ the 2 $[Y_4O(OR)_{10}]$ butterflies connected via 2 $[\mu_3\text{-}Cl(Li\text{-}(\mu\text{-}O)_2Li]$ cycles form a linear chain [553].

4.7.4. Cycles

Cycles are formed by 7-, 8-, and 10-nuclear alkoxides. In the molecule of $[BaCu_6(\mu\text{-}OCEt_3)_8]$ a tetrahedral Ba atom is incorporated into 2 $[BaCu_3(\mu\text{-}OR)_4]$ cycles ($[Cu(OR)_2]$ - linear) [1321]. The tetrahedral $\mu_4\text{-}O$ group in the molecule of $[Cu_2Zr_2(OPr^i)_9]_2(\mu_4\text{-}O)$ connects 2 eight-member rings, each of them containing 2 linear $[CuO_2]$ groups and a $[Zr(\mu\text{-}OR)_3Zr]$ octahedron [1385]. One centrosymmetric cycle of 4 $[Mo_2(\mu_3\text{-}O)]$ triangles connected via $(\mu\text{-}OH)$ is observed in the molecule of $[(MoO)_4(\mu_3\text{-}O)_2(\mu\text{-}OEt)_2(\mu\text{-}OH)_2(OH)Cl_3(EtOH)_2]_2$ [1385, 156].

Finally, a $[Bi_8]$ cycle with a crown shape (close to that of S_8) built up of tetragonal $[Bi(\mu\text{-}OR)_4(OR)]$ pyramids was found in the structure of $[Bi(OEt)_3]_8 \cdot (7+x)EtOH$ (the molecules of alcohol being connected only to the terminal OR) [898]. The decanuclear cycle $[Y(\eta^2,\mu\text{-}OC_2H_4OMe)_2(\eta^1\text{-}OC_2H_4OMe)]_{10}$ is built up of the $[Y(\mu\text{-}O)_4(O\text{-}eth)_2O]$ pentagonal bipyramids [1308]

4.7.5. Fragments of a planar polymer layer

Fragments of a planar polymer layer of CdI_2 type are present in the nonanuclear $[M_9(OR)_{18}(ROH)_2]$ molecules, M = Ca, Cd, R = C_2H_4OMe (not containing oxogroups and not isomorphous with each other). In the first of the central core contains 3 octahedra and the periphery — 6 polyhedra with 7 vertices [654], in the second one there are present 7 octahedra and 2 polyhedra with 5 vertices [183].

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* The analogous cycles have been discovered in the molecules of $[Fe_9O_3(OEt)_{21}] \cdot EtOH$ [1680 *a*] and $Al_{11}O_4(OPr^i)_{25}$[1519]; however, in the structure of the former they are connected via the common Fe atom and $\mu_3\text{-}O$ and $\mu\text{-}OR$ groups, while the structure of the latter contains in its centrum the $[Al(\mu_3\text{-}O)_2(\mu_3\text{-}OR)_2(OR)]$ group connecting the 2 cycles.

4.8. Polymers

4.8.1. Chains

The factors determining the geometry of the polymer chain — linear or zigzag one — are considered in Section 4.3 for the trinuclear alkoxides. The examples of linear polymeric chains are provided by $[Pb(OC_2H_4OMe)_2]_\infty$, composed of $[Pb(\mu\text{-}OR)_4]$ tetrahedra (the ether functions not being involved into coordination) [649]. The linear $[M(\mu\text{-}OBu^t)_2(\mu\text{-}Bu^tOH)_2]_\infty$, M = K, Rb chains are formed of pairs of tetrahedra sharing common $(\mu\text{-}OR)_2$ edges, connected via pairs of μ-ROH [352].The trinuclear linear $[Na_2Zr[OCH(CF_3)_2]_6(\eta^6\text{-}C_6H_6)]_\infty$ molecules ($[Zr(\mu\text{-}O)_6]$ octahedra connected with 2 $[NaO_3F_3]$ groups via common faces) are converted into linear chains via coordination with benzene molecules situated perpendicularly to the chain direction [1387]. Among the linear polymers a special place is occupied by the pseudocarbonyls of alkali metals, erroneously considered initially to be the salts of hexaoxybenzene, that turned out to contain the $M^+[OC{=}CO]^{2-}M^+$ fragments, M = Na, K, Rb, Cs, permitting them to be considered as derivatives of acetylenediol [1728, 1929].

The zigzag chains are formed if the monomeric unit is, for example, a polyhedron with 5 vertices, like in $[Bi(OC_2H_4OMe)_3]_\infty$, built up of $[Bi(\mu\text{-}OR)_4(OR)]$ tetragonal pyramids [1074, 1069]. In the structure of $[NaTi(OPr^i)_5]_\infty$ are present alternating $[Na(\mu\text{-}OR)_4]$ tetrahedra and $[Ti(\mu\text{-}OR)_4(OR)]$ trigonal bipyramids [703,1691]. In the structure of $[K(Pr^iOH)_2(\mu\text{-}OPr^i)_2Al(\mu\text{-}OPr^i)_2]_\infty$ the nonlinearity is introduced by *cis*-arrangement of terminal ROH molecules in the $[K(\mu\text{-}OR)_4(ROH)_2]$ octahedron [1105]. The same feature is observed in the structure of $[LiTa(OMe)_6]_\infty$, composed of alternating $[Li(\mu\text{-}OR)_4]$ tetrahedra and $[Ta(\mu\text{-}OR)_4(OR)_2]$-*cis* octahedra [1519]. The ethoxide analog — $[LiTa(OEt)_6]_\infty$ — has an analogous structure, but the chains are in that case forming helices due, supposedly, to the bigger size of the ligand. This supposition is confirmed by the existence of a spiral chain for a tert-butoxide, $[KSn(\mu\text{-}OBu^t)_4(OBu^t)\bullet 0.5C_7H_8]_\infty$, composed of $[{:}Sn(\mu\text{-}OR)_4(OR)]$ ψ-octahedra and $[K(\mu\text{-}OR)_4]$ tetrahedra [1692].

4.8.2. Layers

The minimal structure demand for the OMe-group is leading to the maximal coordination of the metal atoms resulting in the fact that the majority of methoxides — both crystalline and amorphous — are polymeric. The powder diffraction studies have shown that many methoxides (and sometimes ethoxides and even isopropoxides) form structures related to those of the corresponding hydroxides: the alkaline methoxides to that of LiOH (layers of $[MO_{4/4}]$ tetrahedra)* [507, 1729, 1728, 1737], alkaline earth ones and those of other divalent metals Mg, Ca, Sr, Ba, Cd, Pb, Fe, Ni- $Mg(OH)_2$ (layers of $[MO_{6/3}]$ octahedra) [1367, 1517, 1627, 1646, 1649], and those of trivalent ones — Al, Cr, Fe — $Al(OH)_3$ (layers of $[MO_{6/2}]$ octahedra) [1366]. The Me-groups form layers among the M-O layers placed according to the [MeOMOMeMe...] motive. Thus the value of the *a* parameter turn out to be very close for hydroxides and methoxides, while the *c* parameter increases with 3.4 Å. As the contact between the layers in the $M(OH)_n$ structures (along the *c* axis) is supported by rather strong hydrogen bonding, which is replaced for the metal alkoxides by weak Van-der-Waals interactions, the sequence of the layers should be disturbed for the metal alkoxides, which results in the presence of only rather weak 001 reflections, looking diffuse on the side corresponding to the increase in theta [1646, 1649, 1366].

For the derivatives of di- and trivalent metals, the crystalline phases are embedded into the amorphous matrices and appear sometimes only after several years of storage. This circumstance and also the disorder in the direction perpendicular to the plane of the layer are leading to considerable decrease in the experimentally determined density compared to the theoretical one: the ratio of those decreases from 98 to 60% from $Ba(OMe)_2$ to $Mg(OMe)_2$. It is interesting that on prolonged storage the $Al(OEt)_3$ phase isostructural to $Al(OH)_3$ — bayerite — is transformed into a more stable one analogous to $Al(OH)_3$ – gibbsite; $Fe(OEt)_3$ crystallizes always in this form [1366]. Studies have described the products of partial substitution for OMe-groups with the OH ones in the methoxides of Mg [965], Ca, Cd [59], and $[AlO(OH)_{0.5}(OMe)_{0.5}]$ [965], conserving the unit cell parameters of their hydroxides with only the corresponding increase in the cell height (AlO(OH) — boehmite).

Polymeric layers of 5-member cycles $[MO_2C_2]$ exist in the structures of Zn, Mn, Fe, Co [700, 1329, 1501], and Ni [1568] glyoxides.

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* The structures of the K, Rb, Cs methoxides are very close to that of LiOMe, but the coordinating numbers of the metal atoms in them increase to 5 (distorted tetragonal pyramid). The intermediate situation for NaOMe among the other M^IOMe is reflected by the existence of 2 derivatives. The form isomorphous to LiOMe is very unstable (d = 1.28); it is instantly hydrolyzed by the traces of methyl groups that form layers among the metal-oxygen layers placed according to moisture with the formation of $Na(OMe)_{0.66}(OH)_{0.33}$ (d = 1.63), isomorphous to KOMe [1729].

Tridemensional networks are apparently not common for the structures of the alkoxides. Among the few examples are $Li_{33}H_{17}(OBu^t)_{16}$ network of $[Li_4H_4O]$ cubanes [761]; the structure of $Na_2Cu[\mu\text{-}OCH(CF_3)_2]_4$ contains the network of $[Na_8Cu_8]$cycles [1321]; the molecules of $\{[Na_3La_2(\mu\text{-}OC_6H_4Me\text{-}4)_9Diox_5]$ Diox} are connected in three directions by the dioxane molecules [548].

Comparison of the properties of metal alkoxides with their structures permits a conclusion that the polymeric nature does not always lead to chemical inertness. The major role appears to be played by the nature of the M-OR bonding. Solubility in alcohols and liquid ammonia of the methoxides of alkaline and alkaline earth metals and that in hydrocarbons of the isopropoxides of K, Rb, Cs (isostructural with the corresponding methoxides), and also $M(OC_2H_4OMe)_n$, M = Pb, Bi indicates the easy oligomerization due to solvation or chelation. At the same time the methoxides and ethoxides of Al, Cr, Fe, and so on, forming the strongest covalent bonds in the $[MO_{6/6}]$ octahedra (and not prone to solvation in alcohols), appear almost inert. They can be dissolved only due to complexation or partial destruction with formation of oxobridges.

* * *

In conclusion, it should be noted that the vast majority of the structures of alkoxides, phenoxides, and siloxides can be described using a restricted variety of the most widespread structural types. The initial building blocks are just very few fragments. These are, the binuclear $[M_2O_2]$ fragments (with OR and oxobridges), $[M_3(\mu_3\text{-}O)]$ and $[M_3(\mu_3\text{-}OR)(\mu\text{-}OR)_3]$ triangles, $[M_4O_4]$ cubanes, and also some larger aggregates (for example, $[M_6O]$ octahedra).

A comparison of the number of known structures for different homologs shows that among the homoleptic alkoxides of n-structure those studied (and crystalline) are nearly exclusively the methoxides. The exceptions are represented by $[Ti(OEt)_4]_4$ [800], $[W(OEt)_4]_4$ [364] and $[M(OEt)_n]_\infty$ polymers, M = Ca, Sr, Ba, Ni [1646; 1627, 1367], Al, Cr, Fe [1366]. The ethoxide groups are present mainly in heteroleptic complexes, containing chloride ligands (in binuclear molecules), and also in oxoalkoxides, where the OEt-groups are situated on the surface of $[M_nO_m]$ fragments, preventing the entanglement of the hydrocarbon chains. An analogous role is apparently played by the heteroatoms in the bimetallic complexes. Among the lager-size derivatives it is necessary to mention again the $[MgTaO(OBu^n)_5(^nBuOH)]_4$ [1522]. At the same time most of the described structures are those of the derivatives of branched radicals like Pr^i, Bu^t, $C_5H_{11}^{neo}$ and the sterically hindered ones, such as CR_3, SiR_3, $C_6H_3R_2$-2,6, $C_6H_2R_3$-2,4,6.

The accumulated structural material permits at present reliable predictions in many cases of the structure of the so far unknown derivatives. Exceptions are, however, provided by the oxoalkoxides, which have a great variety of unexpected molecular structures.

Chapter 5

OXOALKOXIDES

Polymeric metal oxoalkoxides — the products of partial hydrolysis or thermolysis of $\mathbf{M(OR)_n}$— have long been applied as refractory and isolating protection coatings. It has been supposed that these amorphous products contain metal-oxygen chains surrounded by OR-groups [199,48].

A new step in this story was linked to the oligomeric oxoalkoxocomplexes, whose role in the chemistry of alkoxides and apparently in sol-gel processing is extraordinarily important. The reliable data on these compounds were received first in the 1960s due to determination of the molecular structures of the "crystalline primary products of hydrolysis" such as $\mathbf{Ti_7O_4(OEt)_{20}}$ [457, 1414, 1719], $\mathbf{Nb_8O_{10}(OEt)_{20}}$ [219, 911], and $\mathbf{Zr_{13}O_8(OMe)_{36}}$ [1173] (Fig. 4.14).

It has been found that all the oxoligands have bridging functions (even the Nb-complex did not contain any terminal "ylic" O-atoms). They were considered to be the condensation points originating from 2 hydroxyl groups. During recent years, due to the development of X-ray studies, a great number of derivatives have been characterized as belonging to this class. Moreover, a good number of derivatives considered earlier as orthoalkoxides $\mathbf{M(OR)_n}$ turned to contain oxoligands (very often the polydentate ones so that the percentage of the replacement of OR-group with O-ones is very small). Examples include the isopropoxides of lanthanides and In, whose molecules contain a pentadentate oxoatom— $\mathbf{M_5(\mu_5\text{-}O)(OPr^i)_{13}}$ (Fig.4.9 *a*), [1309,1607,208,1734], "crystalline ethoxides" of Al and Fe — $\mathbf{M_{10}O_4(OEt)_{22}}$ (see Fig. 6.4) [1785, 1365], "calcium ethoxide disolvate" — $\mathbf{Ca_6O_2(OEt)_8 \cdot 14ROH}$ (Fig. 4.11 *c*) [1653], and so on. The well-known organicchemistry catalyst and reducing agent, $AlCl(OPr^i)_2$ turned out to consist of tetranuclear $Al_4(\mu_4\text{-}O)(\mu\text{-}OPr^i)_5[H(OPr^i)_2]Cl_4$ molecules [1657] (Fig. 12.16).

It was quite unexpectedly found that the amorphous samples of zirconium and hafnium alkoxides $M(OR)_4$ contain several types of oxocomplexes, particularly, $M_3O(OR)_{10}$ and $M_4O(OR)_{14}$ [1612]. The trinuclear $Zr_3(\mu_3\text{-}O)(\mu_3\text{-}OBu^t)(OBu^t)_9$ was isolated in a crystalline form and turned out to be a structural analog of the known isopropoxide clusters of Th, Mo, and U(IV) – $M_3O(OPr^i)_{10}$ [1520] (see also Sections 4.3 and 12.12). The inclusion of the solvent molecules inside the cavities of the structures and formation of alcohol solvates in many cases leads to microanalysis data that does not deviate much from those calculated for $M(OR)_n$.

Although many authors continue to consider these compounds only as the products of uncontrolled hydrolysis, the conditions of their formation indicate the possibility of other decomposition pathways. The most important in this sense was the recent proof of the chemical identity of the $Ti_7O_4(OEt)_{20}$ and $Nb_8O_{10}(OEt)_{20}$ single crystals obtained by two different routes: on hydrolysis of ethoxides and also on spontaneous decomposition of $Ti(OEt)_4$ and $NbO(OEt)_3$ (for example on prolonged storage or on heating of solutions in an autoclave in rigorous isolation from the traces of water) [457, 1177,911].

As one of the possible pathways of their formation it is possible to consider the ether elimination reaction:

$$-\overset{\backslash\,/}{\underset{/\,\backslash}{M}}\!-\!\boxed{OR + RO}\!-\!\overset{\backslash\,/}{\underset{/\,\backslash}{M}}- \longrightarrow -\overset{\backslash\,/}{\underset{/\,\backslash}{M}}-O-\overset{\backslash\,/}{\underset{/\,\backslash}{M}}- + R_2O$$

Condensation of this kind was first observed by Bradley in case of niobium t-butoxide:

$$Nb(OEt)_5 + 5\,{}^tBuOH \longrightarrow NbO(OBu^t)_3 + Nb_2O(OBu^t)_8 + Bu^t_2O$$

The formation of ether has not been proved in this case, but the authors have proposed a decomposition mechanism including the heterolytic cleavage of an O–R bond and a subsequent attack of the carbocation formed on the oxygen atom of the neighboring OR-group [205].

Processes of this kind are very characteristic of the alkoxides of rhenium [168], molybdenum, and to a minor extent in tungsten: of all the $Mo(OR)_6$

series only the methoxide was successfully isolated [812, 1453, 1560]. All $MoO(OR)_4$ are rather unstable and display a trend to transformation into $MoO_2(OR)_2$ [1637]. The solutions of bimetallic Na and Mo alkoxides were found to decompose at room temperature giving nearly quantitatively Na_2MoO_4 and the ether [1638].

The desolvation of alcohol solvates is to some extent always accompanied by the formation of oxoligands, — for example,

$[Ce(OPr^i)_4(^iPrOH)]_2 \rightarrow Ce_4O(OPr^i)_{14}$ [1497];
$[Ce(OBu^t)_4THF_2] \rightarrow Ce_3O(OBu^t)_{10}$ [547];
$[Nd(OPr^i)_3(^iPrOH)]_4 \rightarrow Nd_6O_5(OR)_8$ [726, 1308]

The other product of this reaction at low temperatures might be ether. The formation of ether has been reported, for example, for the decomposition of $Pr(OPr^i)_3 \cdot {}^iPrOH$ into $Pr_5O(OPr^i)_{13}$ [783].

This process is a common one in the fragmentation of the majority of metal alkoxide molecules in the mass-spectra. A typical example of the latter is the fragmentation pattern of zirconium and hafnium oxoalkoxides [1612] (Fig. 5.1).

The elimination of ethers can play an important role in the processes of hydrolysis of metal alkoxides, where the formation of crystalline oxides is observed already at low temperatures. For example, the action of the excess of water on $Bi(OEt)_3$ solution in benzene provides α-Bi_2O_3 and Et_2O [1610].

This decomposition type has supposedly a quite general character. Thus the siloxides of lead and mercury, $Pb(OSiMe_3)_2$ and $Hg(OSiMe_3)_2$ (the latter being the most stable among the mercury alkoxides), decompose at rather low temperatures with the elimination of $(Me_3Si)_2O$ [1417]. The formation of oxobridges is undoubtedly a thermodynamically favored process and is analogous to the well-known process of aging of hydroxides, where the condensation of 2 hydroxide groups occurs with the elimination of a molecule of water.

The other pathway leading to the formation of oxogroups in the coordination sphere of the metal atom is provided by uncontrolled oxidation of the basic alkoxides such as alkali, alkaline earth metal, and quite probably the rare earth metal ones by oxygen dissolved in solvents and present in the atmosphere. The primary oxidation products are peroxides and hydroperoxides — $M(OOR)_n$ and $M(OOH)_n$, whose decomposition gives water among the other

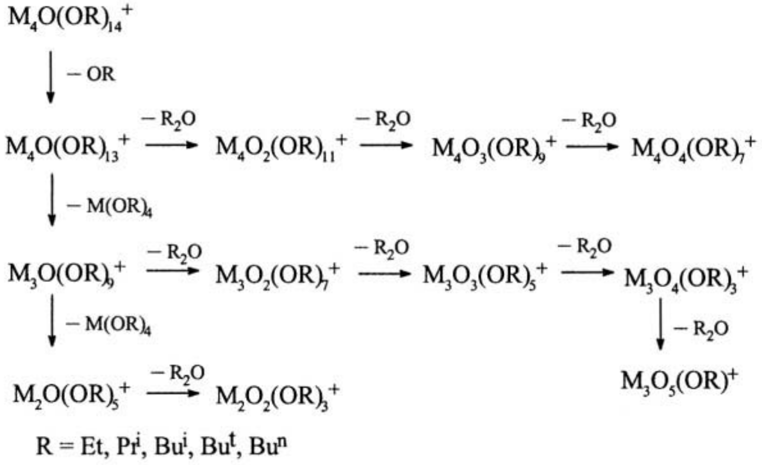


Fig. 5.1. Fragmentation scheme in the mass-spectra of "M(OR)$_4$", M= Zr, Hf [1612].

products [241]. A specific trend to oxidation in comparison with other derivatives has been noticed for 2-methoxyethoxides (for details see Section 12.1). It is interesting to note that among the rare earth derivatives the only one isolable free from oxogroups was found to be **$[Y(OC_2H_4OMe)_3]_{10}$** [1308] — the derivative of the most electronegative element. The 2-methoxyethoxide of gadolinium can be isolated already as **$[Gd_6(\mu_6\text{-}O)(OC_2H_4OMe)_{16}]$** [782]. Caulton *et al.* have even with most rigorous protection from moisture and oxygen obtained **$[Ba_6(\mu_6\text{-}O)(OC_2H_4OMe)_{10}\cdot 4ROH]$** on reaction of Ba metal with 2-methoxyethanol [304].

The controlled oxidation of the low-valent metal alkoxides has in fact been used for the preparation of oxocomplexes. Thus on action of **O_2** on **$Mo_2(OBu^t)_6$** or the red-colored solutions obtained by anodic dissolution of molybdenum metal in alcohols (containing the derivatives of Mo(V)) were obtained the dioxoalkoxides, **$MoO_2(OR)_2$** [356, 908].

The situation with the determination of the input of different reaction pathways into formation of the oxoalkoxide species is rather complicated, as in addition the two last ones — ether elimination and oxidation by oxygen — are catalyzed by the traces of water. The origin of oxogroups in the molecules of alkoxide carboxylates appears to be the formation of esters taking place in the course of their synthesis or in storage (see Section 7.1).

It is quite apparent that the oxocomplexes — homo- and heterometallic ones — play a crucial role in formation of the simple and complex oxide phases and are their true precursors. It therefore is reasonable to consider some examples illustrating the formation conditions and the structures of these compounds (in the order corresponding to the increase in molecular complexity). The dinuclear complex $Ta_2(\mu\text{-}O)(\mu\text{-}OPr^i)(OPr^i)_8 \cdot {}^iPrOH$ (Fig. 4.1) crystallizes from the solution of $Ta(OPr^i)_5$ in the parent alcohol on reflux (due to elimination of R_2O) [1639]. The triangular molecules of $M_3(\mu_3\text{-}O)(\mu_3\text{-}OPr^i)(OPr^i)_9$ (M = Mo and W) (Fig. 4.2 *b*), were obtained on oxidation of $M_2(OPr^i)_6$ with oxygen and $WO(OR)_4$ [356, 357]. The same kind of molecular structure was found for $Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OMe)(OPr^i)_9$ obtained on hydrolysis of $Ti(OPr^i)_4$ [454]. The tetrahedral molecules of $[Pb_4(\mu_4\text{-}O)(OSiPh_3)_6] \cdot C_6H_6$ (Fig. 4.5 *a*) and $[Pb_2Ti_2(\mu_4\text{-}O)(OPr^i)_{10}]$ were formed on alcoholysis of $PbCp_2$ and on complex formation of 2 alkoxides, respectively [608, 447].

$[Li(NbO)(OEt)_4(EtOH)]_2$ is the product of slow decomposition of $LiNb(OEt)_6$ (it was earlier erroneously described as $[LiNb(OH)(OEt)_5]$) [1622, 1621], its structure being an example of the $Ti_4(OMe)_{16}$ type (Fig. 5.2). Its molecule contains a terminal doubly bonded oxoatom ("niobyl" group), which is connected by an intermolecular hydrogen bond with an alcohol molecule at Li atom.

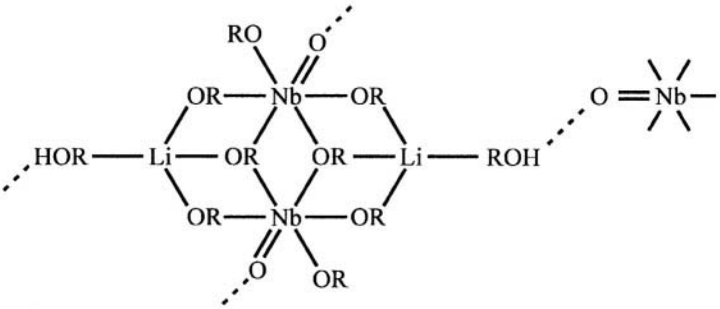


Fig. 5.2. The metal-oxygen core in the structure of $[Li(NbO)(OEt)_4(EtOH)]_2$ [1622, 1621]

The Fig. 5.2 shows clearly that even a very light thermal treatment would lead to the elimination of the solvating alcohol and formation of the Li–O–Nb bridge [1622, 1621].

The already mentioned pentanuclear $[M_5(\mu_5\text{-}O)(OPr^i)_{13}]$ (M = In, Sc, Y, Ln) (Fig. 4.9) crystallize from solutions obtained by all the described techniques (Section 12.7) [208, 1309, 1607]. The $[Ba_5(\mu_5\text{-}O)(OPh)_8(PhOH)(THF)_8]$ complex is formed on the reaction of Ba with PhOH [303], supposedly due to oxidation by the traces of oxygen. From the solutions of $Pb(OPr^i)_2$ (obtained by anodic oxidation of metal or via metathesis reactions) occurs the crystallization of $[Pb_6(\mu_3\text{-}O)_4(\mu_3\text{-}OPr^i)_4]$ (Fig. 4.10 *b*) [1627, 1786]. The formation of oxocomplexes in the latter case occurs either due to hydrolysis or the elimination of ether, which is rather characteristic of lead alkoxides [34,1254]. The metathesis of $GdCl_3$ with NaOR and NaCp provides $[Na_2Gd_4O(OBu^t)_{12}]$ [1441], and hydrolysis of potassium alkoxozirconate gives $[K_4Zr_2O(OPr^i)_{10}]$ [1666] (see also Section 4.6).

A short time refluxing of alcohol solutions of Ba and Ti isopropoxides enables the crystallization of $[BaTiO(OPr^i)_4(^iPrOH)_{7/8}]_4$ containing the metals in 1:1 ratio, which can serve as the precursor of $BaTiO_3$ (in contrast to barium alkoxotitanates containing the metals in 1:4 and 1:2 ratios). The central element in its molecule is the cubic $[Ba_4(\mu_4\text{-}O)_4]$ core, coordinating in its turn the $[Ti(OR)_5]$ residues. Taking into account the exclusively short Ti-O bond lengths (1.71 and 1.79 Å), the structure can be considered as the combination of four ion pairs $[Ba(ROH)]^{2+}{}_4[TiO(OR)_4]^{2-}{}_4$ (Fig. 4.12) [1787, 1631]. Its solutions contain supposedly the single ions or their aggregates in contrast to the molecular $Ba[Ti_2(OPr^i)_9]_2$, $[BaTi_2(OPr^i)_{10}]_2$, $[BaTi_3(OPr^i)_{14}]$ [1686] (see also Chapter 10).

Examples of polynuclear oxoclusters include the products of controlled or uncontrolled hydrolysis such as $Ta_7O_9(OPr^i)_{17}$ [1639, 1784] (Fig. 4.13 *b*), $[M_8O_{10}O(OEt)_{20}]$ (M = Nb,Ta) [219,911,1617] (Fig. 4.14 *b*), $[Bi_9O_7(OC_6F_5)_{13}]$ [851], $[Ti_{10}O_8(OEt)_{24}]$, $[Ti_{11}O_{13}(OPr^i)_{13}(OEt)_5]$, $[Ti_{12}O_{16}(OPr^i)_{16}]$ [457], $Zr_{13}O_8(OMe)_{36}$ [1173] (Fig 4.14 *c*), $[Ti_{16}O_{16}(OEt)_{32}]$ [1177], and $[Ti_{18}O_{28}(OBu^t)_{16}(^tBuOH)]$ [291]. In these molecules the blocks of $[M(OR)_6]$ octahedra are connected by $(\mu_n\text{-}O)$, $n = 2\text{–}4$ forming the structures that closely remind those of the known iso- and heteropolyanions and are often spherical (see also Section 4.7.2).

This family of structures includes also some heterometallic molecules such as $[Sr_6Ti_4(\mu_4\text{-}O)_4(OPr^i)_{20}]$ [1519], $[Zr_3Mo_8O_{12}(\mu_3\text{-}O)_8(\mu\text{-}O)_4(OPr^i)_{12}({}^iPrOH)_4]$ [901], $[Mn_8Sb_4(\mu_5\text{-}O)_4(OEt)_{20}]$ [140], $[Li_8(EtOH)_8Ta_8(\mu_4\text{-}O)_2(\mu_3\text{-}O)_{10}(\mu\text{-}O)_2(OEt)_{20}]\cdot 4EtOH$ and $[LiTa_9O_{13}(\mu\text{-}OEt)_6(OEt)_{20}(EtOH)_2]$ [1519] (Fig 4.13 *a*), [1519], and $[Ba_4Ti_{13}(\mu_5\text{-}O)_6(\mu_3\text{-}O)_{12}(OC_2H_4OMe)_{24}]$ [293].

The characteristic feature of the polynuclear $M_xO_y(OR)_z$ is their slow crystallization from solutions. They are usually soluble in hydrocarbons but can be transferred into solutions in alcohols only on heating (or mechanic crashing in alcohol). The determination of their solubility in alcohols is never providing the reproducible values — the solubility polytherms measured on heating and on cooling of solutions demonstrate hysteresis [911]. These data indicate the solvolytic decomposition of oxocomplexes on transfer into solution in alcohol with formation of pieces of different composition and structure participating in complex equilibria of poly- or oligomerization. The only exclusion appears to be $Ta_2O(OPr^i)_8\cdot{}^iPrOH$, whose binuclear molecules do apparently exist in solutions in alcohol [1639]. At the same time, some of the oxoalkoxides — $Ln_5O(OPr^i)_{13}$ (Fig. 4.9 *a*), $Al_{10}O_4(OEt)_{22}$ (Fig. 6.4), — appear to exist in the gas phase according to the mass-spectrometry data [953, 1785].

In conclusion it is necessary to note the considerable change in chemical activity occurring on transformation from the alkoxides into oxocomplexes. An example is the synthesis of a bimetallic Bi–Ti complex. The complex formation of 2 isopropoxides occurs only in the presence of water ($h = 0.2$–0.7), which leads to the formation of Bi-oxoisopropoxide, which then reacts with $Ti(OPr^i)_4$ already at room temperature providing $BiTi_2O(OPr^i)_9$ [447] (see also Chapter 8). Teyssie *et al.* [760] have proposed a large group of alkoxides of 3*d*-transition metals, and also those of Zn, Al, and Mo as highly effective selective catalysts for polymerization of lactones, isocyanates, and so on.

Chapter 6

SPECIFIC FEATURES OF PHYSICO-CHEMICAL BEHAVIOR: «COORDINATION POLYMERISM»

The structural types described in Chapt. 4 correspond to the crystalline alkoxides. At the same time, $M(OR)_n$ are much more prone to give amorphous samples due, supposedly, to the nonhomogeneity of their molecular composition. Crystallization occurs only in the cases when the samples contain only one type of aggregate or a regular polymeric structure.

The aging processes leading to the changes of the properties of samples over time (such as solidification of liquids, decrease in solubility, increase in evaporation temperature, changes in the composition of the fragments in the mass-spectra, crystallization of amorphous solids) have become wellknown. These processes, very characteristic also for the hydroxides, are caused by aggregation or polymerization and also by condensation of oligomeric molecules.

During the last 30 years the literature has included many reports on the variation of the properties (such as m., solubility, vapor pressure, IR, and mass-spectra) of samples of different alkoxides in time. Such examples were provided by the samples of $Al(OEt)_3$ and $Al(OPr^i)_3$ [1640, 1642], $Ga(OPr^i)_3$ [1234, 1233], $[Th(OPr^i)_4]_n$ [106], $Er(OPr^i)_3{\cdot}xROH$ [1734], and so on. The properties of the polymeric and tetrameric samples of $Ti(OMe)_4$ ("A" and "B" forms) [866] that differ in solubility in hydrocarbons, structure, and IR spectra are compared in Section 12.11. Dioxomolybdates and tungstates $MO_2(OR)_2$ are also prone to polymerization in time: their solubility decreases to practically zero and the IR spectra indicate formation of the M=O...M oxobridges (instead of the terminal M=O groups) [968, 1637].

The most detailed study of the mutual transformations has been carried out for the two types of $Al(OPr^i)_3$ aggregates that very often are present in the samples simultaneously. In the 1960s and 1970s with the aid of IR and NMR spectroscopy it was shown that the freshly distilled liquid samples of $Al(OPr^i)_3$ contained trimeric $[(RO)_2Al(\mu\text{-}OR)_2]_2Al(OR)$ molecules — nonlinear chains with the 5-coordinated central and 2 tetrahedral peripheric Al-atoms [198, 563] (their structural analog was found in the crystal structure of $Al_3Cl_5(OPr^i)_4$ [1781]). On storage the liquid solidifies slowly and after approximately 40 days achieves a m.p. of 140°C [1642, 1043]. The crystalline samples contain $Al[(\mu\text{-}OR)_2Al(OR)_2]_3$ tetrameric molecules [1642] (whose structure was earlier predicted by Bradley [198], see Section 4.4.6). They are preserved in solution at room temperature and are destroyed forming trimers on heating [18, 927]. The process of aging, (i.e., of the increase in the average molecular complexity and m.p. in time) can be illustrated by a melting polytherm in the binary trimer-tetramer system (Fig. 6.1) [1642]. The activation enthalpy of the trimer → tetramer transformation is estimated at ~ 12 kcal/mol [563]. There do not exist, therefore, in contradiction to the literature data [563] any specific polymorphs of $Al(OPr^i)_3$, except, one and the same sample can contain 2 different forms of molecules in different ratios (the m.p. of 117 to 118 °C, provided usually in the literature, corresponds to the crystals formed directly from the alcohol solution and still containing about 12% of the trimer). This ratio is kept in hydrocarbon solutions.

On addition of ^iPrOH to the crystals it is possible first to obtain very concentrated solutions, from which then commences the crystallization of poorly soluble tetrameric form (Fig. 6.2). It can be supposed that the trimer molecule coordinates an additional alcohol molecule along the sixth coordinate of the central aluminum metal in solution and then forms with the aid of hydrogen bonding the intermediates, which transform subsequently into tetrameric molecules already containing the hexacoordinated central Al atom. The incomplete coordination polyhedron of the Al atom is thus responsible for the thermodynamic instability of the phase, where it is present [1642].

At ~110°C the melts of $Al(OPr^i)_3$ contain even dimeric molecules, which quickly transform into trimers on cooling [927]. The kinetics of mutual trans-

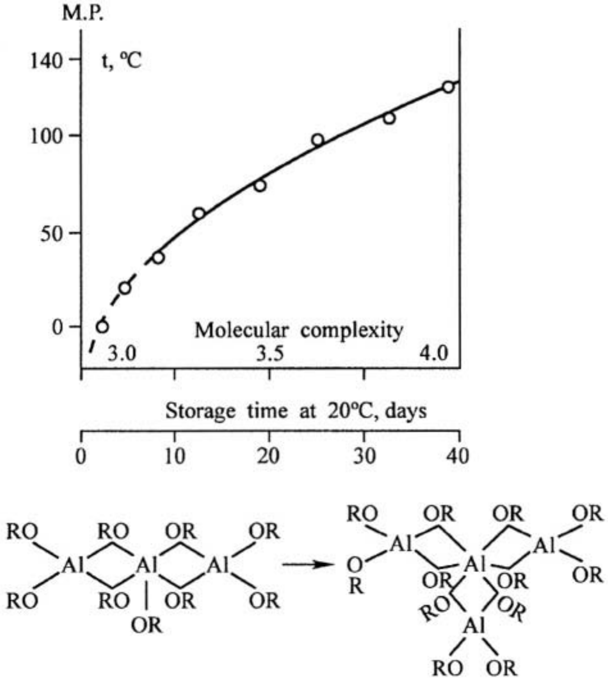


Fig. 6.1. The dependance of melting point on the degree of association of $Al(OPr^i)_3$ [1642].

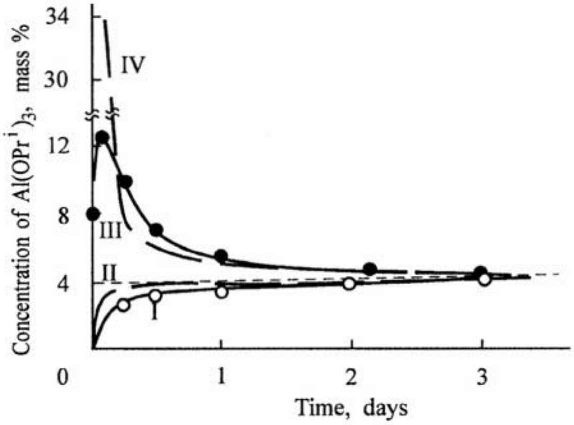


Fig. 6.2. The kinetic curves of isothermal saturation of ^{i}PrOH with various samples of $Al(OPr^i)_3$ at 20°C: m.p. 140°C (I), 118°C (II, III), supercooled melt (IV) [1642].

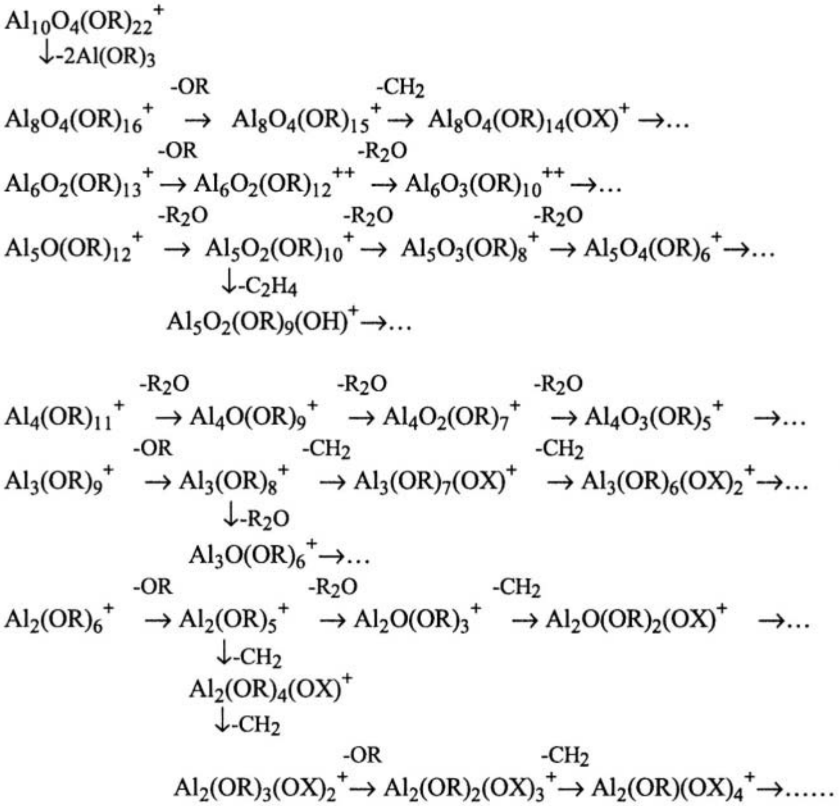
formations of all 3 forms of aggregates has been thoroughly investigated by Shiner, Wittaker *et al.* [1472, 927]. According to the mass-spectroscopic studies, [435, 250], the samples of $Al(OPr^i)_3$ can even contain admixtures of polynuclear oxocomplexes. We have interpreted the mass-spectrum as the fragmentation of a decanuclear molecule analogous in composition to the structurally characterized oxoethoxide $Al_{10}O_4(OEt)_{22}$ (the provided *m/z* correspond to the following ions: 1369, $Al_9O_4(OR)_{18}^+$; 1165, $Al_8O_4(OR)_{15}^+$; 1063, $Al_8O_5(OR)_{13}^+$; 961, $Al_8O_6(OR)_{11}^+$). The latter can result from microhydrolysis, micropyrolysis, or ether elimination from the $[Al(OPr^i)_3]_n$ molecules [1655].

It was found that the molecular composition of the $Al(OR)_3$ samples strongly influences the b. and the vapor pressure over the samples. The irreproducibility of these values was interpreted by some authors as the result of nonequilibrium conditions of distillation or partial thermolysis. Fieggen *et al.* concluded, however, that the major reason lies in the different molecular compositions of the samples [563].

The characteristics of the $Fe(OPr^i)_3$ samples do also vary in a very broad range: the m. change from 88 to 150°C (this latter value was obtained after a year of storage), the color on aging or on action of cold alcohol changes from reddish brown to light yellow, the solubility in alcohol change from ~7% to zero (20°C). The mass-spectra of all the samples contain the $[Fe(OPr^i)_3]_n$, n = 1–3 fragments [1365].

Even greater variation in the molecular composition has been observed for the 2-methoxyethoxides. The presence of the ether function in their molecules provides an alternative possibility for the saturation of the coordination sphere of metal atoms: the aggregation using the OR-bridges is competing with chelation via the ether oxygen atom. Both oxygen atoms, as it can be concluded from the single crystal X-ray data, can be mono-, bi-, or tridentate or not coordinated at all. All these factors provide additional opportunities for the existence of different isomers and aggregates. One of the consequences of this fact is that the majority of the crystalline 2-methoxyethoxides could be obtained only with low yields from the solutions in hydrocarbons.

The much more complex composition of the $Al(OEt)_3$ samples leads to a very broad variation in properties, which led a number of authors to some conclusions about the existence of distinct modifications for this compound.



$$Al_{10}O_4(OR)_{22}^+ \xrightarrow{-2Al(OR)_3} Al_8O_4(OR)_{16}^+$$

$$Al_8O_4(OR)_{16}^+ \xrightarrow{-OR} Al_8O_4(OR)_{15}^+ \xrightarrow{-CH_2} Al_8O_4(OR)_{14}(OX)^+ \rightarrow \ldots$$

$$Al_6O_2(OR)_{13}^+ \xrightarrow{-OR} Al_6O_2(OR)_{12}^{++} \xrightarrow{-R_2O} Al_6O_3(OR)_{10}^{++} \rightarrow \ldots$$

$$Al_5O(OR)_{12}^+ \xrightarrow{-R_2O} Al_5O_2(OR)_{10}^+ \xrightarrow{-R_2O} Al_5O_3(OR)_8^+ \xrightarrow{-R_2O} Al_5O_4(OR)_6^+ \rightarrow \ldots$$

$$Al_5O_2(OR)_{10}^+ \xrightarrow{-C_2H_4} Al_5O_2(OR)_9(OH)^+ \rightarrow \ldots$$

$$Al_4(OR)_{11}^+ \xrightarrow{-R_2O} Al_4O(OR)_9^+ \xrightarrow{-R_2O} Al_4O_2(OR)_7^+ \xrightarrow{-R_2O} Al_4O_3(OR)_5^+ \rightarrow \ldots$$

$$Al_3(OR)_9^+ \xrightarrow{-OR} Al_3(OR)_8^+ \xrightarrow{-CH_2} Al_3(OR)_7(OX)^+ \xrightarrow{-CH_2} Al_3(OR)_6(OX)_2^+ \rightarrow \ldots$$

$$Al_3(OR)_8^+ \xrightarrow{-R_2O} Al_3O(OR)_6^+ \rightarrow \ldots$$

$$Al_2(OR)_6^+ \xrightarrow{-OR} Al_2(OR)_5^+ \xrightarrow{-R_2O} Al_2O(OR)_3^+ \xrightarrow{-CH_2} Al_2O(OR)_2(OX)^+ \rightarrow \ldots$$

$$Al_2(OR)_5^+ \xrightarrow{-CH_2} Al_2(OR)_4(OX)^+ \xrightarrow{-CH_2} Al_2(OR)_3(OX)_2^+ \xrightarrow{-OR} Al_2(OR)_2(OX)_3^+ \xrightarrow{-CH_2} Al_2(OR)(OX)_4^+ \rightarrow \ldots\ldots$$

Fig. 6.3. Fragmentation scheme in mass-spectra of $Al(OR)_3$ (R=Me, Et); X=H for methoxide, Me for ethoxide [1233, 1655].

The mass-spectra of all the forms of **"$Al(OEt)_3$"** were found to contain the 4 to 10 nuclear fragments of the oxoethoxides (Fig. 6.3) in addition to the **$[Al(OR)_3]_n$** (n = 2–4) ones.The relative intensity of ions corresponding to ortho- and oxo-forms indicated that the composition of the samples varied in a rather broad range depending on the conditions of their synthesis and their thermal prehistory.

Certain information concerning the structure of the oligomeric oxoalkoxides present in amorphous samples can be obtained regarding the molecular structures of the crystalline oxocomplexes, treating the oxogroups as the knots in condensation. Thus in the molecule of the "crystalline aluminium ethoxide" **$Al_{10}O_4(OEt)_{22}$** [1785] (Fig. 6.4) it is easy to distinguish the fragments forming tetra-, penta, hexa- and octanuclear oxocomplexes discovered in the mass-spectra. The average molecular complexity in the benzene solutions of **$Al_{10}O_4(OEt)_{22}$** [1661] and in the gas phase [1640], turned out to be the same — 4.4.

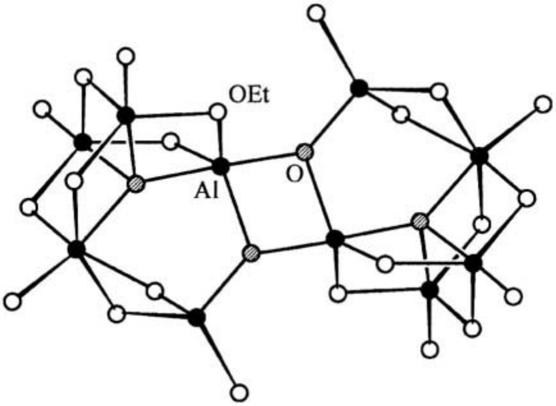


Fig. 6.4. The molecular structure of $Al_{10}O_4(OEt)_{22}$ [1785].

The same kinds of ortho- and oxo-forms were discovered in the mass-spectra of **$Al(OMe)_3$**. Its most reactive (young) forms were also obtained for **$Al(OEt)_3$** obtained under mild conditions — on alcohol interchange from **$Al(OPr^i)_3$** in benzene at 20°C [1640]. In storage in the samples of **$Al(OMe)_3$** and **$Al(OEt)_3$** in the amorphous matrix there occurs crystallization of the polymeric layered structure of **$Al(OH)_3$** bayerite type, which on longer storage (after several years) transforms into the **$Al(OH)_3$** gibbsite phase [1366]. The difference in reactivity of "old" and "young" **$Al(OMe)_3$** is clearly displayed in their complex formation with NaOMe [887].

It can be concluded from the above-mentioned examples that the nonhomogeneity of the molecular composition can be caused not only by the existence of different **$M(OR)_n$** aggregates but also by the presence of oxoligands in them (often to a very low extent) (see also Chapt. 5). The oxoligands appear always on sublimation, distillation or any other thermal treatment. The most thermally stable alkoxides, such as **$Al(OR)_3$**, produce oxocomplexes only at high temperatures in the hydrocarbon media. Thus on prolonged thermal treating at 240°C or on reflux with benzene, the solid $[Al(OEt)_3]_\infty$ can be partially transferred into solution due to oligomerization with formation of $[AlO_n(OR)_{3-2n}]_x$, where $n << 1$. Soluble forms of $Al(OEt)_3$ can also be obtained on the interaction of metal with alcohol in xylene (140°C) [1103, 344]. Action of the excess of the alcohol in this form leads to the precipitation of $[Al(OEt)_3]_\infty$, being supposedly free from oxoligands [1640].

The analogous form of $[Fe(OEt)_3]_\infty$ (yellow microcrystalline powder having a bayerite-type structure) was first obtained by action of $Ti(OEt)_4$ or $Nb(OEt)_5$ on solutions of "$Fe(OEt)_3$" in alcohol, which is containing supposedly much higher amount of oxoligands than "$Al(OEt)_3$" (brownish orange $Fe_{10}O_4(OEt)_{22}$ can be obtained from these solutions by crystallization with good yields; see also Section 12.22) [1365].

The variation in characteristics of "$M(OPr^i)_4$" (M = Zr, Hf) is connected with the presence in their samples of $M_3O(OR)_{10}$ and $M_4O(OR)_{14}$ oxocomplexes, formed on desolvation of $[M(OPr^i)_4 \cdot ROH]_2$ [1612]. Slow decomposition of liquid $NbO(OEt)_3$ or $MoO(OEt)_4$ (with formation of crystalline $Nb_8O_{10}(OEt)_{20}$ or $MoO_2(OEt)_2$) leads also to the variation of the properties of the samples in time. In the latter case a color change from the brownish yellow to a practically colorless takes place; the solubility decreases drastically [911, 1637].

The appearance of microamounts of oxoligands usually leads the alkoxides that have polymer structures to oligomerization and strong increase in solubility and chemical reactivity, in particular, in the reactions of complex formation. Thus $[Ba(OBu^n)_2]$ obtained by reaction of metal with alcohol in hydrocarbon media is insoluble in ^nBuOH and does not react with either $Ta(OBu^n)_5$ or $Ti(OBu^n)_4$. The appearance of the oxogroups in its composition (<0.05 per 1 Ba atom) permits solutions in ^nBuOH with up to ~40%, and in joint solutions with $Ta(OBu^n)_5$ all the ratios of the components can be achieved [1631, 1562]. Thus the absence of solubility or reactivity toward an alkoxide of other metal can serve as an indication of the purity of $[M(OR)_n]$ samples. At the same time, the introduction of oxogroups turns out to be very useful for the preparation of the complex solutions to be applied in sol-gel technology (see Chapt. 10). It brings light on the sol-gel technology recommendation to subject the solutions of several alkoxides (and sometimes even the heterogeneous systems) to prolonged reflux before the introduction of water for hydrolysis.

This treatment leads to increased solubility and the formation of bimetallic complexes.

The influence of the microamounts of oxogroups on the thermal properties of $Al(OBu^t)_3$ and $[Mo(OBu^t)_3]_2$ has been clearly illustrated by the data of Chisholm *et al.* In the atmosphere of highpurity He, both these compounds sublime at 200–220°C under atmospheric pressure. In the presence of traces of water and oxygen at >190°C they decompose forming γ-Al_2O_3 and MoO_2 respectively (an autocatalitic mechanism has been proposed for the decomposition) [124].

For a great number of metal alkoxide derivatives of Al, Ti, Zr, Hf, NbO^{3+}, Ta, MoO^{4+}, MoO_2^{2+}, WO_2^{2+}, $Re_2O_3^{6+}$, Fe, and Ni, we have discovered that variations in the characteristics of the samples dependent on their "prehistory" — temperature of the synthesis, nature of solvent they are isolated from, storage time (age) — have a more or less general character and are caused by the existence of several types of aggregates (different in size and composition) and the possibility of their mutual transformations. All these phenomena we designated by the term *"coordination polymerism"* [1655]. We suppose that the driving force of this process is the sterical instability of oligomeric alkoxides caused by coordination unsaturation of the metal atoms. The trend to saturation of the coordination sphere via polymerization, isomerization, and so on is the reason for the thermodynamic instability of the corresponding crystalline or amorphous phases.

The following general features of the poly- or oligomerization processes were observed:

- The molecular complexity increases in time ("aging") and on action of alcohols due supposedly to solvation of the "young" forms containing coordinatively unsaturated atoms. The second step is connected with the formation of hydrogen bonds between the solvated species and their subsequent condensation with the formation of OR-bridges and the release of the solvating alcohol molecules. The process is associated with increase in m. and b., decrease in solubility (in the alcohols) and lightening of the color. In the mass-spectra, due to the increasing temperature of the transfer, increases the extent of fragmentation products with lower weights.

- Thermal treatment of the samples (melting,* destillation) or dissolution in aromatic hydrocarbons favor oligomerization of the molecules (in the latter case supposedly due to partial rupture of the alkoxide bridges and formation of **π-complexes).** The products of oligomerization display lower thermal constants, higher solubility in alcohols and more intense colors. Their mass-spectra contain ions with higher weights — fragments of oligomeric aggregates existing in the condensed phase. The scheme of these transformations is shown in the Fig. 6.5. Knowledge about these regularities permits in many cases to modify the molecular composition and properties of the samples, which is very important in their technological applications.

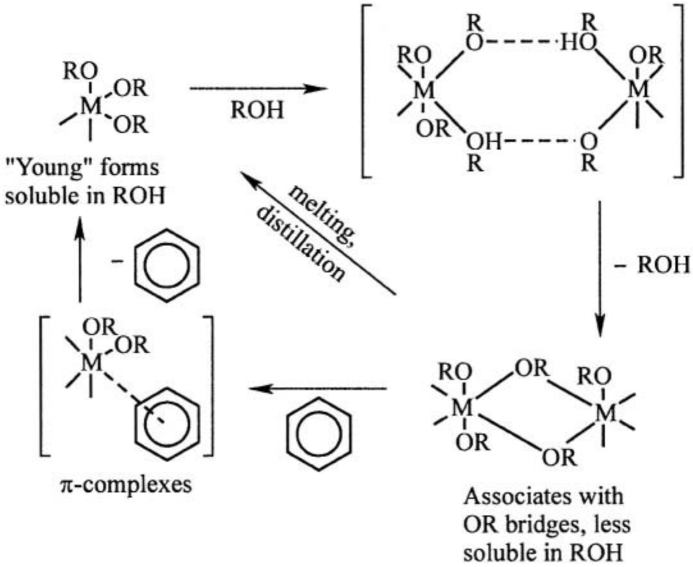


Fig. 6.5. General scheme of changes in molecular composition of $[M(OR)_n]_x$ under the action of different factors [1655].

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*The m. values depend on the technique of determination — heating time, amount of the sample used, and size of the particles (for example, the m.p. for 0.02 g of $Al(OEt)_3$ on heating with the rate of 20°/min was 135, and for 8 °/min was 146° C) [1640].

In conclusion, we should mention that in the description of the behavior of distinct alkoxides it appears very difficult to distinguish the influence of each of the two factors — the inhomogeneity of the molecular composition and the presence of oxoderivatives. In certain cases the reversibility of transformations and reproducibility of the properties of the oligomeric forms can be used as criterion (as for $Al(OPr^i)_3$) indicating the constant chemical composition and the dominance of the first factor. At the same time, an irreversible aggregation/polymerization can result from the both factors.

Chapter 7

HETEROLEPTIC METAL ALKOXIDES CONTAINING CARBOXYLATO-, β-DIKETONATO, AND AMINOALKOXIDE LIGANDS

The studies of the mixed-ligand alkoxide complexes of metals belong to one of the most intensively and dynamically developing directions in the chemistry of metal alkoxides. Interest in these compounds has risen due to a number of reasons. One of the strongest driving forces was the request for the soluble in organic solvents and easy-to-handle derivatives of the transition (Fe, Co, Ni, Cu) and main group (Zn, Cd, Pb) metals — the components of the most important materials applied in the modern industries (such as HTSC and ferroelectrics PZT, PLZT, PZN, and so on) [326]. The other reason that drew the attention to the mixed-ligand complexes turned out to be the much higher stability of the heteroligands to hydrolysis, which provided a possibility to influence the speed of this process and regulate the morphology and properties of its products [1394, 1392]. Such behavior of heteroligands also gave rise to the supposition that the bridging heteroligands can be used to keep the metal ratio in the heterometallic species in the course of hydrolysis and preparation of a desired oxide material [785]. In the present chapter we do not pretend to cover all the information present in the literature on mixed-ligand complexes but try to describe and characterize the most important methods of their preparation, known types of molecular structures, and particular features of their hydrolytic behavior.

7.1. Synthesis

The most important ways to prepare heteroleptic complexes are (1) the reaction of chemical modification, (2) the interaction of an alkoxide with a carboxylate, **β-diketonate,** or other derivative of the same or the other metal, and (3) reactions of alcoholysis of derivatives initially not containing alkoxoligands.

In the background of the chemical modification lies the interaction of an alkoxide with an acidic organic ligand, usually carried out in hydrocarbon solvents or in ethers:

$$M(OR)_n + xHZ \rightarrow M(OR)_{n-x}Z_x + xROH$$

This reaction is analogous to microhydrolysis, and for it as well as for the microhydrolysis in literature have been proposed different mechanisms: the possibilities of both S_N2 [1021], and proton-assisted S_N1 [1056] scenarios have been discussed. The modification often leads in case of alkoxides that are Lewis acids and in the presence of excess of an acidic reagent to heteroleptic oxoalkoxides. It is supposed that their formation is due to the reaction of the alcohol released with the excess of acid leading to formation of esters and water. The latter causes microhydrolysis leading to oxospecies. Thus during storage of the mixtures containing $Ti(OR)_4$, AcOH, and ROH in 1:1:1 ratio the slow crystallization of $Ti_6(\mu_3\text{-}O)_2(\mu\text{-}O)_2(\mu\text{-}OEt)_2(\mu\text{-}OAc)_8(OEt)_6$ **[625]**, $Ti_6(\mu_3\text{-}O)_2(\mu\text{-}O)_2(\mu\text{-}OPr^i)_6(\mu\text{-}OAc)_4(OPr^i)_6$, and $Ti_6(\mu_3\text{-}O)_2(\mu\text{-}O)_2(\mu\text{-}OBu^n)_2(\mu\text{-}AcO)_8(OBu^n)_6$ **[490]**, respectively, occurs (Table 7.1). For the description of the extent of substitution in the complexes formed, the parameter x is equal to the ratio of the number of groups introduced to the number of atoms in the complex. The extent of microhydrolysis is characterized by the parameter h equal to the number of moles of water per mole of alkoxide that is needed to produce the oxocomplex considered. Thus for all the given complexes h is 2/3, while the x values differ. It is 4/3 for the ethoxide and butoxide and 2/3 for the isopropoxide. The x value can be regulated varying the alkoxide:acidic reagent ratio (thus at higher values of this ratio the complex $Ti_6(\mu_3\text{-}O)_2(\mu\text{-}O)_2(\mu\text{-}OPr^i)_2(\mu\text{-}OAc)_8(OPr^i)_6$ **[981]** analogous to those for the derivatives of the primary alcohols can be obtained). The h value can be increased by the introduction of small amounts of water in organic solvent. Thus on the very slow addition of

Table 7.1. Selected examples of heteroleptic alkoxides

Chemical composition. Structure	Synth. route*	Properties	Investig. methods	Ref.
$[Ti_6O_4(OBu^n)_8(OAc)_8]$, 2 $[M_3O]$ trian. connected via 2 μ-O bridges	1	colrl. cr., s. in hc, CH_2Cl_2	IR, ^1H, ^{13}C, X-r	490
$[Ti(OC_5H_{11}{}^{neo})_3(OCOBu^t)]_2$ 2 oct. sharing $(OR)_2$ edge	1	colrl. cr., s. in tol., <175/10^{-3} (subl.)	IR, ^1H, ^{13}C, X-r	194
$[Ti_6O_6(OC_5H_{11}{}^{neo})_6(OCOC_6H_4OPh)_6]$ M_6O_6 - 12-membered ring	1	colrl. cr., s. in hc., CH_2Cl_2	IR, ^1H, X-r	1255
$Ti(OR)_2(\beta\text{-dik})_2$, R= Me, Et, Pr^i, β-dik= acac, thd	1	colrl. cr., s. in hc.	IR, ^1H	535
$[Ce_2(OPr^i)_6(\mu,\eta^2\text{-}OC_2H_4NMeC_2H_4N\ Me_2)_2]$, 2 oct. sharing $(\mu\text{-}OR)_2$ edge	1	or. cr., s. tol, ^iPrOH	IR, ^1H, X-r	786
$[MNb_2(OPr^i)_{10}(OAc)_2]$, M=Mg, Cd, Pb, angular mol., 3 oct. sharing $[(OR)_2(OAc)]$-faces	2	colrl cr., s. in tol.	IR, ^1H, ^{13}C, ^{113}Cd, X-r	181, 779
$PbZr_3O(OPr^i)_{10}(OAc)_2$, $[M_4O]$ tetrah.	2	colrl. cr., s. in hc.	IR, ^1H, X-r	779
$PbSn_2O(OBu^t)_4(OAc)_4$, $[M_3O]$ trian.	2	colrl.. cr., s. in hc.	IR, ^1H, X-r	298
$[BaTi(OEt)_4(thd)_2(EtOH)_2]_2$, struct. type of $Ti_4(OMe)_{16}$	1, 2	colrl cr., s. in hc.	IR, ^1H, ^{13}C, X-r	899
$Pb_2Zn_2(OC_2H_4OMe)_4(OAc)_4$	3	colrl. cr., s. in hc.	IR, ^1H, X-r	583
$W_2(NMe_2)_2(OR)_4$, R= $CMe_n(CF_3)_{3-n}$, ethane-like mol. M≡M bond	3	dark red cr., 90-100 (subl.), s. in hc	IR, ^1H, ^{13}C, ^{19}F, X-r	272

*The numbers of the synthetic routes are corresponding to the particular classification given in this chapter.

water to the solutions of $Ti(OBu^n)_{4-x}(acac)_x$ ($x < 1$) it turns out to be possible to isolate the crystalline complex $Ti_{18}(\mu_5\text{-}O)_2(\mu_4\text{-}O)_2(\mu_3\text{-}O)_{10}(\mu\text{-}O)_8(\mu\text{-}OBu^n)_{14}(OBu^n)_{12}(acac)_2$ [1590] ($x = 0.11$, $h = 1.22$). For the tetravalent metals such as tin [324] and cerium [1590] the chemical modification by symbol β-diketones leads to $[M(\beta\text{-diket})(OR)_3]_2$ and $M(\beta\text{-diket})_2(OR)_2$ with very high yields, no oxo-by-products being noticed in the absence of additionally introduced water. It is also important that the x-value is not always determined by the ratio of the reagents ($M(OR)_n$ and HZ) in the reaction mixture. In many cases the composition of the complex to be formed is determined by the stability or the solubility of the complexes formed. Thus the interaction of $M(OEt)_2(EtOH)_4$ (M = Ca, Sr, Ba) with Hacac leads immediately to the precipitation of insoluble $M(acac)_2$, while that with Hthd as modifier leads to soluble, heteroleptic complexes ($x = 1$), such as $[Ca_4(thd)_4(OEt)_4(EtOH)_4]$, $[Sr(thd)(OEt)(EtOH)_{0.66}]_n$, and $[Ba(thd)_{1.5}(OEt)_{0.5}(EtOH)_{0.33}]_n$ [68]. In the same way the reaction of $LaNb_2(OPr^i)_{13}$ with $N(C_2H_4OH)_3$ H_3 tea leads always to the formation of a more stable complex $La(tea)_2[Nb(OPr^i)_4]_3$, and not to the compounds with lower La : tea ratio [899].

The interaction of the metal alkoxides with the salts of carboxylic acids or with β-diketonates of other metals is especially attractive for the synthesis of bimetallic molecular precursors in the cases, when the preparation of the alkoxide of the other metal is somehow hindered or it is insoluble or irreactive under the conditions applied. This method has been widely used for the sol-gel preparation of HTSC materials (because of low solubility and reactivity of $Cu(OR)_2$) and lead-containing ferroelectrics (in the view of difficult synthesis and low stability of $Pb(OR)_2$). It should be mentioned that the reaction between a metal alkoxide and a functional derivative does far not always lead to the formation of a mixed-ligand bimetallic complex:

$$M(OR)_n + M'Z_m \longrightarrow MM'(OR)_nZ_m$$

as it might be supposed. This approach turned out to be very efficient for the preparation of carboxy-isopropoxides of divalent metals and niobium, $MNb_2(OAc)_2(OPr^i)_{10}$ (M= Mg, Cd, Pb) [181], but the reaction with both carboxylates and β-diketonates leads very often to mixed-ligand oxocomplexes as products. The reaction of acetates with alkoxides appears very often to be associated with the elimination of esters [298], as for example

$$Pb(OAc)_2 + Sn(OBu^t)_4 \xrightarrow{(tol.)} PbSn_2(\mu_3\text{-}O)(OBu^t)_4(OAc)_4 + Bu^tOAc + ...$$

The same reason was given in the literature for the formation of a number of other bimetallic oxocomplexes such as $Cd_4Sn_4(\mu_4\text{-}O)(OCH_2Bu^t)_{10}(OAc)_{10}$ [325] and $[PbTi_2(\mu_4\text{-}O)(OEt)_7(OAc)]_2$ [320]. When the alkoxides of zirconium, hafnium, or cerium are used for this reaction, the formation of the oxocomplexes can be due to the elimination of an unsaturated hydrocarbon from the initial alkoxide [1565], leading to the formation of monometallic oxoalkoxides as intermediates (the latter are formed already on desolvation of $[M(OR)_4(ROH)]_2$ and are always present as admixtures in the samples of desolvated $M(OR)_4$, where R is a primary or secondary radical [1612] (see also Section 12.12). In this case the possible sequence of transformations (taking place usually on reflux in toluene) can look as follows:

$$\begin{gathered}3[M(OR)_4(ROH)] \longrightarrow M_3O(OR)_{10} + 4ROH + R'CH{=}CH_2\ (M{=}Zr,Ce)\\ Pb(OAc)_2 + Zr_3O(OPr^i)_{10} \longrightarrow PbZr_3(\mu_4\text{-}O)(OPr^i)_{10}(OAc)_2\ [779]\\ Fe(acac)_3 + Zr_3O(OPr^i)_{10} \longrightarrow FeZr_3(\mu_4\text{-}O)(OPr^i)_{10}(acac)_3\ [1415]\\ Ba(thd)_2 + Ce_3O(OPr^i)_{10} \longrightarrow Ba_4Ce_2(\mu_6\text{-}O)(OPr^i)_{10}(thd)_4 + ...\ [782]\end{gathered}$$

The analogous explanation can be given for the formation of such bimetallic heteroleptic oxocomplexes as $Gd_2Zr_6(\mu_4\text{-}O)_2(OPr^i)_{20}(OAc)_6$ [443] or $[PbZr_2(\mu_4\text{-}O)(OEt)_6(OAc)_2]_2$ [1040].

It should be mentioned that in many cases it turns out to be impossible to isolate the bimetallic mixed-ligand complex. The isolable reaction products appear to be homometallic heteroleptic species. The composition of the reaction products is often dependent on the polarity and donor properties of the solvent as the molecules of the latter compete with the bridging alkoxo-, carboxylato-, or **β-diketonatoligands** for the place in the coordination sphere of metal atoms. Thus if the reaction of $Pb(OAc)_2$ with $Sn(OBu^t)_4$ mentioned above is carried out in pyridine, it gives $Sn(OBu^t)_3(OAc)Py$ and $Pb(OAc)(OBu^t)$ as the major products and not the bimetallic complex [298]. $Sn(OBu^t)_3(OAc)Py$ turns also to be the major product of the reaction of $Sn(OBu^t)_4$ with Me_3SiOAc

in pyridine [298], while the same reaction in toluene leads via the ester elimination to the mixture of $Me_3SiOSn(OBu^t)_3$ and $(Me_3SiO)_2Sn(OBu^t)_2$. The composition of the reaction products can also be dependent on the nature of the atom that should act as the donor of alkoxide groups. Thus the reaction of copper acetylacetonate with sodium or yttrium alkoxides in pentane gives a homometallic mixed-ligand derivative $[Cu(acac)(OR)]_4$, $R = C_2H_4OPr^i$ [1498, 1307], while that with the aluminium alkoxide produces a bimetallic complex $(acac)Cu(\mu\text{-}OR)_2Al(OR)_2$, R= $SiMe_3$ [1498]. In the latter case the stability of the intermediate bimetallic derivative turns out to be higher.

The alcoholysis of derivatives that do not initially contain alkoxide ligands is of special importance for the preparation of alkoxide halids. It is also an efficient synthetic route to mixed-ligand complexes of chromium [538, 523, 1189]:

$$[Cr(acac)_2(H_2O)_2] + \text{exc.}ROH \rightarrow [(acac)_2Cr(OR)]_2,\quad R = Me, Et, Ph$$

The latter cannot practically be prepared by any other way because of low solubility and insufficient reactivity of chromium(III) alkoxides. The alcoholysis by the alcohols with rather high boiling points such as 2-alkoxyalkoxides can even lead to replacement of such ligands as an acetate group [583]:

$$2Pb(OAc)_2 + 2Zn(OAc)_2 + \text{exc.}ROH \longrightarrow Pb_2Zn_2(OAc)_4(OR),$$
$$R = C_2H_4OMe$$

The formation of a mixed-ligand alkoxoacetate complex takes place presumably also on reflux of the pure led acetate with 2-methoxyethanol [985], while in this case the reaction products have not been characterized by the X-ray single-crystal study.

7.2. Molecular structures

The major types of the molecular structures for the heteroleptic derivatives appear to be the same or very close to those characteristic of homoleptic alkoxides. They can be classified as follows:

- Mononuclear complexes in the cases when the number of donor atoms in the ligands is not less than is necessary for the saturation of the coordination sphere of the central atom. These compounds are of interest as molecular precursors of oxide materials in the MOCVD technique, such as, for example, $Sn(acac)_2(OPr^i)_2$ [324] $Sn(OBu^t)_3(OAc)Py$ [298] or $Ti(thd)_2(OPr^i)_2$ [535], or as specific catalysts of stereoselective processes as $HB(3\text{-}^tBuPz)_3MgOEt$ [353].

- Binuclear complexes, whose molecules usually contain a $M(\mu\text{-}OR)_2M$ group. This structure is characteristic, for example, of $M_2(\mu\text{-}OPr^i)_2(OPr^i)_4(acac)_2$, M= Ce [1590], Sn [324]; $Ce_2(OPr^i)_6(\mu\text{-}OC_2H_4NMeC_2H_4NMe_2)_2$ [786]; $(acac)Cu(\mu\text{-}OR)_2Al(OR)_2$, R = Me_3Si [1498]; $Cr_2(\mu\text{-}OR)_2(acac)_4$ [538, 523, 1189], $[Ti(OR)_3(\beta\text{-}dik)]_2$, R=Me, Et, Pr^i, β-dik= acac, thd [535]. Application of specific heteroligans (that form usually a M–C bond and that lay beyond the scope of this book) can lead to the formation of dimers with three alkoxide bridges such as $LSn(\mu\text{-}OBu^t)_3InL'$ (L,L' — a ligand acting as an acceptor of an electron pair, type $Mo(CO)_5$) [1695], and dimers with one bridging heteroligand such as, for example, $(tea)Ge(\mu\text{-}CH_2)Ge(OEt)_3$ [687].
- Trinuclear aggregates are represented by triangular molecules such as $Y_3(\mu_3,\eta^2\text{-}OR)_2(\mu,\eta^2\text{-}OR)_2(\mu_3,\eta^1\text{-}OR)(acac)_4$, R= C_2H_4OMe [1307], $PbSn_2(\mu_3\text{-}O)(OBu^t)_4(OAc)_4$ [298], or linear chains, where the metal atoms are bound by three bridging groups, such as $[(Pr^iO)_3Nb(\mu\text{-}OPr^i)_2(\mu\text{-}OAc)]_2M$, M = Mg, Cd, Pb [181].
- The tetranuclear molecules of heteroleptic derivatives demonstrate with a few exceptions all the structural types described for alkoxide- and oxoalkoxide tetramers of homoleptic alkoxides. Among the homoleptic compounds that are the cubane type that appears to be the leading one. It is represented, for example, by the structures of $Cu_4(\mu_3,\eta^1\text{-}OC_2H_4OPr^i)_4(acac)_4$ [1498], $Ni_4(\mu_3\text{-}OMe)_4(dbm)_4(MeOH)_4$ [377], $Ca_4(thd)_4(\mu_3\text{-}OEt)_4(EtOH)_4$, $Ca_4(thd)_6(OC_2H_4NMe_2)_2$, $H_2Ba_4(thd)_6(OC_2H_4OPr^i)_4$ [68]. The $Ti_4(OMe)_{16}$ methoxide type is represented by such complexes as $Ba_2Cu_2(acac)_4(OR)_4(ROH)_2$, R= C_2H_4OMe [1406], $Zr_2Co_2(\mu_3\text{-}OPr)_2(\mu\text{-}OPr)_4(OPr)_4(acac)_2$ [1415], $Ba_2Ti_2(thd)_4(OR)_4(ROH)_2$, R= Et [899]. The $[Al(OPr^i)_3]_4$ type is displayed by $La(tea)_2[Nb(OPr^i)_4]_3$ [899]. The substitution for 2 bridging acetate groups in molybdenum(II) acetate structure by two bridging isopropoxoaluminate ligands gives $Mo_2(\mu\text{-}OAc)_2[\mu\text{-}Al(OPr^i)_4]_2$ [760]. Closo-fragment of 4 same or different metal atoms with a μ_4-bridging oxygen atom in the center was discovered in the structures of $Zr_3Fe(\mu_4\text{-}O)(\mu\text{-}OPr)_6(OPr)_4(acac)_3$ [1415], $PbZr_3(\mu_4\text{-}O)(\mu\text{-}OPr^i)_6(OPr^i)_4(OAc)_2$ [779],

$Zr_4(\mu_4\text{-}O)(\mu\text{-}OPr)_6(OPr)_4(acac)_4$ [1590]. The complex nature of the bridging ligands permits the realization of the structures that belong to the structural types that are close but not identical with those known for homoleptic derivatives, such as, for example, that of $Pb_2Zn_2(\mu,\eta^2\text{-}OC_2H_4OMe)_4(OAc)_4$ [583] — a rhombus of metal atoms connected only by doubly-bridging ligands.

- Pentanuclear complexes are represented by the pairs of triangles with a common vertex ($MM'_4(OR)_{18}$ type). This type is displayed by the structure of $BaCu_4(thd)_4(OR)_2(ROH)_4$, $R = C_2H_4OMe$ [150].
- Hexanuclear molecules can appear as closo-structures with an oxygen atom in the center, such as $Co_4Zr_2(\mu_6\text{-}O)(\mu\text{-}OPr^i)_8(OPr^i)_2(acac)_4$ [1415], $Ba_4Ce_2(\mu_6\text{-}O)(thd)_4(OPr^i)_{10}$ [782], or result from the condensation of triangle aggregates via bridging ligands as $Ti_6(\mu_3\text{-}O)_2(\mu\text{-}O)_2(\mu\text{-}OAc)_4(\mu\text{-}OPr^i)_6(OPr^i)_6$ [490], $[PbTi_2(\mu_4\text{-}O)(OAc)(OEt)_7]_2$ [320], $[PbZr_2(\mu_4\text{-}O)(OAc)_2(OEt)_6]_2$ [1040]. A ring of 6 metal atoms not identical to that observed for the previous type was also found in the structures of $Ti_6(\mu_3\text{-}O)_2(\mu\text{-}O)_2(\mu\text{-}OAc)_8(\mu\text{-}OR)_2(OR)_6$, $R = Et, Pr^i, Bu^n$ [625, 490, 981].
- Octanuclear aggregates have been so far represented by the combination of two tetrahedra as, for example, in $Cd_4Sn_4(\mu_4\text{-}O)_2(OAc)_{10}(OCH_2{}^tBu)_{10}$ [325].
- There is now known a number of bigger heteroleptic aggregates such as, for example, $Ti_{18}(\mu_5\text{-}O)_2(\mu_4\text{-}O)_2(\mu_3\text{-}O)_{10}(\mu\text{-}O)_8(\mu\text{-}OBu^n)_{14}(OBu^n)_{12}(acac)_2$ [1590].

7.3. Particular features of hydrolysis and thermolysis

A number of rather thoroughly written and detailed reviews have been devoted to the problems associated with hydrolysis and thermolysis of heteroleptic complexes authored mainly by Sanchez [1394, 1021].

The application of weakly acidic organic ligands for chemical modification has been initiated itself by attempts to influence the processes in the course of hydrolysis of metal alkoxides (see Chapter 9). It turned out that the hydrolysis of the complexes incorporating the ligands forming stable chelate cycles (such as carboxylate or **β-diketonate**) effects nearly exclusively the alkoxide groups, leaving the functional ligands intact. The chemical modification is thus limiting the h value that can really be achieved as the excess of water does not permit to remove the heterogroups, while its influence on the formation of hydrogen bonds and solvation of the hydrohyde aggregates formed (i.e., the key parameters influencing the subsequent polycondensation step) cannot be excluded completely. On the other hand, polycondensation occurs in a quite different manner even at very low *x* values as the development of the polymer chain turns out to be limited in the directions in space that are shielded by the heterogroup strongly attached to the metal center. Finally, the gel formation for the chemically modified precursors occurs much more slowly than for the homoleptic alkoxides, the gels formed are much more stable, while the particles forming them (when the x value is chosen properly) are more uniform in size. As the elimination of the chelating ligands occurs at rather high temperatures (500 to 600°C as it is shown by TGA [320, 1040]), the morphology of the initial particles formed on hydrolysis is kept during the subsequent steps of the preparation of materials, even on the thermel treatment. The chemical modification appears therefore to be the key to the preparation of the oxide materials with the prescribed morphological characteristics. The most illustrative demonstration of the influence of x and h values on the structure and morphology of the particles obtained in the sol-gel process has been demonstrated by Sanchez in [1394] for cerium alkoxides. For the achieved *x* value, the solutions obtained by the addition of Hacac to cerium(IV) isopropoxide can contain the following structurally characterized molecular precursors: $\mathbf{Ce_2(OPr^i)_8(^iPrOH)_2}$ (I), $\mathbf{Ce_2(OPr^i)_7(acac)(^iPrOH)}$ (II), $\mathbf{Ce_2(OPr^i)_6(acac)_2(^iPrOH)_2}$ (III), $\mathbf{Ce_2(OPr^i)_4(acac)_4}$ (IV), which can be present simultaneously in different ratios. In the absence of a modifier ($x = 0$) the compound I is the only precursor present, and its hydrolysis is followed by polycondensation in all directions, leading to the formation of a precipitate, whose particles vary a great deal in size and morphology. At low $x (x < 0.5)$ the solutions contain both I and II, and thus there appear some limitations in the polycondensation process, whose products consist of large areas with a high extent of condensation connected by branched polymer chains. The latter become the main product at x close to 0.5 (both slightly lower and slightly higher than this value), when II becomes the main component in solution. When *x* reaches 1, III becomes the major molecular precursor, and the structure of the polymer starts to incorporate small, well-formed blocks. The bonds inside them occur via oxo- and hydroxobridging groups, while the surface becomes covered by the molecules of modifier.

When x exceeds 1, the free aggregates of this type appear in solution after hydrolysis. When $x = 2$ (i.e., in the situation when IV becomes the main molecular precursor), such aggregate was characterized by X-ray single crystal study, and it was shown to have $Ce_6(\mu_6\text{-}O)_4(\mu_3\text{-}OH)_4(acac)_{12}$ composition [1590].

The fact that the groups of the modifier are kept in the coordination sphere of the metal atom gave rise to the concept of creating organic-inorganic hybride materials using chemical modification and subsequent hydrolysis followed by the polymerization (or polycondensation) of the organic residues, not affected by hydrolysis [1392]. As such ligands there have been tested the metacrilic and related unsaturated organic acids or β-diketones, containing unsaturated radicals.

As it has been mentioned above, the elimination of the organic residues corresponding to the modifying ligands incorporated into the coordination sphere of the metal atoms occurs at rather high temperatures. This fact gave rise to numerous recent attempts to apply the heteroleptic heterometallic complexes as precursors in the MOCVD. It has been supposed that the thermally stable bridging ligands can guarantee the conservation of the metal-metal ration on transition into the gas phase, which will permit such derivatives as single-source precursors to be used in the deposition of films with rather complex composition [779].

Chapter 8

ADDUCTS AND HETEROMETALLIC ALKOXIDES

As has been mentioned above, of the many works devoted to the studies of the chemical properties of metal alkoxides, we here can consider only the reactions of partial substitution for the alkoxide groups (Chapter 7), decomposition with formation of oxocomplexes (Chapter 5), and hydrolysis with the formation of homo- and heterometallic hydroxides (Chapters 9 and 10). We discuss here the complex formation products of metal alkoxides — the adducts with neutral ligands, **$M(OR)_n \cdot mL$,** and the bimetallic alkoxides, precursors of complex oxides in sol-gel technology.

8.1. Solvate complexes

The high donor activity of the oxygen atoms of the OR-groups makes formation of the aggregates, where the coordination spheres are filled with the oxygen atoms of bridging ligands, much more common than the formation of solvates with "alien" donor molecules. In fact the solvates with such strong donors as normal-chain alcohols are known nearly exclusively for the derivatives of alkaline and alkaline-earth metals (R= Me, Et, Bu, Ph) (see Tables 12.1 and 12.2). The alkoxides of more electronegative elements were reported to form solvates if the branched alcohols are involved (for example, for M = Sn, Ce, Zr, Hf, **$R = Pr^i$,** and for Pb, Bi, **$R = CBu^t_3$, $C_5H_{11}^{neo}$**). Of special interest is the structure of *bismuth ethoxide,* which turned out to be a solvate of **$[Bi(OEt)_3]_8 \cdot (7+x)EtOH$** composition, where a **$[Bi_8]$** crown is solvated by a high number of ethanol molecules, of which only 7 in the first solvation sphere could be located by the single crystal X-ray study [898].

The exact composition of the solvates was established in a number of cases by the study of solubility (melting) polytherms and desolvation vapor pressure polytherms in the systems $M(OR)_n - L$ (solvent) [1234, 1655], while the most accurate determinations could be achieved only using the X-ray single crystal method: for example, the exact composition of the solvate known as $Mg(OMe)_2 \cdot 4MeOH$, turned to be 1:3.5 [1524]. For the derivatives of transition metals, the low-temperature solubility studies have revealed the existence inthe $M(OR)_n$ — ROH systems of $Ti(OEt)_4 \cdot EtOH$ [1615]and $Ta(OMe)_5 \cdot MeOH$ [1639] monosolvates. They eliminate the solvating alcohol molecule peritectically at –10 and +21°C, respectively; the analogous transformation has also been observed for $LiOR \cdot 2ROH$ (Fig. 3.1). However, in the majority of cases the desolvation is accompanied by solvolysis and formation of oxoalkoxides. An illustrative example is provided by the decomposition of the isopropoxides (and, supposedly, isobutoxides) of quadrivalent metals, $[M(OPri)_4 \cdot {}^iPrOH]_2$, M = Sn, Ce, Zr, Hf forming $M_3O(OR)_{10}$ and $M_4O(OR)_{16}$, whose composition and structure have been determined by mass-spectrometry and X-ray techniques (see Fig. 4.2 *b*) [1497, 1612, 1803]. It can be supposed that the solvates of other homologues of these metals are less stable and transform to oxocomplexes already at room temperature (see Sections 12.9, 12.7, 12.12, and Tables 12.8, 12.10, 12.13). Among the derivatives of trivalent metals, the $[Nd(OPr^i)_3({}^iPrOH)]_4$ solvate decomposed in a vacuum at 20°C forming $Nd_6O_5(OPr^i)_8$ [1308] (see also Chapter 5).

Quite unexpected turned out to be the recently discovered molecular nature of the solvates of the most electropositive metals, such as $LiOMe \cdot 2MeOH$ [1521, 1643] (Fig. 4.6 *b*) and $Mg(OMe)_2 \cdot 3.5MeOH$ [1524] (the single molecules being connected by the hydrogen bonding). The polymer structures have been observed for the $[K(\mu\text{-}OBu^t)(\mu\text{-}{}^tBuOH)]_\infty$ [352] and also the adducts of phenoxides with phenols, water, alcohols, and crown-ethers [482, 548, 858, 974, 1483, 1720] (see Table 12.1).

The most numerous are their adducts with THF, PR_3, Py and other amines of 2,6- and 2,4,6-substituted phenols and also the derivatives of the most branched radicals Ditox, Tritox, CPh_3, $C_5H_{11}^{neo}$, $CMe_n(CF_3)_{3-n}$, and so on. These molecular compounds — monomers or dimers — have been described for almost all metals — Li, Na, Mg, Ca, Ba, Ga, Ln, Th, V(III), Cr (II and III), Mo(II-VI), Mn, Co, Fe, and Pt-metals.

8.2. Heterometallic complexes

Bimetallic alkoxides (“Meerwein salts”) have been known for more than 70 years, since the report made by Meerwein and Bersin [1101] on the formation of alkoxosalts (analogs of hydroxosalts $\mathbf{MM'_m(OH)_n}$) on titration of alcohol or benzene solutions of acidic alkoxides by those of basic ones to the equivalence points determined using the acid-base indicators:

$$\mathbf{NaOR + Al(OR)_3 = Na[Al(OR)_4]}$$

Subsequent studies by physicochemical methods — and initialy the structure studies — have shown that the majority of the derivatives of this class are molecular compounds, many of them being soluble in nonpolar solvents, volatile, their structures belonging to the same types as those of the homometallic ones described in Chapter 4.

As has been mentioned above, the special interest in these derivatives is connected with their application in the synthesis of the complex oxide materials (see Chapter 10 for details). The heterometallic alkoxides have been discussed in a number of reviews, the most complete of those (at different moments in time) being the corresponding chapter in the book by Bradley *et al.* [223] and articles of Mehrotra [1138] and also of Caulton and Hubert-Pfalzgraf [306].

The data on properties of the single compounds are presented in Chapter 12 in the tables by the more electronegative element but mentioned even in the tables describing the properties of derivatives of the other one (at the bottom).

The synthesis of bimetallic alkoxides can be achieved using the 2 routes first described by Meerwein and Bersin [1101]: complex formation of 2 alkoxides and the methathesis of a metal halide with an alkali metal alkoxide.

8.2.1. Complex formation of two alkoxides

$$\mathbf{M(OR)_n + pM'(OR)_m \rightarrow MM'_p(OR)_{mp+n}}$$

turns out definitely to be more effective if one of the reactants is an alkoxide of an alkaline or alkaline earth metal and the other one is an alkoxide of a multivalent metal (transition or main-group one). It is necessary, however, to take into account that the application of the aged forms of, for example, $Al(OMe)_3$ hinders its interaction with NaOMe [887].

A modification of this route is a simultaneous reaction of two metals with alcohol that can be considered as the *in situ* reaction of the alkoxides formed. Thus the interaction of Mg and Al with ethanol (leading to the formation of the perfectly soluble $MgAl_2(OEt)_8$) occurs very rapidly and does not need activation, in contrast with the reactions of individual metals with alcohol, leading to polymeric $Mg(OEt)_2$ and $Al(OEt)_3$ [1101, 887] (see Section 2.1). The preparation of the heterometallic derivatives has been achieved even via anodic oxidation of one metal in solution of the other (the complex solutions obtained have been used for the deposition of films in sol-gel technique) [1777].

Many examples have been described where the specific stability of one or both multivalent alkoxides hindered the complex formation. In all these cases the application of a corresponding oxocomplex instead of the alkoxide makes the reaction more facile. Thus, if the products of partial hydrolysis of the polymeric $Pb(OPr^i)_2$ or $Bi(OPr^i)_3$ were used instead of the homoleptic alkoxides in reaction with $Ti(OPr^i)_4$, the heterometallic products — $Pb_2Ti_2O(OPr^i)_{10}$ and $BiTi_2O(OPr)_9$ — could be obtained quite quickly and already at room temperature [447] (without a long period of refluxing) (see Chapter 5). The polymeric $Ba(OBu^n)_2$ reacts with $Ta(OBu^n)_5$ in alcohol only in the presence of the products of uncontrolled oxidation forming well-soluble bimetallic oxocomplexes, which permitted the preparation of butoxide solutions with different concentrations and broad variety of metal ratios [1562]. The isopropoxides of Zr, Hf, or Ta react with $Al(OPr^i)_3$ only on prolonged refluxing of solutions in alcohol accompanied supposedly by the appearance of the oxoalkoxide products [334, 1608]. It can be suggested that reactions of M^IOR or $M^{II}(OR)_2$ do not require preliminary activation because of the presence in the sample a small amount of oxogroups.

To determine the composition of bimetallic alkoxides formed via complex formation in solution and in the solid phase and to estimate their stability, we have applied physicochemical analysis — the investigation of the solubility isotherms in the systems $M(OR)_m - M'(OR)_n - L$ (solvent: alcohol, ether, hydrocarbon, *etc.*). This method, common for the studies of the interaction of inorganic salts in water solutions, turned out to be rather fruitful in the chemistry of alkoxides. It permitted the study of the interaction of the components in all the range of possible [M]:[M'] ratios and the composition of all complexes formed in solution and in the solid phase [1635]. Fig. 8.1 shows the examples of different kinds of interaction, represented graphically in the Gibbs-Roseboom triangle diagrams:

- In the **$NaOMe–Fe(OMe)_3–MeOH$** system no complex formation takes place, the polymeric **$Fe(OMe)_3•MeOH$** not being transferred into solution at any concentration of NaOMe, and its crystallization curve being situated therefore on the side of the triangle [1365] (Fig. 8.1 *a*).
- The polymeric **$Ba(OBu^n)_2$** is transferred into alcohol solutions of **$Ti(OBu^n)_4$** due to formation of the **$Ba[Ti_2(OBu^n)_9]_2$** complex (not discovered in the solid phase), and thus the line corresponding to crystallization of **$Ba(OBu^n)_2$** is situated along the section with the Ba:Ti = 1:4 ratio [1631] (Fig. 8.1 *b*).
- Both components — **$Bi(OEt)_3$** and **$WO(OEt)_4$** — are poorly soluble in alcohol, but dissolve due to formation of two complexes in solution having 3:2 and 1:1 metal ratios (not isolated in the solid phase): the lines corresponding to the crystallization of the components going along the corresponding transsections of the triangle [1638] (Fig. 8.1 *c*).
- In the following four systems the crystallization of the bimetallic complexes — **$NaAl(OMe)_4$, $Ba_3Al_2(OEt)_{12}$** and **$BaAl_2(OEt)_8$, $HfAl_2(OPr^i)_{10}$, $CaTi_4(OEt)_{18}$** — is observed (Fig. 8.1 *d–g*). The first of them exists in the excess of the alkaline alkoxide and undergoes solvolysis on the action of alcohol (in analogy with hydrolysis of sodium aluminate). The eutonic point (the one corresponding to the equilibrium of two solid phases and solution) is situated on the cross-section corresponding to the 1:1 ratio [887]. **$CaTi_4(OEt)_{18}$** crystallizes in the excess of **$Ti(OEt)_4$**, as the latter is much more acidic than **$Al(OEt)_3$** and the difference in acidity for the two components in this system is higher than for those in the previous one [1626]. And, finally, in the system formed by two acidic alkoxides — those of Hf and Al—the complex, **$HfAl_2(OPr^i)_{10}$**, can coexist with the solutions of both components and does not undergo solvolysis on action of alcohol [1608].

The results of investigation of more than 50 systems, in which there has been observed the formation of alkoxoaluminates, -titanates, -zirconates, -hafnates, -niobates, -tantalates, -molybdates, -tungstates, and -ferrates — permit-

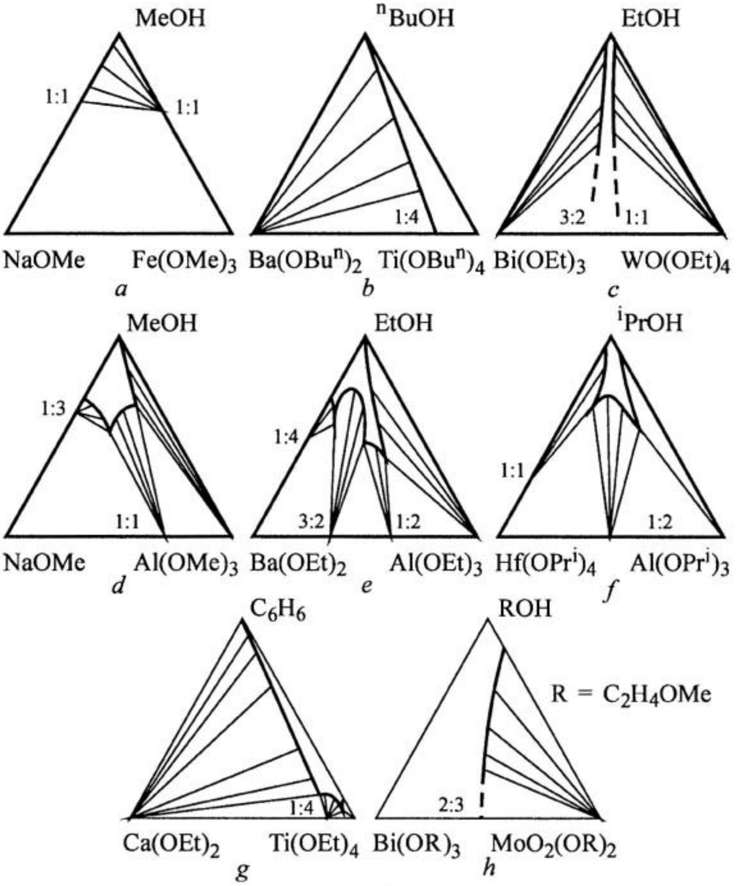


Fig. 8.1. Solubility isotherms in $M(OR)_n$ –$M'(OR)_m$–L systems at 20°C (wt %):
a **[1365];** ***b*** **[1631];** ***c*** **[1638];** ***d*** **[887];** ***e*** **[1629];**
f **[1608];** ***g*** **[1626];** ***h*** **[1638].**

ted the optimization of the conditions of their synthesis and the preparation of solutions to be used in sol-gel technique [1655].

There are many examples where the formation of stable heterometallic complexes can occur only via the formation of a M–O–M' bridge (oxocomplex), while the homoleptic nonoxo complexes cannot be isolated in the solid state. Thus the interaction of $Ba(OEt)_2$ and $M^V(OEt)_5$ (M^V = Nb, Ta) leads to $[BaM^VO(OEt)_5(EtOH)_{1.5}]_4$ formed apparently via oxidation of Ba ethoxide by the traces of oxygen in solvents (the corresponding isopropoxides forming under the same conditions quite stable $[BaM^V_2(OPr^i)_{12}({}^iPrOH)_2]$ [1522, 1562, 1621,1622]) (see also Section 12.16). A specific trend to decomposition in the presence of alkali alkoxides (via the ether elimination mechanism) has been observed for the derivatives of Mo and W. Thus, on the reaction of $MoO(OR)_4$ with NaOR (R = Et, Pr^i) in alcohol solutions, the $[NaMo_2O_4(OR)_5(ROH)]_2$ complexes (containing one O-ligand more per each molybdenum atom) have been isolated. The treatment of the solutions of these complexes with the excess of NaOR at room temperature leads to crystallization of Na_2MoO_4. The same reaction leads to the formation of the crystalline phases of Na_2WO_4, Bi_2MoO_6, and cubic solid solutions in the Bi_2O_3–WO_3 system (the solid-state synthesis of these compounds takes place only on prolonged heat treatment at over 700°C) [1638]. (Concerning the formation of heteroleptic bimetallic complexes accompanied by elimination of esters, see Section 7.1).

The stoichiometry and structure of the oxoalkoxometallates are often quite different from those of the compounds not containing oxoligands. That allowed them to be applied in the sol-gel technology of many important materials. The above mentioned oxoalkoxotantalates and niobates of 1:1 composition, in difference of the complexes of 1:2 composition free from oxygen ligands, can be used as precursors of $LiNb(Ta)O_3$-type phases, $BaTiO_n(OR)_{6-2n}$ complexes as precursors of $BaTiO_3$ (formed on reflux of the solutions containing $BaTi_4(OR)_{18}$), and so on.

From the solutions definitely containing oxocomplexes can, in certain cases (with often far not quantitative yields), be crystallized the bimetallic complexes not containing the oxoligands. The examples are provided by $HfAl_2(OPr^i)_{10}$ [1608], $Ba[Zr_2(OEt)_9]_2$ [1609], $LaM^V_2(OPr^i)_{10}$ (M = Nb, Ta) [334, 1622], possessing, supposedly, the minimal solubility among the components of solutions (including $M^{IV}_3O(OR)_{10}$ or $La_5O(OPr^i)_{13}$).

8.2.2. Methathesis reaction of a metal halide with an alkali metal alhoxide

$$MCl_n + n\,M^IM'(OR)_m \rightarrow MM'_n(OR)_{mn} + n\,M^ICl\downarrow$$

is usually applied in the cases, when one of the alkoxides is difficult to access (the halide being used instead). In principle, this is also an example of complex formation *in situ.* The other important aspect in application of this method is thus the inertness of one of the alkoxides to the complex formation. Thus the reaction of $Al(OPr^i)_3$ with rather stable $M_5O(OPr^i)_{13}$ (M= Sc, Y, Nd) is hindered[1308, 1309, 1607]. At the same time, according to Mehrotra *et al.* [223, 1118], the reaction

$$MCl_3 + 3KAl(OPr^i)_4 \rightarrow M[Al(OPr^i)_4]_3 + 3\,KCl$$

easily provides the alkoxoaluminates of the rare earth metals (volatile and well soluble in alcohol and benzene).

An important development of this method has recently been carried out by Mehrotra and Veith. The reaction with the excess of halide was found to provide bimetallic alkoxide halides. Their interaction with the alkoxometallate of the third metal provided access to trimetallic alkoxides:

$$\begin{tikzcd}
MHal_n + (n-1)NaM'(OR)_m \arrow[r] & HalMM'_{n-1}(OR)_{m(n-1)} + (n-1)NaHal\downarrow \arrow[d, "+\,NaM''(OR)_y"] \\
 & M_xM'_yM''_z(OR)_m
\end{tikzcd}$$

Among the large number of compounds of this class described [143, 501, 618, 1138, 1509], only a few have been unequivocally proved to exist and be characterized by the X-ray single-crystal method, among them $[CdM^{II}M^{IV}_2(OPr^i)_{12}]_2$, M^{II} = Ca, Sr, Ba, M^{IV} = Sn, Ti, Zr, Hf [1686, 1687, 1690, 1691], $LiMo_4Ta_3O_{14}(OPr^i)_9(OC_2H_4OMe)_3$ [847] and also $[NaPb_2Ti_2O(OPr^i)_{10}]^+Cl^-$ [782] (see also Section 12.16)

In addition to the synthetic routes to the bimetallic alkoxides described above, in some cases the redox reactions have been applied, such as:

$W(OPh)_6 + Li + PhOH + THF \longrightarrow LiW(OPh)_6(THF)_2$ [453]
$Ti(OC_6H_3Pr^i_2\text{-}2,6)_4 + Na/Hg + THF \longrightarrow NaTHF_2Ti(OC_6H_3Pr^i_2\text{-}2,6)_4$ [509].

Veith has also applied the transmetallation in the synthesis of t-butoxides of the Group III and IV metals:

$Tl(OBu^t)_3M^{IV} + InBr \rightarrow In(OBu^t)_3M^{IV}$ (M^{IV} = Ge, Pb) [1695].

A convenient approach to alkoxoaluminates is provided by the alcoholysis of the corresponding alumohydrides:

$$MAlH_4 + 4\,ROH \rightarrow MAl(OR)_4 + 2H_2$$

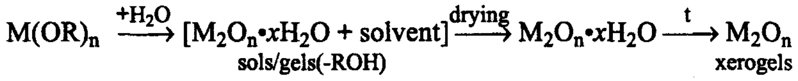
(this reaction has also been applied for the volumetric determination of the active hydrogen in alcohols) (Section 12.5).

Chapter 9

HYDROLYSIS OF METAL ALKOXIDES AND SYNTHESIS OF SIMPLE OXIDES BY THE SOL-GEL METHOD

Hydrolysis of metal alkoxides is the basis for the sol-gel method of preparation of oxide materials; therefore, reactions of metal alkoxides with water in various solvents, and primarily in alcohols, may be considered as their most important chemical properties. For many years the sol-gel method was mostly associated with hydrolysis of $Si(OR)_4$, discussed in numerous original papers and reviews [242, 1793, 243]. Hydrolysis of $M(OR)_n$, in contrast to hydrolysis of $Si(OR)_4$, is an extremely quick process; therefore, the main concepts well developed for $Si(OR)_4$ cannot be applied to hydrolysis of alcoholic derivatives of metals. Moreover, it proved impossible to apply classical kinetic approaches successfully used for the hydrolysis of $Si(OR)_4$ to the study of the hydrolysis of metal alkoxides. A higher coordination number of metals in their alcoholic derivatives in comparison with $Si(OR)_4$ leads to the high tendency to oligomerization of metal alkoxides in their solutions prior to hydrolysis step as well as to the continuation of this process of oligomerization and polymerization after first steps of substitution of alkoxide groups by hydroxides in the course of their reactions with water molecules. This results in extremely complicated oligomeric and polymeric structures of the metal alkoxides hydrolysis products.

The process of formation of oxide from metal alkoxide can be presented by the following scheme:

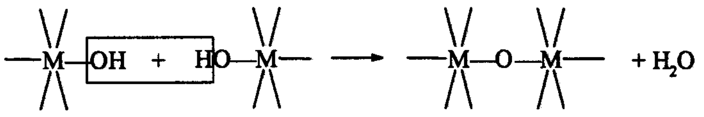


$$\mathrm{M(OR)_n} \xrightarrow{+\mathrm{H_2O}} \underset{\text{sols/gels(-ROH)}}{[\mathrm{M_2O_n{\cdot}xH_2O} + \text{solvent}]} \xrightarrow{\text{drying}} \mathrm{M_2O_n{\cdot}xH_2O} \xrightarrow{t} \underset{\text{xerogels}}{\mathrm{M_2O_n}}$$

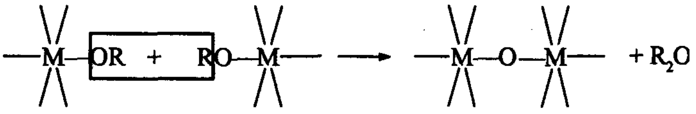
As a rule amorphous hydrated products containing alkoxide groups are formed on the first stage (so called xerogels); their drying and thermal treatment leads to crystalline products. It is now a well established that the main properties of oxide materials are to a considerable extent determined by reactions taking place during the first steps of the hydrolysis process. Molecular structure and complexity of metal alkoxide in solution as well as the tendency to form oxoalkoxocomplexes play important roles in the character of the future hydrolysis product The structural peculiarities of monometallic and heterometallic oxocomplexes have been discussed earlier in Chapters 4 and 5. Oxo-bridges in the molecules of oxoalkoxide complexes probably are the centers of formation of future crystalline structures of metal oxides. Formation of the M–O–M' group in the case of heterometallic precursors ensures chemical homogeneity on molecular level of complex oxide phase formed in the course of metal alkoxide hydrolysis.

Although different classes of chemical compounds are used as precursors in the sol-gel method, metal alkoxides or modified metal alkoxides (with partial substitution of alkoxide groups by other organic ligands) are by far the ones used most frequently. The stability of colloids obtained during hydrolysis of metal alkoxide solutions is usually much higher than that prepared from aqueous solutions of inorganic salts (due to the absence of destabilizing anions).

Formation of M–O–M' bonds in the hydrolysis products may proceed in two different ways. The first way is the typical process of aging of hydrated oxides; their central metal atoms are coordinated by hydroxo-, oxo-, and aqua-groups. Dehydration of such product results in irregular amorphous oxide structures, such as

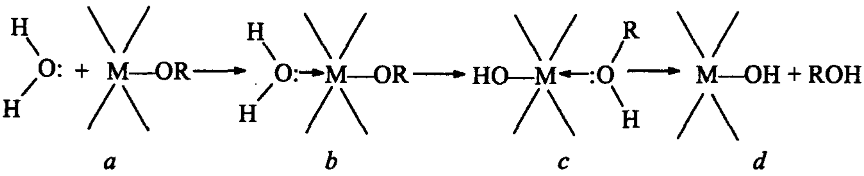


The second way is characteristic only of metal alkoxides and involves the elimination of ethers:



The presence of water most probably catalyzes this reaction, which is especially accelerated by refluxing of the reaction mixture. As a result, crystalline phases are formed at very low temperatures (in comparison with the conditions of dehydration and crystallization of usual gels).

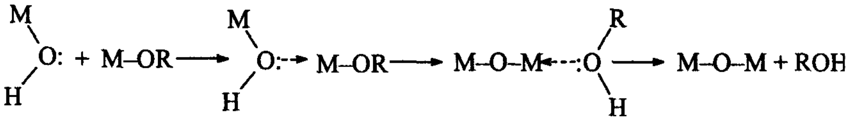
The main principles of metal alkoxide hydrolysis were formulated by Livage in his reviews [1020]. On the addition of water or a water-alcohol mixture to the solutions of alkoxides in organic solvents, nucleophillic attack of H_2O molecule at the positively charged metal atom occurs (a), which leads to an intermediate state (b):



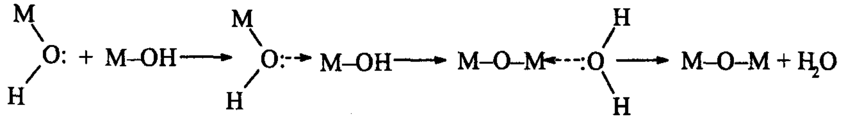
The shift of the proton from water molecule to the negatively charged oxygen atom of the neighboring OR-group results in the intermediate state (c) followed by elimination of alcohol molecule. Thus, the whole process follows the mechanism of nucleophillic substitution. The thermodynamics of the reaction is determined by the nucleophilicity of the attacking group and the electrophilicity of the metal atom [$\delta(O) \ll 0$ and $\delta(M) \gg 0$]. The rate of the substitution process depends on the coordination insaturation of the metal atom in the metal alkoxide $N - z$ (N is the maximum coordination number of the metal atom of the oxide, z is the oxidation state of the metal atom), and the possibility of the proton transfer within the transition state (b). The higher the $N - z$ value, the lower the activation energy of the nucleophillic attack.

Immediately after hydroxide groups are introduced into the coordination sphere of the metal atom, condensation occurs that may proceed in one of three possible ways:

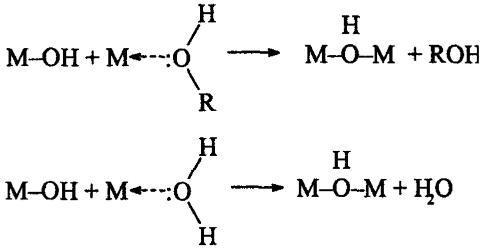
- Alkoxolation with elimination of alcohol:



- Oxolation with elimination of water molecule:



- Olation with elimination of solvent molecule (alcohol or water):



It has been traditionally assumed that condensation is a much slower reaction than substitution of the alkoxide group by the hydroxide; however, quite recently it was shown that the rates of these processes are actually very close. Kinetic study of hydrolysis of titanium and zirconium alkoxides by means of a quick mixing technique with FTIR, SAXS, and conductivity measurements monitoring has shown that hydrolysis is a very quick reaction followed by condensation, which is also a very fast process and occurs after from 25 to 50% of alkoxide groups are substituted by hydroxides (under the experiment conditions this occurs in 80 milliseconds after the beginning of mixing of the reagents) [709].

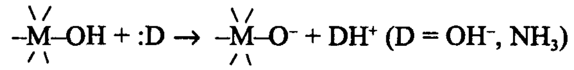
Study of hydrolysis and condensation of $Ti(OBu^n)_4$ by means of ^{17}O NMR spectroscopy has also shown that formation of oxobridges occurs immediately after addition of water, which indicates the extremely high rates of both reactions; these rates are comparable even in the presence of such reaction inhibitors as acids and complexation ligands [158].

Rate of hydrolysis depends primarily on the size and structure of the alkoxide group, — for example, it decreases in the series titanium butoxide tertiary >

secondary > normal [1755]. The nature of the OR- group also affects the condensation process, — for example, on hydrolysis of $Ti(OR)_4$, precipitates are formed very quickly in case of $R = Et, Pr^i$, wheras in the case of $R = Bu^n, Am^n$ precipitation takes much longer.

The rates of hydrolysis and condensation reactions may be regulated by pH of water used for hydrolysis (by addition of acids —HCl, HNO_3 or alkali — NH_3, NaOH) [1020]. The role of acid catalysis lies in the quick protonation of the negatively charged OR groups by H_3O^+ groups; therefore, proton transfer and elimination of the ROH molecule do not limit the hydrolysis rate; this theoretically allows the substitution of all OR-groups. Nevertheless, OH-groups are mostly formed at the ends of the chains, which results in the formation of linear polymers. In the strongly acidic medium $([H^+] \sim [Ti])$ condensation process is considerably slowed down; protonation of hydroxide groups becomes possible and results in the formation of hydrated hydroxocomplexes.

In the course of the basic catalysis, activation of condensation process occurs via formation of highly nucleophillic fragments such as $M{-}O^-$:



$$-\overset{\backslash\,/}{\underset{/\,\backslash}{M}}-OH + :D \rightarrow -\overset{\backslash\,/}{\underset{/\,\backslash}{M}}-O^- + DH^+ \quad (D = OH^-, NH_3)$$

This reactive precursor attacks the positively charged metal atom; as a result of this process dense compact polymer species are formed.

Condensation of metal alkoxides occurring as a result of uncontrolled hydrolysis greatly influences further hydrolysis; therefore, the properties of the products are highly dependent on the content of residual water in the anhydrous solvents used for the preparation of metal alkoxide solutions, as well as on the time and conditions of storage of the solutions prior to hydrolysis. This fact was demonstrated by the study of hydrolysis of $Zr(OR)_4$, which are especially sensitive to water [1015].

Nevertheless, the main parameter that affects the course of hydrolysis reaction is the molar ratio of reactants (i.e., the water to metal alkoxide ratio $h = [H_2O]:[M(OR)_n]$). This h value determines the composition and the properties of the hydroxides and oxides formed on hydrolysis and thus allows them to be obtained in different forms of powders, films, glasses, and fibers.

In the rest of this chapter we focus on the peculiarities of hydrolysis process for different groups of metal alkoxides.

9.1. Alkoxides of the metals of Groups I and II

Few data are available on the hydrolysis of simple metal alkoxides of these elements. Alkoxides of alkaline and alkaline earth metals are mostly used as precursors for the preparation of complex oxides or solid oxide solutions. Commercial production of pure magnesium oxide by hydrolysis of $Mg(OMe)_2$ with formation of transparent gel has been described [715], as well as hydrolysis of $Mg(OC_5H_{11}{}^i)_2$ with the following thermal treatment to produce a fine MgO powder that sinters at low temperatures [1766]. Solutions prepared by dissolving magnesium in methoxyethanol are by far the most convenient precursors for preparation of magnesium oxide films.

$Zn(OR)_2$ are hard to produce, and in reality they are not used for preparation of oxides. On the other hand, highly soluble $[RZnOR']_4$ can be easily prepared by alcoholysis of ZnR_2, and therefore they are the main precursors for the preparation of ZnO powders for sintering of varistor ceramics [725]. Hydrolysis of $EtZnOBu^t$ in toluene followed by drying of the precipitate under vacuum at 90 to 110°C results in the crystallization of zincite. On hydrolysis porous species of the amorphous powder of regular spherical shape with the size of about 0.2 μm are obtained. These species are indeed comprised of fine crystallites (150Å), which explains the very high specific surface area of the powder ($30\ m^2/g$). Washing of the powder with water drastically changes its morphology (pseudohydrothermal recrystallization), the species acquire bipyramidal shape, their size increases approximately four times, and the surface area decreases down to $10\ m^2/g$, which considerably improves their sintering properties.

9.2. Aluminum alkoxides

First investigations of hydrolysis of aluminum alkoxides were performed in the 1950s and 1960s [1252, 285]. Stolarek [1536] studied hydrolysis reactions with the aim of the preparation of aluminum oxide as a carrier for catalysts.

The investigations on the preparation and properties of alkoxy-derived sols and gels of Al_2O_3 performed by Yoldas [1793], along with the numerous works on hydrolysis of $Si(OR)_4$, laid the foundation of the sol-gel method as the technique employing the process of continuous transformation from colloid (sol) to gel. The structures of sols and gels prepared in accordance with the procedures described by Yoldas were in detail characterized by means of NMR, Raman, and IR spectroscopy [243]. $Al(OR)_3$, $R = Pr^i, Bu^n, Bu^s$ are normally used as precursors. Hydrolysis in an acidic medium at 20°C results in stable sols with mixed octahedral and tetrahedral coordination of aluminum atoms. Decrease of acidity results in amorphous hydroxide precipitate with considerable content of residual alkoxides. Hydrolysis at 80°C leads to sols with octahedral coordination of all Al atoms. In a neutral medium, precipitate of δ-$AlO(OH)$ (boehmite) is formed. This precipitate is easily peptized by the addition of small amounts of acid, which cannot be achieved on heating to 80°C of precipitate obtained by hydrolysis with cold water. Gradually, sols are transferred into continuous transparent gels, which, however, shrink on elimination of solvent to give porous nontransparent bodies. [327]. Dried gels are in chemical composition very close to $AlO(OH)$, which is in agreement with the data of FTIR analysis [327]. The structure of gels, size, and morphology of pores is determined by the amount of the introduced acid. About 60% of the volume of porous bodies is occupied by pores; their very small size (2 to 8 nm), however, ensures preservation of their transparency. Thermal treatment of dry gel results at first in the formation of-Al_2O_3; further temperature increase up to 1200°C gives crystalline α-Al_2O_3. Despite shrinkage the material does not crack due to uniform volume crystallization. In the course of thermal treatment, however, it looses transparency. Despite numerous hydrolysis techniques varying quite considerably in hydrolysis conditions, the sequence of phase formation in all of the cases can be summarized by the following scheme [1400, 512]:

$$Al(OR)_3 + H_2O \xrightarrow{<100^\circ C} \delta\text{-}AlO(OH) \xrightarrow{350^\circ C} \gamma\text{-}Al_2O_3 \xrightarrow{950^\circ C} \delta\text{-}Al_2O_3 \xrightarrow{>1200^\circ C} \alpha\text{-}Al_2O_3$$

Aluminum oxide sols are successfully used for application of films [1794, 1793], such as high area films for hybrid circuits [1236]. The same technique was used for the preparation of β-Al_2O_3 ($NaAl_{11}O_{17}$); in this case alcoholic solutions of NaOR were added to aluminum alkoxide solutions [1795, 1038]. To increase the stability of sols, aluminum alkoxides are frequently modified with acetic acid [1570] or **β-diketones** [1659]. Alumina sheets are commercially produced by the sintering of high-purity fine Al_2O_3 powders prepared by hydrolysis of modified $Al(OPr^i)_3$ [1236]. To prepare powders with spherical species from dilute solutions, hydroxopropylcellulose was added to prevent agglomeration [1555]; an alternative option is to perform hydrolysis in hydrophobic solvents, such as in the mixture of n-octanol with acetonitrile [1164]. These sols were used for preparation of ultrafiltration layer (with the pore size of 4 to 100 nm) of the inorganic ceramic membranes for filtration of liquids and gases [1801, 993].

9.3. Alkoxides of rare earth elements

Hydrolysis of $Y(OR)_3$ solutions was used mostly together with hydrolysis of $Zr(OR)_4$ or $Al(OR)_3$ for the preparation of powders and further sintering of stabilized ZrO_2 (solid solution ZrO_2-Y_2O_3) or Al_2O_3–Y_2O_3 (see Chapter 10) ceramics. On hydrolysis of "$M(OPr^i)_3$", M=Y, La, Ce with further crystallization at 500°C submicron M_2O_3 powders were obtained [1541, 878]. The authors suggest a diffusion-limited particle-growth mechanism. Hydrolysis study of the modified cerium isopropoxide $Ce(OPr^i)_{4-x}(acac)_x$ ($0.15 < x < 1.0$) by means of IR, EXAFS, SAXS has demonstrated that the properties of the hydrolysis products are controlled by the value of x: precipitation occurs for $x < 0.15$; for $0.15 \leq x < 1$ the sols that undergo transformation into gels with time are formed (gels are formed even at very low temperatures); in the case of $1 \leq x \leq 2$ stable micellar sols based on oligomeric molecules are obtained [1351].

9.4. Germanium, tin, lead alkoxides

Voigt [1705] prepared transparent GeO_2 glasses on hydrolysis of $Ge(OEt)_4$; the temperature of glass formation is about 100°C lower in comparison with that used in conventional methods. On crystallization of amorphous oxide prepared on hydrolysis of $Ge(OPr^i)_4$, a mixture of two phases, crystoballite and α-quartz, is formed. On further thermal treatment, phase transition of crystoballite to **α-quartz** occurs, while grinding in air results in the transition to a rutile-type structure; on treatment at temperatures higher than 1050°C all phases are tranferredto **α-quartz** [1766].

Although hydrolysis of tin alkoxides and alkoxochlorides, especially in the mixture with indium alkoxides, is used extensively, such as for preparation of conductive ITO (solid solution of indium and tin oxides) layers, only few fundamental works on hydrolysis of $Sn(OR)_4$ are known, and they have been summarized in a comprehensive review [702]. Bradley proved the formation of oligomeric molecules as first hydrolysis products of $[Sn(OPr^i)_4{}^iPrOH]_2$ by ebulioscopy measurements. Further hydrolysis of tin isopropoxide as well as $Sn(OBu^t)_4$ and $Sn(OEt)_4$ results in the formation of crystalline SnO_2, even without additional thermal treatment; calcination at 400°C increases the crystallinity of the product. Spherical SnO_2 species 250 ran in size consist of irregular grains 20 to 30Å in diameter. Hydrolysis of $Sn(OBu^t)_4$ was used for preparation of gels [641] and high-quality conductive SnO_2 films [662, 1601].

Looking for convenient precursors for lead containing perovskites, Teff and Caulton [1565] isolated in the course of hydrolysis of $Pb(OR)_2$ at h = 0.5 and 1.33 two series of oxoalkoxides, $Pb_4O(OR)_6$ and $Pb_6O_4(OR)_4$, $R = Pr^i, Bu^t$ with tetrahedral and octahedral "cluster" molecules respectively; these oxoalkoxides enter reactions with $Zr(OR)_4$ to form bimetallic oxoalkoxides [1563]. Hydrolysis of the solution of $Pb(OC_5H_{11}^t)_2$ in THF (synthesized by alcoholysis of $Pb[N(SiMe_3)_2]_2$) at room temperature results in the crystalline hydroxide $3PbO{\bullet}H_2O$ ($=Pb_6O_4(OH)_4$ — structural analogue of oxoalkoxide). Increasing the hydrolysis temperature up to 66°C leads to 2 crystalline modifications of PbO, tetragonal, litharge, and rhombohedral, massicot. Prolonged refluxing of the reaction mixture increases the yield of massicot, which is thermodynamically more stable [649]. In the earlier studies of hydrolysis of $Pb(OPr^i)_2$ in ^iPrOH solution, formation of litharge and massicot was also registered at very low temperature; however, massicot was reported to be the main product. This difference may be due to the presence of considerable amounts of sodium in the initial solution in the latter case, as precursors for hydrolysis were prepared by the exchange reaction of $Pb(OAc)_2$ and $NaOPr^i$ without isolation of individual $Pb(OPr^i)_2$ [1767, 1197]. In general, the presence of traces of sodium in $Pb(OR)_2$ becomes a very serious obstacle for the application of lead alkoxides as precursors for ferroelectric films.

9.5. Titanium and zirconium alkoxides

$Ti(OR)_4$ and $Zr(OR)_4$ are the most thoroughly studied alkoxides from the point of view of their hydrolytic decomposition. Depending on the hydrolysis technique, different products such as films, fibers, glasses, and powders of TiO_2 and ZrO_2 may be obtained, numerous preparation techniques are described in dozens of patents. On the other hand the physico-chemical aspect of hydrolysis received considerably less attention.

In the course of calorimetry study of hydrolysis of $\mathbf{Ti(OR)_4}$, at different concentrations and h ratios the values of enthalpies of hydrolysis reaction were measured: $(-\Delta H_h)$ at 298.15K as 14.2, 64.9, 19.3 kJ/mol for R = Et, $\mathbf{Pr^i}$, $\mathbf{Bu^n}$ respectively [660]. These values grow linearly at the first stage when h increases from 0 to 1 and practically do not undergo any changes with further introduction of water. Therefore, the first step of hydrolysis should be regarded as reaction with stoichiometry of h = 1:

$$\mathrm{Ti(OR)_4 + H_2O = Ti(OR)_3(OH) + ROH,}$$

This step is immediately followed by condensation:

$$n\mathrm{Ti(OR)_3(OH)} \rightarrow \mathrm{Ti}_n\mathrm{O}_x\mathrm{(OR)}_{4n-2x}.$$

Further hydrolysis proceeds much slower with very small heat evolution (for R = Et and $\mathbf{Bu^n}$ its value is zero within the accuracy of the experiment , while for $\mathbf{R = Pr^i}$ it does not exceed 20% of the overall reaction heat). Composition of the hydrolysis products for all h values approximately corresponds to $\mathbf{TiO_{1.5}(OR){\cdot}\mathit{y}ROH}$, where y = 0.15–1 depending on the nature of alcohol and concentration of alkoxide. Solvating alcohol in the hydrolysis products was confirmed by chemical analysis and IR spectroscopy of the products of their thermal decomposition. Residual carbon on thermal treatment in air is eliminated in two steps — at 300°C with formation of amorphous black powder and then in the process of crystallization at 400 to 500°C. A mixture of anatase and rutile is usually thus formed, calcination at higher temperature gives pure rutile.

The formation of metal oxoalkoxides in the course of hydrolysis of Ti and Zr alkoxides was first described by Bradley [214, 203]. Later Day and Klemperer performed structural and NMR-spectroscopy studies of the multinuclear titanium oxoalkoxides in crystalline form and in solutions (see Chapter 5). Crystalline oxoalkoxides of varying complexity, ranging from 7-nuclear $\mathbf{[Ti_7O_4](OEt)_{20}}$ to $\mathbf{[Ti_{12}O_{16}](OPr^i)_{16}}$ containing 12 Ti atoms, were isolated on controlled hydrolysis of titanium ethoxide and isopropoxide [1651, 457]. Boyd and Whiter reported the formation of polytitanoxane complexes in the course of hydrolysis of $\mathbf{Ti(OBu^n)_4}$ [1755, 185]. It has been shown that average complexity of the hydrolysis products depends on the reagents ratio. At $\mathbf{h \leq 1}$ the products are linear polymers, and their composition may be evaluated from the following equation:

$$n\mathrm{Ti(OBu)_4} + (n-1)\mathrm{H_2O} \longrightarrow \mathrm{(RO)}_{2(n+1)}\mathrm{Ti}_n\mathrm{O}_{n-1} + 2(n-1)\mathrm{H_2O}$$

The last alkoxide group cannot be eliminated even at h = 4. Excess of water results in the cross-linked polymers either in the form of gels or precipitates, the average complexity and molecular weight are mostly affected by the h value.

In 1986 Yoldas performed one of the first detailed studies of the morphology of $Ti(OR)_4$ and $Zr(OR)_4$ hydrolysis products as a function of their thermal treatment, metal alkoxides concentrations in solutions, h ratio, and pH or acid content in the hydrolysis agent. [1793]. The range of concentrations where fibers could be drawn in the system $Ti(OPr^i)_4–H_2O–EtOH–HCl$ was determined by Kamiya [872].

The SAXS study of the influence of mineral acids on the growth of titanium oxoalkoxopolymers in the course of hydrolysis of $Ti(OR)_4$ ($R=Pr^i$, Bu^n) has demonstrated that the structure of the polymers changes gradually from open network to dense gels [869]. Densification occurs as a result of the 2-step process: large polymer molecules formed at the first step absorb free monomers. At high acid concentration, growth of polymer chains occurs as a result of recombination of the fragments close in size, densification takes place only by the end of the process and leads to gel formation. On the other hand, at low acid concentrations only a few of monomers undergo condensation; after that, oxopolymers densify very quickly, resulting in gradual precipitation.

Raman spectroscopy and SAXS studies of structural changes, which occur in the course of hydrolysis of "$Zr(OPr^n)_4$" in solutions in ^iPrOH, indicate the instant hydrolysis, while formation of gels is a result of gradual aggregation of primary clusters formed on mixing of the components. Their drying leads to xerogels, amorphous hydrated oxides that on thermal treatment at 400°C for 2 hours give tetragonal ZrO_2. Only on further thermal treatment at 1000°C for 2 hours is the monoclinic ZrO_2 crystallized, even though it represents the thermodynamically stable phase at room temperature [81]. Calcination in nitrogen hinders considerably the phase transition from tetrahedral to monoclinic [1250].

Acetic acid is also used as an acidic catalyst, which increases gelation time and leads to transparent homogeneous gels. This effect can be explained by partial substitution of OR- by OAc- groups chelating metal atoms [1391]. In the course of hydrolysis, the OAc-groups remain bonded to titanium atom and consequently hinder formation of gels. Interaction of "$Zr(OPr^n)_4$" with acetic acid liberates ^nPrOH, which enters esterification reaction with acetic acid and water thus formed hydrolyzes metal alkoxide. This allowed Larbot *et al* to use gas chromatography of the evaluated ^nPrOH as an efficient tool to study the hydrolysis process [993]. Introduction of acetic groups considerably decreases the tendency of "$Zr(OPr^n)_4$" to hydrolysis: the polymer product that contains alkoxide and acetic groups is stable even to excess of water. As a result of this reaction, transparent gel is formed; however, acetic groups can be eliminated only in the course of thermal treatment at 200°C [33].

Acetylacetone and other β-diketones are much stronger chelating agents. In this case precipitation does not occur even with a big excess of water, as chelating ligands cannot be completely eliminated. Blanchard and Sanchez used complex formation to slow down condensation in the course of $Ti(OBu^n)_4$ hydrolysis [158]. Transparent monolithic ZrO_2 gel was obtained by controlled hydrolysis of "$Zr(OPr^n)_4$" in the presence of acetylacetone [468]. After drying at 40°C, amorphous microcrystalline monolith is obtained with the pores < 1.5 nm. Stable acidic sols, prepared on hydrolysis of zirconium alkoxides modified by acetylacetone, contained linear polymers [458] and were used for the preparation of fibers about 165 cm long with the diameter of 3 to 30 μm. The sequence of phase formation in the course of thermal treatment of the fibers is the same as in the course of thermal treatment of gels: at first at 500°C metastable tetragonal phase is formed, which at 1000°C undergoes transfer to monoclinic ZrO_2.

For many years it has been discussed in the literature if hydrolysis of metal alkoxides can be used as a convenient way for the preparation of ideal nanopowders (powders with spherical submicron species 0.1 to 1.0 μm in size), which can find numerous applications (e.g., for sintering of ceramics of special applications). Different techniques are described in dozens of patents. Among fundamental works in this direction, studies of Barringer and Bowen aimed at the synthesis of TiO_2 on hydrolysis of $Ti(OEt)_4$ are of special interest [110, 557]. The required condition for the synthesis of ideal powders by the sol-gel method is the homogeneous nucleation — complete mixing of the components ($M(OR)_n$ solution and water) prior to the beginning of precipitation. Therefore, special attention should be paid to the conditions for solutions preparation, storage, and filtration in the inert atmosphere to avoid uncontrolled hydrolysis, which leads to the formation of heterogeneous nucleation centers. To achieve complete mixing prior to precipitation, the authors used dilute metal alkoxide and water solutions in ethanol (0.1 to 0.2 M) and (0.3 to 1.5 M) at $h \geq 3$. Mean particle diameter was about 0.3 to 0.6 μm, and increases with the decrease of water and alkoxide concentration, the species are quite uniform in size ($r_{max}/r_{min}<3$, $r_{max}/r_{mean}<2$). According to the authors, these are the most uniform species ever reported in the literature. As mixing of dilute solutions under the static conditions is a very inefficient and time-consuming technique a few variations of dynamic hydrolysis have been suggested [1357, 1674, 1227]; these methods are also used for the kinetic studies of hydrolysis reactions.

Assuming that the formation of uniform fine TiO_2 powders in the course of $Ti(OEt)_4$ hydrolysis occurs in accordance with the LaMer homogeneous nucleation mechanism [987], many authors following Barringer and Bowen considered time after mixing of the components before precipitation (induction time) as a qualitative measure of the rate of hydrolysis reaction [840, 659, 712, 1357]. Having applied this approach to the study of hydrolysis of "$Zr(OPr^n)_4$" in EtOH and in ^nPrOH, Smit [1503] and Bartlett *et al.* [113] have proven that hydrolysis occurs with the substitution of only three alkoxide groups:

$$Zr(OR)_4 + 3H_2O \longrightarrow Zr(OR)(OH)_3 + 3ROH$$

thus supporting the mechanism suggested by Smit for hydrolysis of $Zr(OPr^n)_4$ in PrOH [1503].

The mechanism of particle growth in the course of hydrolysis and condensation of Ti, Zr, and Ta alkoxides has been frequently discussed. Nevertheless, the discussion so far remains open. Ring suggested a diffusion-limited model for growth of particles [484, 1357]; other authors, however, assume a growth mechanism limited by reaction on the surface of the growing species [1228, 708, 477].

Species prepared by hydrolysis of $Ti(OEt)_4$ in accordance with the technique suggested by Barringer and Bowen were studied by Edelson and Gleiser [517] by means of high-resolution electron microscopy; the latter studied also sintering ability of the powders. They paid attention to the drastic discrepancy between the specific area (310 to 350 m^2/g) and the mean particle size (0.35 μm) of the species. High-resolution electron microscopy proved that the species, earlier observed by Barringer, indeed consisted of minute fragments 6 to 10 nm in size; this result is in agreement with the specific area measurements. It is therefore no surprise that the volume shrinkage of the powders during sintering in the temperature range from room to 1200°C amounted to 87%. According to the authors, approximately half of this value is due to the densification of the internal structure of the agglomerates, which occurs in the temperature range of 425 to 600°C. Porosity of the particles hinders their sintering ability: sintering of dense species 0.35 μm in size should have occurred at far lower temperatures.

The SAXS study of the $Ti(OBu^n)_4$ hydrolysis product has demonstrated it to be a multilevel system, its primary structural element being an oligomeric molecule of titanium oxobutoxide with the size of 1.6 nm [659, 1247]. Components concentration and ratio determine the character of further condensation of these species and may result in various morphological forms of the final hydrolysis product: uniform dense particles are precipitated from dilute solutions; hydrolysis of concentrated solutions at high h results in polydisperse precipitates with open porosity and high surface area. Gradual densification of the precipitate occurs with time due to filling of the volume with the condensation products. By analogy with the well-known structures of metal oxoalkoxides in crystals, and on the basis of the data of chemical analysis, it has been suggested that the molecule of primary hydrolysis product consists of 6 hexa- and 6 penta-coordinated titanium atoms, supported by 12 μ_3-O and 6 μ-O bridges.and bonded to 12 terminal OR-groups.. Refinement of the structure of the primary hydrolysis species was performed by HyperChem® (version 5.01), Hypercube, Inc. The mean diameter of the calculated structure of the primary particle is 1.6 nm, which corresponds to the value determined from the SAXS experiment.

Uniform submicron particles cannot be obtained by hydrolysis of concentrated $Ti(OR)_4$ solutions, as the increase of concentration results in agglomeration of the hydrolysis product, these agglomerates cannot be redispersed. Agglomeration is a result of the sticking together of the particles in the course of Brown movement, which can be overcome electrostatically (it assumes introduction in the solution of electrolyte ions) or sterically by introduction of surface active components, which should be able to diffuse from solution and bind with the surface of the particle by physical adsorption. To prevent agglomeration, Ring suggested adding hydroxopropylcellulose (HPC) to the $Ti(OEt)_4$ solution prior to hydrolysis in concentrations of about 10^{-3} to 10^{-4} g/cm^3 [840, 1076, 328]. This approach proved very fruitful, and was subsequently used in different hydrolysis techniques to prevent agglomeration, which was described in numerous patents. It was also suggested that organic acids be used with not less than 6 carbon atoms in the molecule as agglomeration preventing agents [1026]. Acids probably act as both electrostatic and steric stabilizers.

Hydrolysis of $Ti(OPr^i)_4$ does not allow the obtaining of "ideal" TiO_2 powders [1394]. In contrast to oligomeric titanium ethoxide and butoxide, titanium isopropoxide is a monomeric molecule; condensation of its hydrolysis product occurs very quickly and results in quick nonuniform particle growth; and minute particles quickly agglomerate into polydisperse species.

Hydrolysis of $Zr(OR)_4$ results in considerably denser particles, in comparison with the $Ti(OEt)_4$ hydrolysis products. Having studied hydrolysis in different alcohols Kotova *et al.* [944] demonstrated that well-shaped regular particles precipitate only at the first step from diluted solutions in ethyl alcohol at moderate h values. Hydrolysis of solutions containing both titanium and zirconium alkoxides leads to the species homogeneous in chemical composition, and the metal ratio in the precipitated species corresponds to that in the starting solution [708, 659]. This is a fairly unexpected result, in particularly taking into account quite different hydrolysis rates of titanium and zirconium alkoxides; it is also noteworthy that no chemical complexes between the alkoxides of the two elements were registered, although the attempts to synthesize such compounds were indeed made [945]. It further turned out that even a very small addition of zirconium alkoxide to $Ti(OBu^n)_4$ solutions in ^nBuOH results in drastic densification of the particles.

Therefore, the review of the studies of hydrolysis of Ti and Zr alkoxides indicates that "ideal" oxide powders can be obtained only when very dilute solutions are used, at low h values with homogeneous mixing of solutions before precipitation, which indeed means that nucleation of solid precipitate should occur from homogeneous solution and high yields could never be achieved. The size of the particles can be regulated by pH of water used for hydrolysis, modification of alkoxides by introduction of RCOO or acac- groups, and addition of hydroxopropylcellulose. Despite a series of publications discussing the growth mechanism, it still remains obscure. Even hydrolysis with excess of water results in amorphous precipitate containing residual alkoxide groups. The regular species observed by electron microscopy demonstrate porosity that is very high in the case of hydrolysis products of titanium alkoxides and far less pronounced in the case of hydrolysis of zirconium alkoxides. An interesting peculiarity of these hydrolysis products lies in the preservation of their morphology on thermal treatment with crystallization of corresponding oxides.

9.6. Bismuth alkoxides

The interest in bismuth alkoxides emerged only in the last decade, mostly in connection with high-temperature superconductivity and layered perovskites, especially for thin films applications. Phase composition of Bi_2O_3, formed on hydrolysis of $Bi(OR)_3$, depends on the nature of alkoxide radicals and solvents and the h ratio. Thus refluxing of sols obtained on reaction of $Bi(OC_2H_4OMe)_3$ in methoxyethanol with excess of water gives crystalline β-Bi_2O_3. Hydrolysis of the same bismuth alkoxide in THF resulted in amorphous powders [1074.]. Crystallization of δ-Bi_2O_3 from amorphous powder precipitated on hydrolysis of $Bi(OBu^t)_3$ solution in THF occurs only after prolonged thermal treatment at 550°C[1069]. When $Bi(OEt)_3$ is used as the precursor, α-Bi_2O_3 is always formed as hydrolysis product. If hydrolysis of solution in benzene is performed by excess of water, the crystalline phase is formed immediately in the course of hydrolysis. Precipitates obtained from ethanol or methoxyethanol are amorphous and crystallize after subsequent refluxing with water or thermal treatment at 450°C. The extent of crystallinity of the products isolated from EtOH is always higher than that of the products isolated from $MeOC_2H_4OH$. Crystallization, probably simultaneously, follows two patterns: “aging” of the precipitate of hydrated oxide and elimination of R_2O. The second pattern results in formation of crystalline precipitate with a high extent of structural perfection already in the course of hydrolysis in benzene. There is a lot of speculations in the literature concerning elimination of ether in the course of hydrolysis of metal alkoxides, and many indirect observations supported this assumption; however, the above described reaction is its first direct experimental proof [1610].

9.7. Vanadium alkoxides

Hydrolysis of vanadium alkoxides has attracted the attention of scientists for several decades. Back in 1913 Prandtl and Hess [1313], who suggested using hydrolysis for the preparation of vanadium acid sols, assumed existence of $V_6O_{13}(OEt)_4$–$V_3O_6(OEt)_3$ equilibrium in solutions. In the 1960s Jahr and Fuchs [814, 591] applied hydrolysis of $VO(OR)_3$ in the presence of different cations for synthesis of new polyvanadates (at the same time, an analytical technique for measuring of traces of water in organic solvents by precipitation of [AmH]$[H_2V_{10}O_{28}]$ was suggested [814]). Because of application of $VO(OR)_3$ as a precursor for catalysts and oxide materials, lately considerable attention has been paid to the preparation of gels from these metal alkoxides. It has been demonstrated that the addition of stoichiometry amount of water to $VO(OPr^i)_3$ (h = 3:2) results in transparent orange gel, whereas $VO(OC_5H_{11}{}^t)_3$ under the same conditions gives sol. Excess of water (h > 100) leads to red gels, which in contrast to the orange ones do not contain residual OR-groups. The gels with the composition of $V_2O_5{\bullet}1.8H_2O$, are polymeric ribbons involving, in accordance with ^{51}V NMR spectroscopy data, decavanadate groups. Vanadium is in square-pyramidal $[VO_5]$ environment with one short V=O bond along z axis. Residual alkoxide groups are always absorbed in the branched structure of gel, and they can be eliminated only after thermal treatment at the temperature not less than 300°C. Dehydration of gels occurs in two steps: at first at about 120°C water is reversibly eliminated; nonreversible dehydration is accomplished by 250°C. Hydrolysis is always accompanied by partial reduction of V(V) by alcohol and appearance of V^{4+} in $V_2O_5{\bullet}nH_2O$; this results in green coloring of gels. In organic solvents the process plays a very important role. It is interesting that V^{4+} ensures polymerization of $V_2O_5{\bullet}nH_2O$ and formation of gels, probably as a result of higher radius and coordination abilities of V^{4+} in comparison with V^{5+}. The electron microscopy photographs of the gels show fibers ~ 10 nm tick. According to the X-ray data, gel has a layered structure. $V_2O_5{\bullet}nH_2O$ gels are conductors with mixed electron and ion anisotropic conductivity. Polycrystalline VO_2 films were obtained by the application of V(IV) solutions to the substrates with subsequent thermal treatment at 600°C; they undergo reversible phase transition semiconductor metal at 72°C. Structures and properties of gels were discussed in detail in a special review by Livage [1019]; an interesting review of the photovoltaic effect on vanadium pentoxide gels is given in the paper [511].

9.8. Niobium and tantalum alkoxides

Niobium and tantalum ethoxides are commonly used as precursors for the corresponding oxides. Formation of Nb_2O_5 gels on partial hydrolysis of $Nb(OEt)_5$ has been described in [28]. Sols prepared by hydrolysis of $NbCl_2(OEt)_3$, in accordance with the data of X-ray absorption at the niobium K edge (EXAFS), contain polymers built of octahedra $[NbO_6]$ sharing common vertices [1667]. Some edge-sharing species were also observed, and the short-range order around Nb atoms appeared to be quite similar in both the crystalline Nb_2O_5 phase and the niobium pentoxide gels. Crystallization occurred on heating up to about 700°C, when all water molecules were removed. Analogous results were obtained when $Nb(OC_5H_{11})_5$ modified by acetic acid up to the composition of $Nb(OC_5H_{11})_{5-x}(OAc)_x$ ($x = 0.1$) was used as a precursor [680].

It has also been demonstrated that ideal spherical particles can be obtained by hydrolysis of $Ta(OEt)_5$ in the alkaline medium or by addition of hydroxopropylcellulose to the initial alkoxide solution [1190, 840, 1227]. The size of the particles thus formed may be controlled in the range of 0.05 to 1 μm by increasing NH_4OH concentration and decreasing h (nevertheless, at $h < 4$ no precipitation is observed). The amorphous precipitate is assumed to have composition of $Ta_2O_5 \cdot H_2O$; however, in accordance with the exothermic peak at about 400°C, accompanied by weight loss, it contains residual alkoxide groups. Crystallization of Ta_2O_5 occurs only on heat treatment in air at 800°C, and the oxide species inherit the morphology of the hydrolysis product.

Hydrolysis of tantalum alkoxide and preparation of Ta_2O_5 in the form of powders and films gains much more attention in comparison with hydrolysis of $Nb(OR)_5$. This is primarily due to the fact that Ta_2O_5 is used much more extensively in electronics due to its higher stability and better dielectric properties. Sols prepared by partial hydrolysis of $Ta(OEt)_5$ are used for deposition of amorphous Ta_2O_5 films. They crystallize at the temperature higher than 650°C. Ta_2O_5 layers with high dielectric permittivity (20 to 40) are good candidates for insulators in large-scale integration (LSI) devices, electroluminescent devices, film capacitors. Dielectric characteristics of the films prepared by sol-gel method are not lower than that of Ta_2O_5 films deposited by CVD [1487, 1229, 1016].

9.9. Molybdenum and tungsten alkoxides

Yamaguchi was the first to study hydrolysis of $W(OEt)_6$ [1766]. Hydrolysis performed *in situ* at 20 and 80°C yielded amorphous blue precipitate or green-yellow crystals of $WO_3 \bullet H_2O$, respectively. The final crystallization product formed on thermal treatment of both precipitates was monoclinic WO_3, while in the course of thermal treatment at 350°C, the cubic WO_3 was also registered.

Yanovskaya *et al.* [1774] have demonstrated that the hydrolysis products of tungsten oxoalkoxides, $WO(OEt)_4$, and $WO_2(OEt)_2$, contain two phases — crystalline $WO_3 \bullet H_2O$ and amorphous $WO_{3-x}(OEt)_{2x} \bullet nH_2O$. The SAXS and UV-spectroscopy study of colloid and solid hydrolysis products of $MoO_2(OEt)_2$ and $WO(OEt)_4$ have demonstrated that hydrolysis of tungsten oxoethoxide and the structure of sols formed in the course of its hydrolysis are absolutely analogous to the hydrolysis products of $Si(OEt)_4$ (the latter have been described in detail by Brinker [242]). Sols have a network structure, which densifies and becomes three-dimesional with time. The structure of the network is primarily determined by the h ratio in solution: when it is low, networks are very porous; increase of h results in formation of porous balls. Formation of oxide is accompanied by an increasing of polycondensation extent — branching of the W–O core ultimately resulting in the three-dimensional WO_3 structure based on W–O–W bridges.

Hydrolysis of $MoO_2(OEt)_2$ leads to micellar sols with the isopolymolybdate ion $[Mo_2{}^{V}Mo_4{}^{VI}O_{18}]^{2-}$ nuclei. Drying of the sols gives xerogels of crystalline molybdenum blues $MoO_{2.88} \bullet H_2O$ transferring into rhombohedral MoO_3 on thermal treatment at 280°C. MoO_2 groups of $MoO_2(OEt)_2$ are inherited in all hydrolysis products, and they can be further subjected to thermal treatment until MoO_3 also containing MoO_2 group is formed [1774]. Molybdenum and tungsten oxide sols prepared by hydrolysis of the corresponding alkoxides were successfully used for application of photo- and electrochromic oxide films.

9.10. Iron ethoxide

In the first study of hydrolysis of $Fe(OEt)_3$ carried out by Thiessen *et al.* [1577], the precipitate of cubic crystals $Fe_2O_3 \bullet 4H_2O$ was obtained after refluxing of diluted alcoholic solution of iron ethoxide for a few hours. Hydrolysis of iron ethoxide by excess of water results in amorphous precipitate, which on thermal treatment at first gives γ-Fe_2O_3 and then α-Fe_2O_3 (in contrast to the precipitates of α-$FeOOH$, which precipitate from aqueous solutions) [1776].

Chapter 10

SYNTHESIS OF COMPLEX OXIDES FROM METAL ALKOXIDES

Over the last few decades, the preparation of complex oxides from metal alkoxides has become one of their major applications. Almost all the studies of bimetallic metal alkoxides or interaction between metal alkoxides are aimed at the synthesis of precursors for complex oxides, either volatile for MOCVD or soluble in organic solvents for sol-gel synthesis. The number of works describing the different preparative techniques and properties of complex oxides synthesized from metal alkoxides already exceeds by many times the number of works on the synthesis and properties of metal alkoxides themselves. Many reviews and books cover in substantial detail the application of metal alkoxides to metal oxide synthesis, and some of the most important references to our best knowledge are given in Chapter 1. Among the most interesting compositions include the spinel powders – $MgAl_2O_4$ [1148, 1224, 1680, 1765], Co_2TiO_4 [804], Al_2TiO_5 — refractory ceramics with zero expansion coefficient (which cannot be obtained by conventional techniques because of the poor sintering ability of the oxides) [861, 890]. The refractory construction materials also include the cubic ZrO_2 (used also as solid electrolyte). The preparation of the Y_2O_3–ZrO_2 solid solution was achieved by hydrolysis of the isopropoxides of the 2 metals. The properties of the transparent ceramics obtained by alkoxide technology turned out to be much better than those of the product of solid-state synthesis [844, 1084]. Recently, the application of the sol-gel techniques was shown to be successful for the preparation of ferrites in the Fe_2O_3–Y_2O_3 system [1776], cathode materials (films and powders) based on $Li_{1+x}V_3O_8$ bronzes [1630].

Therefore, in this book we do not by any means intend to provide a comprehensive treatise on the subject. The aim of this chapter is rather to show a few illustrations of the application of metal alkoxides in the synthesis of complex oxides.

In particular, we have chosen to have a close look at the synthesis and properties of ferroelectrics and related materials, where the sol-gel method with application of metal alkoxide precursors seems to have produced the most promising results. In most cases we have selected for discussion in this chapter those works on the preparation of complex oxides, emphasized that the chemistry of the precursors and its role for the properties of complex oxide phases.

Synthesis of complex oxides from metal alkoxides includes the preparation of the initial solution, hydrolysis, drying, and thermal treatment of the product. Despite the apparent simplicity and versatility of the scheme, the properties of oxides are extremely sensitive to the conditions of their preparation. The commonly used precursor for oxides preparation is a solution of $M(OR)_n$ in organic solvents. The heterogeneous precursor usually affects the homogeneity of the future oxide phase.

At first, it seemed that the only problem lies in the preparation of the precursor solution containing alkoxides of all the elements of future oxide composition: molecular distribution of the components in the initial solution was supposed to ensure homogeneity of the future oxide phase. It soon turned out, however, that this is far from being the only condition. In fact, this apparently logical assumption did not take into consideration different hydrolysis rates of $M(OR)_n$, which indeed present a considerable obstacle. Even if true bimetallic complexes are formed in solutions, homogeneity of the future oxide phase on the atomic scale may be achieved only if the stoichiometry of alkoxo-complexes in solutions corresponds to that in the future oxide phases. For example, the only stable bimetallic complex in the ternary systems $Ba(OR)_2$–$Ti(OR)_4$–ROH ($R = Et, Pr^i, Bu^n$) is $BaTi_4(OR)_{18}$ rather than $BaTi(OR)_6$, as it has been postulated in literature (see Section 12.11). Indeed, hydrolysis of the freshly prepared solutions of $Ba(OR)_2$ and $Ti(OR)_4$ with Ba:Ti = 1:1 gives $BaTiO_3$ powders always containing admixtures of Ba_2TiO_4 and polytitanates. On the other hand, hydrolysis of solutions containing $BaTiO(OR)_4$ (formed as a result of the partial decomposition of $BaTi_4(OR)_{18}$) results in pure $BaTiO_3$, containing no admixtures.

Therefore, in the course of the studies of bimetallic alkoxides it turned out that one of the most important features for their application in sol-gel films preparation lies in their ability to undergo partial decomposition via hydrolysis, oxidation, or elimination of ethers or esters with formation of M–O–M' bridges (see, e.g., Section 10.1), fragments of future complex oxide phases. Formation of bimetallic oxoalkoxides ensures homogeneity on the atomic scale of the complex oxide formed in the process of the transformation $M(OR)_n \rightarrow M_2O_n$.

Certainly, most of the ideas concerning the rates of hydrolysis and their impact on the forms and morphologies of the hydrolysis products comply with those discussed earlier for monometallic alkoxides (Chapter 9).

Ozaki [1245] in his review classified perovskites prepared from metal alkoxides according to conditions of their crystallization. He described the following three possibilities of crystallization of perovskites: (1) direct crystallization in the course of hydrolysis, (2) one-step process of thermal treatment of the amorphous hydrolysis products, and (3) crystallization as a result of the solid-state reactions between the first crystallized oxides. At present, it has become evident that the careful choice of processing conditions (which includes pre-hydrolysis and hydrolysis stages) allows most of the perovskites enumerated by Ozaki to be obtained without thermal treatment after hydrolysis. If the thermal treatment is, nevertheless, necessary, it is important to choose the appropriate atmosphere (air, oxygen, or oxygen-water vapor flow).

Some examples of application of metal alkoxides for synthesis of ferroelectrics such as $BaTiO_3$-based materials, complex niobates and tantalates, PZT and PLZT-materials, and high-temperature superconductors are discussed below.

10.1. Barium titanate and $BaTiO_3$-based solid solutions

Barium titanate and $BaTiO_3$-based materials are most commonly used for ceramic capacitors with high dielectric permittivity. $BaTiO_3$ powder of extremely high quality (in respect of its purity, stoichiometry, particles morphology) is required for most of the modern applications. This characteristic may be considerably improved by the application of alkoxide precursors. Thus, it is of no surprise that synthesis of $BaTiO_3$ and $BaTiO_3$-based materials from metal alkoxides attracted considerable attention for several decades. The first works on preparation of $BaTiO_3$ in reaction of $Ba(OH)_2$ with $Ti(OR)_4$ date back to 1955 [571]; hydrolysis of the solution of alkoxides was used for preparation of $BaTiO_3$ by Mazdiyasni in the late 1960s [1083]. By the end of the 1980s, we witnessed a new upsurge of interest to synthesis of $BaTiO_3$ via decomposition of metal alkoxides presumably caused by the attempts of commercial application of these methods. These attempts were realized on a small scale; so far there are no data reporting major production of $BaTiO_3$ powders with application of metal alkoxides.

All techniques based on the application of titanium alkoxides as titanium component precursors may be subdivided into three groups in accordance with the methods of introduction of barium in the system — the application of salts (organic or inorganic), $Ba(OH)_2$, and $Ba(OR)_2$.

Barium salts BaX_2 (X = Cl, Br, OAc) do not react with organic solutions of $Ti(OR)_4$, which explains why the products of thermal treatment of the hydrolysis products always contain $BaCO_3$; its decomposition is completed only at 1200°C [450]. It is thus quite natural that the reaction product contains along with $BaTiO_3$ admixtures of numerous complex oxides of the $BaO–TiO_2$ system together with oxohalogenides (in the case when barium halogenides are used as precursors). Application of $Ba(OAc)_2$ solution in acetic acid or other barium carboxylates turned out to be fruitful for sol-gel application of thin films, and thus will be discussed in connection with thin films preparation, however, small-angle X-ray scattering, IR- and Raman spectroscopy data demonstrated that Ba and Ti species coexist in the sol and gel separately [1203]. Thermolysis at 200 to 400°C results in the formation of $BaCO_3$ and TiO_2; crystallization of $BaTiO_3$ occurs only after annealing at 650°C as a result of solid-state reactions [1178].

The alkoxide-hydroxide route summarized by the following reaction

$$Ti(OR)_4\ (\text{solution}) + Ba(OH)_2\ (\text{solution}) \longrightarrow BaTiO_3\downarrow$$

leads to crystallization of $BaTiO_3$ from solutions and is probably one of the most promising methods for synthesis of $BaTiO_3$ fine powders.

The surprisingly low temperature of $BaTiO_3$ formation, below 100°C, makes this reaction very attractive for regulating the particle sizes and paves the way for preparation of submicron uniform species. This method was subsequently used for the synthesis of other perovskites [329]. As to the reaction mechanism, it was at first assumed that hydroxotitanate anion $[Ti(OH)_6]^{2-}$ was the first hydrolysis product, which under the decomposition by the alkaline-earth cation crystallized to form $M^{II}TiO_3$ ($M^{II} = Ba^{2+}, Sr^{2+}$) [329, 571]:

$$[Ti(OH)_6]^{2-} + M^{2+} \longrightarrow M^{II}TiO_3 + H_2O$$

Hydroxotitanate anion, however, has never been detected in the course of hydrolysis of titanium alkoxides. On the basis of electron microscopy data, Diaz-Guemes *et al.* [477] suggested the two-step adsorption mechanism for the above reaction. According to his assumption hydrolysis of titanium alkoxide results in a gel of hydrated titanium oxide, which is further diffused by M^{2+} cations to form crystalline $M^{II}TiO_3$:

$$Ti(OR)_4 + 2H_2O \longrightarrow TiO_2\text{ (gel)} + 4ROH$$
$$TiO_2\text{ (gel)} + M(OH)_2 \longrightarrow M^{II}TiO_3 + H_2O$$

A series of patent publications reflect the attempts made by different companies to commercially develop this method [261, 1264, 1013, 921]. The conditions for the preparation of highly crystalline powder with precise stoichiometry were determined, and the main problem concerning preparation of fine and uniform powders was addressed. In recent studies it was demonstrated that the morphology of perovskite species $M^{II}TiO_3$ (M = Sr, Ba) prepared by the alkoxide-hydroxide route is mostly governed by the rate of the second reaction, the adsorption of alkaline-earth metal by the $Ti(OBu)_4$ hydrolysis product. Thus, to prepare uniform species with the size of about $0.5\ \mu m$, it is important to slow down the adsorption rate. Therefore, for each alkaline-earth titanate or solid solution, separate experiments are required to determine concentrations of the components and temperature regimes to achieve necessary morphology [658]. Anyhow, the alkoxide-hydroxide method is undoubtedly a promising route to $BaTiO_3$ and $BaTiO_3$-based solid solutions. Powders produced by the alkoxide-hydroxide route sinter at temperatures significantly lower than the conventional powders; ceramic materials demonstrate considerably improved dielectric properties. A few data on the sintering and dielectric properties of the materials prepared by this method presented below are presented as illustrations.

More than 30 years ago, Mazdiyasni [1083] suggested preparing $BaTiO_3$ by hydrolysis of $Ti(OC_5H_{11}{}^t)_4$, obtained by alcoholic exchange from $Ti(OPr^i)_4$, and $Ba(OPr^i)_2$. Solutions containing Ba and Ti alkoxides were refluxed for several hours and then slowly hydrolyzed, which led to crystallization of $BaTiO_3$. After calcination at 800°C the powder was characterized by high purity, uniformity, and being sintered into dense ceramic with $\varepsilon = 2500$ (t = 20°C, f= 1 kHz) at 1300°C. This remarkable technique may be considered the first brick in the chemistry of preparation of complex oxides from metal alkoxides. Nevertheless, it remains obscure which of the conditions described in the technique were indeed important. First of all, the choice of the alkoxide precursor is quite unusual: it is not clear if the authors believed it indeed essential to perform alcoholic exchange and to synthesize $Ti(OC_5H_{11}{}^t)_4$ instead of using $Ti(OPr^i)_4$ for further complexation with $Ba(OPr^i)_2$ and hydrolysis. Speculation that $BaTi(OR)_6$ is formed as a result of refluxing of Ba- and Ti-containing solutions seems highly improbable. Bimetallic alkoxide with such stoichiometry has never been registered. Besides, no details concerning the hydrolysis conditions, such as $[H_2O]:[M(OR)_n]$ ratio or hydrolysis temperature, were given; on the other hand, in the works of other authors it was demonstrated that hydrolysis conditions indeed control the phase composition of the powders [922].

Interaction between $Ba(OPr^i)_2$ and $Ti(OPr^i)_4$ in ^iPrOH was studied in detail by Kirby [920]. He isolated single crystals with the ratio of Ba:Ti = 1:1; thermal decomposition of these crystals resulted in the formation of tetragonal $BaTiO_3$ in one step. Moreover, even the shape of big complex oxoalkoxide crystals was preserved in $BaTiO_3$ formed on their decomposition. Nevertheless, the true chemical composition of the crystal as $BaTiO(OPr^i)_4 \cdot 7/8\,{}^iPrOH$ was determined only in the further X-ray structural study of these crystals and revealed the existence of Ba–O–Ti bridges in their structure [1787] (see Section 4.7.1); these are presumably preserved in the course of further thermal treatment with formation of complex oxide. This study provided the first example, where the role of complex oxoalkoxides as precursors for complex oxides was clearly demonstrated by crystallographic data; besides, it provided an explanation of why in many techniques the refluxing of metal alkoxide solution or other methods of partial decomposition of alkoxides leading to oxoalkoxides is essential and facilitates formation of complex oxides on hy-

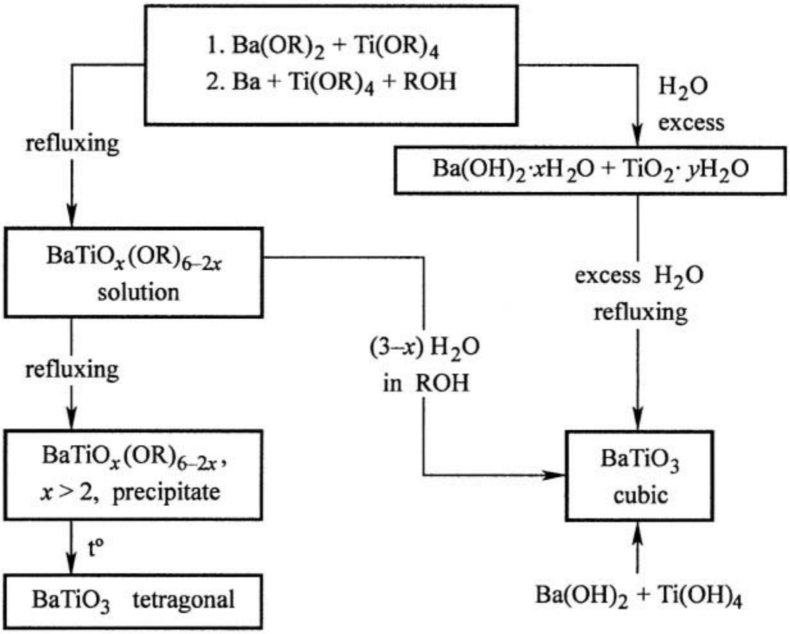


Fig. 10.1. Summary of the chemical processes, that take place under different conditions suggested in techniques for $BaTiO_3$ preparation.

drolysis. This fact also emphasizes the utmost sensitivity of the complex oxide crystallization conditions to the precursor solution preparation prior to hydrolysis. Indeed, it is necessary to ensure the formation of oxoalkoxide species in solutions: only in this case further hydrolysis results in the formation of complex oxide in one step. If the necessary precursor is not "preconstructed" in solution, a mixture of hydrated oxides is formed in the course of hydrolysis of the metal alkoxide solution, and complex oxide is formed only in the course of solid-state reactions that occur on thermal treatment. In this case, however, the chemical homogeneity, actually one of the major advantages of metal alkoxides application as precursors, will be lost (Fig. 10.1).

Crystallization of **$BaTiO_3$** and **$Ba_{1-x}Sr_xTiO_3$** solid solutions may also occur on aging at 30 to 90°C of gels prepared by hydrolysis in methoxyethanol of complex metal alkoxides; usually Ba and Sr ethoxides and **$Ti(OPr^i)_4$** are used [588, 1470, 1474].

Crystalline $BaTiO_3$ prepared by hydrolysis of the alkoxide solutions in the form of dispersion without drying was successfully used to make a ceramic slip formulation, which was then cast as a ceramic green body for microcapacitors 1 to 50 μm thick.

Metal alkoxides are traditionally widely used in the sol-gel method as precursors for preparation of film-forming solutions. $BaTiO_3$ was probably the first ferroelectric complex oxide prepared in the form of thin films from metal alkoxide solutions back in the 1960s [1539, 1161]. It was, however, only much later that ferroelectric properties of the films were actually measured [1780, 1709,1605]. Due to the necessity of high-temperature annealing, the first ferroelectric $BaTiO_3$ films were obtained on Pt substrates. Recently, the films of the $Ba_xSr_{1-x}TiO_3$ (BST) system, as high permittivity materials for high-density dynamic access memories (DRAMs) and millimeter microwave integrated circuits (MMIC), attracted substantial attention. Moreover, these films seem to be among the most promising sol-gel applications for the near future; they are widely considered to be a particular target, where sol-gel method can successfully compete with other well-known techniques for thin-film applications.

Either pure titanium alkoxides or titanium alkoxides stabilized by addition of acetylacetone (usually 2 moles per mole of $Ti(OR)_4$) are used as titanium precursors. Barium and strontium can be introduced in the form of alkoxides or carboxylates in methoxyethanol. Recent study [717] has been devoted to the systematic investigation of application of different alkaline-earth carboxylates as precursors. Series of $MTiO_3$ (M = Ba, Sr) thin films were prepared in identical conditions using alkaline earth acetates, propionates, 2-methylpropionates, and 2-ethylhexanoates. In all cases the ceramic thin films of $BaTiO_3$ and $SrTiO_3$ with high permittivity were prepared. In the course of thermal treatment, however, titanium precursor was shown to decompose earlier than alkaline-earth carboxylate, which leads to a mixture of amorphous titanium oxide matrix with finely distributed alkaline earth carboxylate. Then decomposition of the alkaline-earth carboxylate occurs in the temperature interval of 375 to 500°C (depending on Ba or Sr derivative and the chemical nature of carboxylate), crystallization requires further temperature treatment at above 600°C. During layer-to-layer deposition, $SrTiO_3$ and $BaTiO_3$ show epithaxial growth resulting in columnar film structure [843]. The dielectric measurements were performed on $BaTiO_3$ films with different morphologies grown on Pt-coated

Si substrates. The change of morphology from grainy to columnar resulted in an increase of room temperature permittivity for the films with the thickness of 0.2 μm from 500 to 900 (measurements were performed at 10 kHz), which clearly emphasized the necessity and possibility to control the morphology by film formation process.

In [1677] complex alkoxides and alkoxide-carboxylates were compared as precursors for preparation of BST films. In contrast to the introduction of alkaline earth carboxylates in the form of preliminary isolated salts, in this work metal alkoxide solution in methoxyethanol containing titanium and alkaline-earth metal was modified by addition of 2-ethylhexanoic acid with subsequent slow distilling off the solvent and repeated dilutions with fresh portions of methoxyethanol. During the distillation process, part of the alkoxide groups are substituted by the 2-ethylhexanoate ligands. The exchange reaction of $Ti(OPr^i)_4$ with acid was studied in different solvents, and it was demonstrated that in the course of distillation the titanium oxoisopropoxy-2-ethylhexanoate is formed with elimination of ester:

$$Ti(OPr^i)_4 + MeOC_2H_4OH + C_7H_{15}COOH \longrightarrow$$
$$\longrightarrow TiO_x(OPr^i)_y(C_7H_{15}COO)_{4-2x-y} + C_7H_{15}COOC_2H_4OMe + {}^iPrOH$$

Oxoalkoxocomplexes are oligomers of varying molecular complexity. The extent and conditions of distillation allow to control the nature of the species in solution, thus influencing the film-formation process [1368]. This process of *in situ* modification of metal alkoxide solution by carboxylate ligand may have certain advantages with respect to the chemical uniformity as compared to the techniques based on simple mixing of a titanium alkoxide with alkaline-earth carboxylates.

IR spectra measurements as well as variation of the film thickness, shrinkage, and refractive index demonstrated substantial differences in the mechanisms of thermal decomposition of films prepared from the exclusively metal alkoxide precursor and from the metal alkoxides modified by 2-ethylhexanoic acid. These differences affect the evolution of film microstructure and thus determine the different dielectric properties of the obtained films. The dielectric permittivity of the films prepared from metal alkoxide solutions was relatively low (about 100) and showed weak dependence of the bias field. This fact may be explained by the early formation of metal-oxide network (mostly in the course of hydrolysis during application of solution to the substrate) in this case. This hinders structural relaxation and causes high mechanical stresses in the films. As a result, the crystallization starts at lower temperatures but results in a structure with defects and distortions. By contrast, in the case of modified metal alkoxide precursors, the metal-oxide network is created after pyrolisis of organics at a much higher temperature when atoms with higher energy and mobility ensure better conditions for crystallite growth in a porous non-stressed structure. In general, the higher extent of solvent distillation during solution preparation results in the higher permittivity and more pronounced nonlinearity with application of the bias voltage.

The dielectric permittivity of BST films (measured at the frequency of 1 MHz at 20°C without application of bias electric field) as a function of the strontium content in the films is shown in Fig. 10.2. The maximum value of dielectric permittivity is observed for the films with Ba/(Ba+Sr) = 0.3 in accordance with single-crystal behavior. The values of dielectric permittivity increase with the increase of annealing temperature of the films (from 700 to 800°C), as well as with the increase of film thickness.

Recently, an attempt to use $OC_5H_{11}^{neo}$ derivatives for preparation of BST films was made [191]. According to the authors, $OC_5H_{11}^{neo}$ ligands were chosen because they facilitate the "cross-linking" decomposition pathway, and thus the formation of uniform films, besides the t-butyl moiety due to the steric hindrance, minimizes oligomerization and increases the solubility of the alkoxide species. Indeed, the titanium precursor $[Ti(\mu\text{-}OC_5H_{11}^{neo})(OC_5H_{11}^{neo})_3]_2$ (isolated by the alcohol exchange reaction of $Ti(OPr^i)_4$ with $^{neo}C_5H_{11}OH$) is the smallest crystallographically characterized homoleptic titanium alkoxide isolated to date. Barium and strontium derivatives were prepared by reactions of metals with $^{neo}C_5H_{11}OH$ in THF, and the precursor solution was made by mixing of Ba, Sr, and Ti alkoxides. It is interesting that although an attempt to prepare a ternary single-source precursor was made, the crystals isolated from the precursor solution containing all three metal alkoxides represented a binary complex with the Ba:Ti ratio of 1:2. Films with the thickness of ~0.3 μm deposited on platinized silicon demonstrated dielectric constant of 120 (tg δ = 0.03) at 10 kHz.

In the present time Veith *et al.* have made detail investigation on the synthesis of the powders and ceramics $BaTiO_3$, $BaZrO_3$, and $BaTi_{0.5}Zr_{0.5}O_3$ based

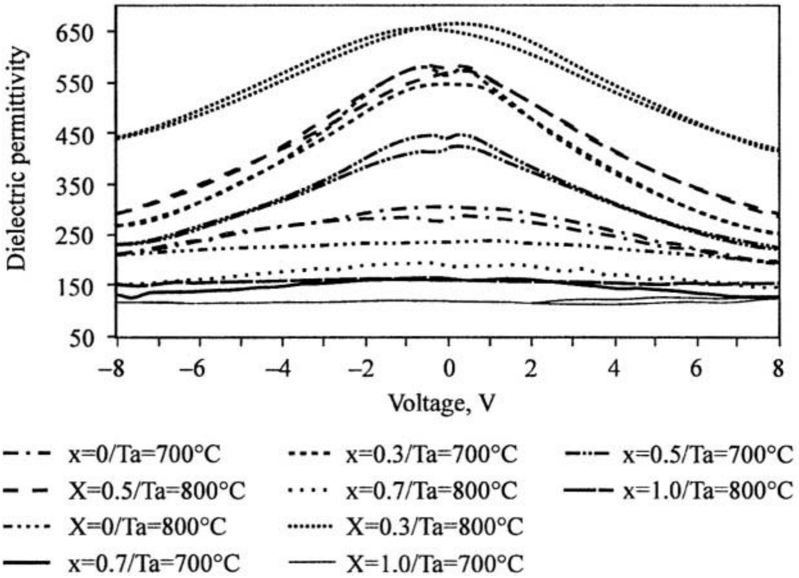


Fig. 10.2. Dielectric permittivity of $Ba_{1-x}Sr_xTiO_3$ films versus x and annealing temperature.

on isopropoxides of Ti and Zr and complex $Ba_2TiZr(OPr^i)_{12}$ useing three Ba precursors — $Ba(OH)_2$, $Ba(OAc)_2$, and $Ba(OPr^i)_2$ [1689].

Thin-film dielectrics $(Ba_{0.92}Ca_{1.08})(Ti_{0.92}Zr_{0.08})O_3$ for the thin-film capacitors were prepared using Ba, Ca, and Zr ethoxides and Ti isopropoxide in refluxed methoxyethanol solutions as precursors. Films were deposited on a usual platinized Si substrate. Crystalline thin films after heat treatment at 800°C demonstrated dielectric permittivity of 1200, dielectric loss of 0.5%, nonlinear coefficient $\alpha = 0.92$, and break-down voltage of 980 V [1595].

10.2. Complex niobates and tantalates

Synthesis of niobates and tantalates of alkaline metals at high temperatures may result in the products with unintended stoichiometry because of high volatility of alkaline metal (especially lithium) oxides. Therefore, their synthesis in the form of efficiently sintering powders presents a serious problem. Films of alkaline niobates and tantalates can find wide range of applications in acousto- and optoelectronics and are usually prepared by rf-sputtering techniques, also giving rise to stoichiometry problems.

Application of metal alkoxides for the preparation of niobates and tantalates in the form of both powders and films has been first performed by Dändliker [475]. In our study of hydrolysis of LiOEt and $Nb(OEt)_5$ solutions in anhydrous EtOH, it was demonstrated that although the freshly prepared powder is amorphous for X-ray, it already contains microcrystallites of $LiNbO_3$ [1778]. In addition to conventional techniques, the properties of the powder in the course of thermal treatment were studied by the second harmonic generation of the laser beam, which is a sensitive technique for detection of noncentrosymmetric phase; the first signal was registered at 350°C.

Studying the preparation of alkaline niobates and tantalates in the form of powders and films, Hirano [756] demonstrated that in order to prepare pure phase of complex oxide, the refluxing of the precursor alkoxide solutions prior to hydrolysis or film application is beneficial. He explained this fact by the formation of $LiNb(OEt)_6$ in solution during refluxing. However, according to [1622], the above bimetallic complex is formed immediately on the mixing of lithium and niobium ethoxides. Refluxing or storage of the solutions leads to bimetallic oxoethoxoniobates. (The structure of the crystalline $[LiNbO(OEt)_4(EtOH)]_2$ has been reported in [1621]). Formation of oxoalkoxide is facilitated by direct reaction of alkaline metal with the alcoholic solution of niobium ethoxide. Application of partially hydrolyzed solutions is also preferable to control morphology of the species formed. Formation of $LiTaO_3$ via the gelation step allows oxide species of regular shape with high sintering ability to be prepared [1324]. Crystallization of alkaline niobates occurs at lower temperature (250 to 300°C) if calcination of the hydrolysis products and films is performed in a flow of oxygen mixed with water vapor.

Although in most papers concerning the preparation of $M^IM^VO_3$ (M^I = Li, Na, M^V = Nb, Ta) Li and Na are introduced as alcoholic derivatives, a few workers suggest introducing alkaline elements in the form of their acetates, while $M^V(OEt)_5$ are used as Nb and Ta precursors [95, 373, 840, 931].

The same metal alkoxide precursor solutions in EtOH and methoxyethanol, which were used for preparation of powders were also suggested for application of $LiNbO_3$ and $NaNbO_3$ films on Pt and quartz substrates [524, 1778]. The choice of solution concentration and thickness of the layer, which undergoes calcination, is very important for the preparation of films without cracks or bubbles. Oriented $LiNb_xTa_{1-x}O_3$ $(0 \leq x \leq 1)$ films were obtained on the sapphire substrates (012), (110), or (001) [96; 1540]. Partially hydrolyzed solutions were used for the preparation of stoichiometric crystalline lithium niobate fibers [755]. Other oxide phases of the $Li_2O - Ta_2O_5$ system can be synthesized from alkoxide precursor solutions with different $[LiOEt]:[Ta(OEt)_5]$ ratios [1548]. Potassium niobate powders and thin films $KTaO_3$, $KNbO_3$, as well as solid solutions of $KTa_{1-x}Nb_xO_3$ were also prepared from metal alkoxides [1760, 36, 1658].

Perovskites $AB_{1/3}C_{2/3}O_3$ (A = Ba, Sr; B = Zn, Mg, Co, Ni; C = Nb, Ta) are promising compounds for microwave applications. It is important to synthesize these complex oxides as pure perovskite phases because the slightest admixture of a second phase hinders drastically the dielectric properties of ceramics, which sinter only at very high temperatures (1400 to 1500°C). The precursor chemistry resembles greatly that of $BaTiO_3$ formation by alkoxide or alkoxide-hydroxide routes. Below we summarize the 3 approaches to the synthesis of these perovskites by the sol-gel method:

- *First approach.* Ba and Zn, are introduced in the form of inorganic salts suspended in the alcoholic solution of $Ta(OEt)_5$, and the dispersion is hydrolyzed and annealed. Uniform distribution of Ba and Zn in this gel is achieved by vigorous stirring of the reaction mixture [805]. A high degree of dispersion and reactivity of $Ta_2O_5 \bullet H_2O$ ensures the formation the complex oxide at temperatures ~150°C lower than those necessary for solid-state reactions. In the variation of the above procedure, all 3 elements are dissolved in the organic solvent, Ba and Ta as alkoxides, and Zn as acetylacetonate, its most available organic derivative. While metal alkoxides are hydrolyzed, $Zn(acac)_2$ remains unaffected and reacts with the products of metal alkoxides hydrolysis only at the thermolysis time. Thus, formation of the complex oxide in this case also occurs only as a result of the solid-state reaction between the components at ~1030°C.
- *Second approach.* Mg is introduced into the alcoholic solutions of liquid Nb or Ta alkoxides either in the form of solid Mg alkoxide or as metal that readily dissolves in the alcoholic solution of $M(OR)_5$ with elimination of hydrogen. This solution is then hydrolyzed by aqueous solution of $Ba(OH)_2$:

$$Ba(OH)_2 + 1/3Mg[Nb(OR)_6]_2 \xrightarrow{t \geq 80°C} BaMg_{1/3}Nb_{2/3}O_3$$

Just as in the above described case of $BaTiO_3$ preparation, the reaction can be performed in two steps: at first bimetallic alkoxide is hydrolyzed, and then $Ba(OH)_2$ is adsorbed by the precipitate of hydrated oxides. Crystallization of the perovskite phase under these conditions occurs at 80 to 100°C [1779, 805].

- *Third approach.* The precursor solution in alcohol, methoxyethanol, or alcohol-benzene mixture contains all elements of the future oxide composition in the form of metal alkoxides. In the case of the synthesis of individual Zn, Co, Ni alkoxides presenting certain difficulties they may be introduced in methoxyethanol solution containing other metal alkoxides by anodic dissolution of the corresponding metals. Hydrolysis of the solutions at room temperature results in amorphous precipitates of hydrated oxides that are dehydrated on thermal treatment and crystallize in the perovskite phase at 800 to 1000°C. If hydrolysis is carried out on refluxing, which is continued with stirring for several hours, and residual solvent is isolated at $t \geq 100°C$, the crystalline perovskites are obtained without additional thermal treatment [805]. The crystalline products obtained directly by hydrolysis were successfully used for sintering of ceramic sheets [707]. Lead-magnesium niobate $PbMg_{1/3}Nb_{2/3}O_3$ was prepared by decomposition of gel produced by mixing of magnesium alkoxoniobate with lead acetate and subsequent hydrolysis [583]. Crystallization of the amorphous powder prepared after drying of gel occurs at 470°C with crystallization of pyrochlore; perovskite crystallizes only on further thermal treatment at a higher temperature of about 700°C. It is interesting that the rate of phase transition from pyrochlore to perovskite depends not only on the annealing conditions but rather on the gelation process. The same precursor solutions were used for application of films on platinized silicon wafers. Ferroelectric perovskite films crystallized at 800°C [583]. Porous $PbMg_{1/3}Nb_{2/3}O_3$ was prepared by drying the gel under supercritical conditions [329]. In the search for the precursors for this class of complex oxides, Hubert-Pfalzgraf studied reactions between niobium alkoxides $Nb(OR)_5$ ($R = Et, Pr^i$) and anhydrous acetates $M(OAc)_2$ (M = Mg, Ba, Pb, Cd). With the exception of barium acetate, which remains inert even under refluxing or in the presence of acetic acid, the reaction proceeds at room temperature in non-polar solvents. Acetates are dissolved to give $MNb_2(\mu\text{-}OAc)_2(OR)_{10}$ species. Isopropoxides are more reactive than ethoxides. X-ray structural data confirmed that two different metals are clamped together by the acetate ligand. Formation of pure $MgNb_2O_6$ and $CdNb_2O_6$ after hydrolysis and thermal treatment of $MNb_2(\mu\text{-}OAc)_2(\mu\text{-}OPr^i)_4(OPr^i)_6$ (M = Mg, Cd) occurs at 600°C [779].

10.3. Lead zirconate-titanate (PZT) and lead-lanthane zirconate-titanate (PLZT) solid solutions

The first studies on the synthesis of PZT and PLZT materials from metal alkoxides date back to the early 1970s. They dealt primarily with the preparation of powders for sintering of the electrooptic PLZT ceramics [252]. Although Mazdiyasni et al. suggested hydrolyzing the solution containing all 4 elements as alkoxides, in most of the subsequent studies lanthanum alkoxides have not been used. Instead, the hydrolysis of the solution in organic solvent was performed by aqueous solution of lanthanum acetate. Different lead derivatives, such as lead alkoxides, dissolved in alcohols together with titanium and zirconium alkoxides, PbO-powder vigorously stirred in the alcoholic solution of titanium and zirconium alkoxides during the hydrolysis stage, or aqueous solution of lead acetate, were also used.

Application of all four alkoxides resulted in a powder with the purity of 99.95% and the particle size in the range of 75 to 300 Å, which sintered into dense optically transparent ceramics at 1050 to 1175°C without hot pressing. However, for large-scale synthesis, another technique using PbO and aqueous $La(OAc)_3$ was introduced [506]. The following investigations demonstrated that hydrated Ti and Zr hydroxides, which are formed on the hydrolysis of corresponding metal alkoxides, are extraordinarily active and react readily with suspended PbO to form amorphous matrix with uniform distribution of elements [1779]. Crystallization of PZT from this matrix occurs in one stage at 600°C. The sintered ceramic is characterized by the absence of composition fluctuations and residual porosity and therefore demonstrates very good optical properties. The introduction of lead in the form of its acetate did not give very good results as decomposition of $Pb(OAc)_2$ occurs only on calcination and the perovskite phase is thus formed only as a result of the solid-state reactions between the components.

Comparison of different commercially available ZrO_2 samples in sintering of PZT ceramics has demonstrated that crystallization of PZT occurs in one step only if samples prepared by hydrolysis of alkoxides are used [1697].

Despite good laboratory results, metal alkoxides did not find commercial application for sintering of piezoelectric ceramics, presumably because of their high cost. On the other hand, the last decade has been characterized by a tremendous growth of interest in the sol-gel PZT or doped PZT films. In the early 1990s, the sol-gel route to high-quality ferroelectric Pb-based films still was questionable, as films were mostly characterized by poor or variable microstructure and lack of control of the perovskite phase formation. However, after extensive studies performed by numerous research groups, which were aimed at the improvement of solution synthetic methods, hydrolysis and heat treatment parameters, dielectric film/substrate interface, and high-quality textured films were prepared. While solution deposition may not prove useful for all applications of PZT and related films because of potential problems with coating conformity, fabrication of this type has many advantages associated with low capital cost, rapid processing, reasonable reproducibility, and excellent compositional control. When used in conjunction with spin-casting, it is compatible with existing semiconductor fabrication processes. A great variety of techniques for the preparation of the precursor solutions was reported. These techniques, along with the attempts to explain the chemistry of the precursor solutions, are summarized in reviews [1442,1409, 1442].

The most frequently applied and well-known technique is based on the reaction of lead acetate with titanium and zirconium alkoxides suggested by Budd and Dey. It was probably the first successful technique used for preparation of PZT films, which has been tested by numerous subsequent applications by different authors. It is also so far the most widely used conventional technique for PZT films applications [269, 476]. Titanium isopropoxide and zirconium n-butoxide are separately subjected to the exchange reaction with methoxyethanol. Lead acetate trihydrate $Pb(OAc)_2{\cdot}3H_2O$ is dehydrated by dissolution in methoxyethanol and subsequent 3 times distillations of the solvent with repeated addition of fresh portions of methoxyethanol. As a result, acetate groups are partially substituted by methoxyethoxide. To achieve a higher extent of substitution of acetate groups (up to about [OAc]:[Pb] = 0.83) by methoxyethanol, the last distillation may be performed under vacuum. Stoichiometric amounts of Ti and Zr precursors are then added to the lead-containing solution. Before film casting, the stock solution is mixed with the hydrolysis solution.

In the following years many attempts were made to isolate ternary Pb–Ti–Zr complex; however, so far none of them has been successful. On the other hand, many authors have reported the crystallographically characterized bimetallic Pb–Ti and Pb–Zr complexes of different stoichiometry [120, 320, 779, 784, 555]. It is clear that in the system suggested by Dey, numerous chemical reactions proceed, thus making the chemistry of precursors very complicated and strongly dependant on the reaction conditions, which affects the reproducibility of the properties of the films obtained. Several attempts to gain better understanding of the chemistry of the techniques suggested by Dey [985, 1332, 269, 924] were undertaken. Dehydration of lead acetate under different conditions was studied in [1775], and in contrast to the above technique, it was suggested that $Pb(OAc)_2$, obtained in mild dehydration conditions by reaction of $Pb(OAc)_2 \cdot 3H_2O$ with acetic acid anhydride should be used. Anhydrous lead acetate obtained under these reaction conditions does not contain Pb–O–Pb bonds, which hinder further reactivity of $Pb(OAc)_2$ in reactions with Ti and Zr alkoxides. The same work suggested using the electrochemically prepared Ti and Zr methoxyethoxide solutions as precursors, thus avoiding the exchange reactions of aliphatic alkoxides with methoxyethanol. It has also been suggested that lead should be introduced in the form of 2-ethylhexanoate [924].

Modification by acetylacetone is a powerful route, that allows precursor solutions to be stabilized. Interaction of titanium alkoxides with acetylacetone was extensively studied and reviewed in [1391,86]. Study of reactions, occurring on interaction of $Zr(OPr^n)_4$ and Ti–Zr alkoxide mixture with acetylacetone, was performed in [1448] and allowed the authors to simplify the technique for preparation of precursor solution for PZT films application and to overcome the requirement of prolonged refluxing, which certainly decreases reproducibility. After dissolution of titanium and zirconium alkoxides in methoxyethanol, acetylacetone is added to form stable zirconium and titanium stock solutions. The introduction of acetylacetone allowed aqueous lead acetate (and lanthanum acetate for PLZT films) solutions to be added to mixed titanium and zirconium solutions. No reaction steps involving elevated temperatures or distillation or long reaction times are required. The solution could be used both immediately on mixing or after storage for several months. Such solutions were successfully used for application of ferroelectric films.

Another approach to sol-gel PZT precursors involves the reaction of alkoxide mixture with glacial acetic acid [1442, 1790]. Lead acetate and titanium and zirconium propoxides or butoxides are dissolved in acetic acid; the solution is afterward diluted, usually by propanol or methanol containing certain amount of water. **β-Diketones** such as acetylacetone are sometimes added to the precursor solutions to increase their stability. Acetic acid or acetylacetone "modify" $M(OR)_4$ with the formation of oxoalkoxoacetates or oxoalkoxoacetylacetonates with oligomeric structures extensively discussed in literature (see Chapter 7). The characteristic structural feature of these precursors is the metal-oxygen core surrounded by acetate or acac ligands.

Solutions prepared by any of the above-described techniques are spun onto the rotating substrate and dried at the temperature ranging from 150 to 450°C. Spin coating and drying are usually repeated several times. The coated films are finally annealed at 650°C for crystallization. Rapid thermal annealing (RTA) is frequently used for crystallization, demonstrating a positive impact on perovskite phase crystallization. It was also demonstrated by numerous workers that excess of lead (about 10% over stoichiometry) has to be introduced to compensate for the partial evaporation of volatile PbO during thermal treatment. This also allows the formation of pyrochlore admixtures, which represents the major obstacle in the course of PZT films crystallization, to be overcome.

It may thus be concluded that application of metal alkoxides for preparation of PZT-based thin films in many aspects may be nowadays considered to be a routine technique widely used in many laboratories. The research work is presently mostly focused on electrical and microstructural aspects of these films rather than on chemical routes of their preparation. Irrespective of the technique for the precursor preparation, when 10% excess of Pb is introduced (to prevent loss of lead due to the PbO volatility) the ferroelectric perovskite PZT films are obtained after annealing at about 700°C, demonstrating nonlinear properties of the level acceptable for most of the desired applications. Their typical microstructure is presented in Fig .10.3.

10.4. Bismuth strontium tantalates and niobates $SrBi_2M^V_2O_9$ (M^V = Nb, Ta)

Volatility of PbO leads to the so-called fatigue of Pt/PZT/Pt capacitor structures: polarization drastically decreases after the structure is exposed to repeated (about 10^8 cycles) polarization cycles. The fatigue problem may be overcome by application of ferroelectrics without volatile components leading to

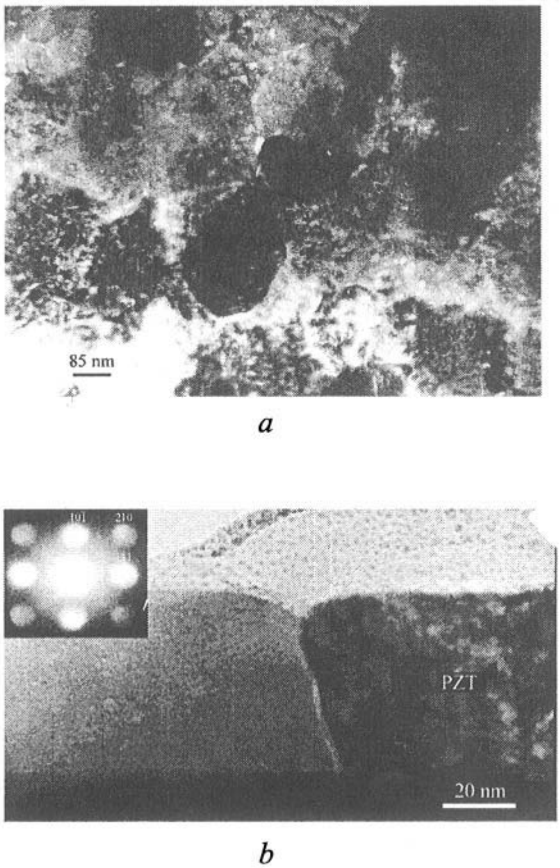


Fig. 10.3. Electron micrographs (*a,* cross-section; *b,* surface) of PZT film prepared from solution containing 10 mole % excess of Pb.

stoichiometry variations [78]. $SrBi_2Ta_2O_9$ (SBT) is such an alternative to PZT. $SrBi_2Ta_2O_9$ films with the thickness of 0.2 to 0.5 μm were applied from solutions in alcohol or xylene of metal alkoxides $Bi(OEt)_3$, $Sr(OPr^i)_2$, and $Ta(OBu^n)_5$ or $Ta(OEt)_5$ and Sr and Bi 2-ethylhexanoates [1029]. Ferroelectric properties are registered after films are crystallized by annealing at 800°C. About 10% excess of Bi is essential for the preparation of perovskites without admixtures. The main admixture is the phase with pyrochlore structure. The main problem for more extensive application of these films is lower remanent polarization than that of PZT films and crystallization temperature of 800 to 850°C, which is too high for microelectronic applications. A few attempts to decrease crystallization temperature were made. Thus, it has been suggested that films be deposited on an intermediate $PbBi_2Nb_2O_9$ layer or that thermal treatment be performed under reduced pressure. To optimize the choice of the alkoxide derivatives for application of these films, the interaction between different Bi and Ta alkoxides was studied. It was demonstrated that Bi and Ta ethoxides were the best alkoxide precursors [1710]. On complete elimination of EtOH used as a solvent, the viscous pastes containing $Bi(OEt)_3$ and $Ta(OEt)_5$ are formed. Such pastes can be stored for a long time without any alteration of their properties or solubility. On the other hand, they are readily dissolved in most organic solvents and allowed to prepare a convenient precursor for films application, when combined with strontium 2-ethylhexanoate. Crystallization of $SrBi_2Ta_2O_9$ in the films obtained by application of these solutions occurred at 700°C. $Si–SiO_2–Ti–Pt–SrBi_2Ta_2O_9–Ni$ structures annealed at 700 and 750°C demonstrated a coercive field of about 50 kV/cm and the remanent polarization Pr*–Pr of 7 to 9 $\mu C/cm^2$.

Kato et al. have prepared solutions in EtOH with the necessary stoichiometry compositions and claimed that corresponding ternary complexes were thus formed; although no evidence for formation of the complexes was given, the solutions were successfully used for the application of $SrBi_2Ta_2O_9$ films [890]. With the ethoxide precursor, after annealing of films in the mixture of water vapor and oxygen, the crystallization occurred at 650°C, and the prepared film with the thickness of 0.12 μm demonstrated switching polarization of 7.7 $\mu C/cm^2$.

Another approach implies the application of glacial acetic acid as a solvent [190,984]. $Bi(OAc)_3$ was mixed and stirred with pyridine. Separately, $Sr(OAc)_2$ and $Ta(OEt)_5$ were mixed and dissolved in glacial acetic acid, then Bi-containing precursor was added, and $Bi(OAc)_3$ was completely dissolved. Deposition on variety of substrates followed by heating at 700°C allowed crystalline films to be prepeared with dielectric parameters suitable for integration.

10.5. High-temperature superconductors

Soon after the discovery of high-temperature superconductivity in 1987, the first data on the preparation of $YBa_2Cu_3O_{7-\delta}$ powders and films were published [1469, 957, 755, 1169, 1559, 1221]. Single crystalline MgO and $SrTiO_3$ were most commonly used substrates; later, Y_2O_3 doped with ZrO_2 was also introduced. Different $Y(OR)_3$ and $Ba(OR)_2$ (R = Me, Et, Pr^i, C_2H_4OMe) were used. The introduction of a Cu derivative into this solution presents the most complex problem.The $Cu(OR)_2$ alkoxides irrespective of R are practically insoluble in organic solvents due to their polymeric nature. A few variations of the technique were suggested to overcome this problem; they mostly take advantage of special conditions known to enhance the solubility of copper alkoxides. Thus, $Cu(OBu^n)_2$ has a very limited solubility in BuOH (about 2%), $Cu(OR)_2$ as well as $Cu(acac)_2$ can be dissolved in methoxyethanol in the presence of $Y(OR)_3$ and $Ba(OR)_2$, and $Cu(OR)_2$ are soluble in alcohols in the presence of ethanolamines $H_nN(OC_2H_4OH)_{3-n}$. In [1614] $YBa_2Cu_3O_{7-\delta}$ powders and films on MgO single-crystal substrates were obtained from the partially hydrolyzed solutions of all 3 metal alkoxides in methoxyethanol. Nevertheless, application of metal alkoxides did not give any substantial decrease of crystallization temperature in comparison with the conventional preparation techniques. This fact is due to the thermolysis mechanism: on thermal treatment at first just simple oxides are formed; crystallization of the 1:2:3 phase occurs only as a result of further solid-state reaction between simple metal oxides. The only advantage of the method is, therefore, the uniform mixture of oxides participating in solid-state reaction. Nevertheless, the sol-gel method became one of the techniques that, along with other methods, is used for the application of thin films for studies of physical properties as well as application of sublayeres in heterogeneous structures.

The Bi-containing high-temperature superconductors received considerably less attention. The $Bi_2Sr_2CaCu_2O_x$ films and ceramics with ($T^K{}_C$80 K) were obtained; films with higher $T^K{}_C$110 K could be prepared only in the Pb-doped system, where a mixture of 2 superconducting phases $Bi_2Sr_2CaCu_2O_x$ (T^K_c 80 K) and $Bi_2Sr_2Ca_2Cu_3O_x$ (T^K_c110 K) was registered. Layered films are always highly (001) textured. The crystallization mechanism did not show any dependence of the precursor compounds and was similar whether metal alkoxides, stabilized metal alkoxides, or 2-ethylhexanoates were used [923, 932, 1587, 1620].

Very careful regulation of the thermal treatment parameters allowed Nonaka to prepare films containing only a high-temperature superconducting phase with T^K_c=110K [1221].

Chapter 11

HYBRID ORGANIC-INORGANIC MATERIALS

During recent decades the metal alkoxides have been used in the quickly developing new area of hybrid organic-inorganic materials. This direction has emerged on the edge of such areas of chemistry as materials science, polymer chemistry, chemistry of metalorganic compounds, and alkoxide-based sol-gel processing. The first detailed report on this topic was made by Sanchez and Ribot [1393], and was followed by a larger review article [860].

Hybrid materials are a new generation of multifunctional materials with a broad spectrum of useful properties and diverse possibilities of application. The very name indicates the presence of both organic and inorganic components. The inorganic part is formed from silicon or transition metal alkoxides via hydrolysis, while the organic is represented by different molecules. These 2 components are difficult to combine (ionic hydrophilic oxides and covalent hydrophobic organic molecules), and to achieve the interaction between them special reaction conditions should be applied. Application of high temperatures is excluded because of low thermal stability of the hybrid systems. The most effective approach to hybrid materials appears to be the sol-gel technique with its specific ability to create the spacious network (macromolecular net) containing M–O bonds under mild conditions using organic solvents and low temperatures.

Inorganic and organic parts of the nanocomposite are multidimensional interpenetrating nets bound to each other by the chemical bonds. The formation of the inorganic part occurs due to polymerization-polycondensation reactions that take place on hydrolysis of metal alkoxides (see Chapter 9), while the organic net originates due to the polymerization of organic monomers. Depending on the extent of interaction between the components, the size of the particles of materials obtained can vary from nano- to submicron size. The properties of the composite obtained are not a simple combination of those of the components but are noticeably modified and improved due to interphase interactions and size effects (being most pronounced in the case of nanocomposites).

The interphase interaction is the key issue, and it has now become common to classify the hybrid materials into two major classes. The first one includes the systems with weak chemical interaction between the components. The organic oligomeric or low molecular weight polymeric molecules are in this case simply introduced into an inorganic matrix and are bound to it mainly due to Van der Waals or hydrogen bonds. The other class contains materials where organic and inorganic components are connected by covalent bonds. In this case the organic components may play both the role of the net and of the modifiers of the net.

The chemistry of hybrid materials applies mainly tetraalkoxysilanes, the metal alkoxides being used at much lower scale because of their much higher reactivity in hydrolysis compared with $Si(OR)_4$ (leading often to the quick formation of precipitates in their case instead of the desired slow gel formation). The mechanism of hydrolysis of metal alkoxides and the means permitting to regulate its speed are described in Chapters 9 and 7. We provide here only some examples demonstrating the developed synthetic approaches to different groups of hybrid materials of the first and the second classes using the metal alkoxides. The numerous literature data dealing with the application of $Si(OR)_4$ and their derivatives for this purpose are not summarized here.

11.1. Systems with weak chemical interactions

Inorganic oxopolymers can easily be generated in situ inside a soluble organic polymer as well as an organic component can easily be introduced into the oxide gels on simultaneous dissolution of the organic substances and the alkoxides. Both approaches lead to the formation *of amorphous composites.*

11.1.1. Introduction of the organic dyes

In the case of the organic dye rhodamine, it has been demonstrated that the interaction of the molecules of dye with the oxide net in the course of formation of the composite turns to be stronger than their interaction with each other. This hinders therefore the formation of dimers (which can lead to the disappearing of the fluorescent properties of the dye). The rhodamine molecules are supposedly absorbed inside the micropores, and the dimerization is negligible even at high concentrations of the dye [80, 483]. Different rhodamine dyes, such as R640, were introduced into the matrix obtained by hydrolysis of the $Si(OEt)_4$–$Zr(OBu^n)_4$ mixed solutions. The low water concentration favors the formation of monomers of rhodamine and their interaction with the inorganic matrix. These materials demonstrate constantly the induced optical anisotropy, which is linearly increased with the concentration of the dye.

11.1.2. Polymers inside the amorphous inorganic sol-gel matrices

There are several kinds of such composites, including the polymers filled in situ by inorganic particles, hybrids formed on simultaneous formation of interpenetrating organic and inorganic networks, and materials obtained by the introduction of organic substances into the polymer inorganic networks.

Practically all these hybrid materials are derived from $Si(OR)_4$. Metal alkoxides are sometimes applied in the reactions of the first type on homogeneous *in situ* generation of the filling by hydrolysis of $M(OR)_n$. Thus poly(n-bytilmethacrylate)-titanium oxide [1080] and polyphosphazenemetaloxide (M = Ti, Al, Zr) [989, 408] were obtained in situ by hydrolysis of solutions of an organic polymer and $M(OR)_n$ in organic solvents (ROH, THF). The hybrid composites obtained are transparent materials with improved physical properties.

11.13. Introduction of organic molecules into an anisotropic inorganic network

Examples of such materials include the composites based on layered vanadium oxides, where the organic molecules are intercalated according to the host-guest principle. Hydrolysis of $VO(OR)_3$ leads to different vanadium oxide structures dependent on the h, influencing not only the size of the particles but even the structure and properties of the oxides formed. Within several hours after water is added to the 1 M solutions of $VO(OPr^n)_3$ in alcohol at h > 100, red tixotropic gels (consisting of negatively charged flat bands) demonstrate a strong trend to intercalation [1019]. Xerogels obtained on their drying at room temperatures — $V_2O_5{\bullet}nH_2O$ — have layered structures and mixed electron-ionic conductivity. Treatment of the gel with solutions of alcohols, alkylamines, sulfoxides, benzidines, and so on leads to facile intercalation of the organic

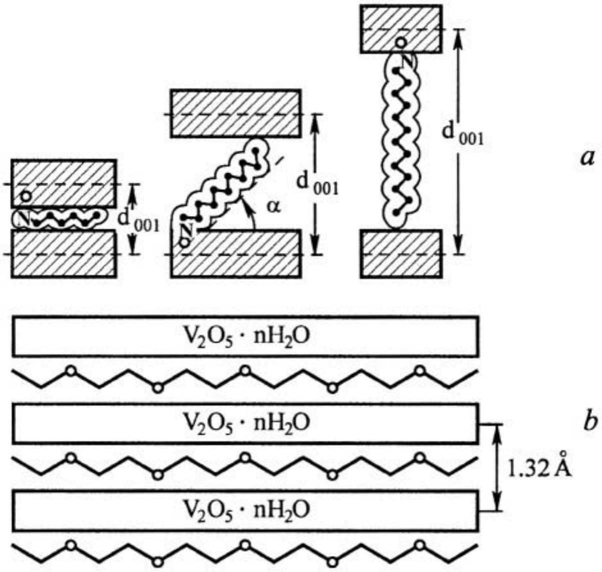


Fig. 11.1. Intercalation of organics into a V_2O_5 xerogel: Orientation of intercalated long-chain $C_nH_{2n+1}NH_2$ [179] (*a*); Intercalated PEO [1373] (*b*).

component. Its driving forces, dependent on the nature of the guest, can be cation or solvent exchange or acid-base or redox interactions. The introduced organic molecules are oriented in the interlayer space in distinct directions, determined by the lattice energies and the energies of Van der Waals and electrostatic interactions. An example is the introduction of $C_nH_{2n+1}NH_2$ alkylamines, where the orientation is dependent on the chain length. At $n < 6$ the molecules are placed parallel to the layers, which minimizes the energy of their shift. At $n > 12$ the organic molecules lay perpendicular to the oxide layers to maximize the Van der Waals interaction between the alkyl chains [179] (Fig. 11.1 *a*).

The gels can incorporate even polymers such as, for example, water-soluble polyethylene oxide (PEO), polyvinylpyrrolidone (PVP), and polypropyleneglycol (PPG). For the PEO/V_2O_5 system the interlayer broadening achieved 13.2 Å, which corresponds to more probable placement of the polymer molecules along the layers [1373] (Fig. 11.1 *b*).

Vanadia xerogels are especially interesting for their redox properties, which promote the catalytical activity of enzymes such as glucose oxydase [644] or induce the oxidative polymerization of organic monomers, such as aniline, pyrrol, and thiophene [873].

11.1.4. Introduction of inorganic oxide clusters into an organic polymer with pores developed by mechanical crazing

The films of organic polymers like polypropylene or polyethyleneterephtalate, when subjected to mechanical tensions, develop systems of micro- and mesopores that make them "transparent" for the diffusion of solutions in solvents not dissolving the polymers itself. The counterflow diffusion of solutions of $MO_2(OC_2H_4OMe)_2$ (M = Mo, W) in $MeOC_2H_4OH$ (from one side) and water solutions (from the other side) permitted composites to be obtained where the metal (Mo, W) oxohydroxide particles were formed *in situ* inside such organic polymer films and remained there after the removal of the solvents [171].

11.2. Systems with strong chemical interactions between components

Their synthesis is based on 2 main approaches — the formation of a new network in the matrix of an initially formed network or during the simultaneous formation of two networks.

In the first case, the initially formed network should contain the functional groups that would be able to react with the other component. Here can be used both macromonomers with inorganic functional groups and a metal-oxygen core with organic functional ones. In the first case, the preparation of hybrid materials is achieved mainly by co-condensation of alkoxides with previously formed macromonomers containing the active terminal groups like OH, $Si(OR)_3$. The most often used organic net-forming macromonomers are the derivatives of trialkoxysilyl (like $HO(SiMe_2O)_nSiMe_2OH$), polystyrene, polyoxazolines, polyethylene oxides, polytetramethyleneoxide, and so on.

Among the few examples of hybrid materials using the metal-oxygen core for their construction is the composite obtained from $BuSn(OPr^i)_3$. The hydrolysis-polycondensation reactions are quite fast for the derivatives of tin (as the increase in the coordination number takes place), but the Sn–C bond is quite stable against the attacks of nucleophilic reagents like water. It makes possible the addition of the organic molecules to the oxopolymers — the tin-

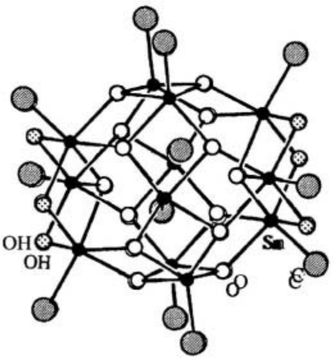


Fig. 11.2. The structure of cation $[(BuSn)_{12}(\mu_3\text{-}O)_{14}(\mu_2\text{-}OH)_6]^{2+}$ [528].

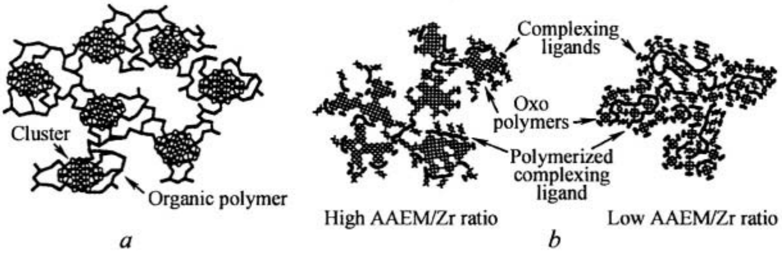


Fig. 11.3. Schematic structure of hybrid materials on the bases: $(Butenyl)Sn(OC_5H_{11}{}^t)_3$ [1393] (a); $Zr(OR)_4$-(AAEM) [1392] (b).

containing oligomers. Thus the hydrolysis of $BuSn(OPr^i)_3$ at h > 3 leads to the formation of the crystalline $[(BuSn)_{12}(\mu_3\text{-}O)_{14}(\mu\text{-}OH)_6](OH)_2({}^iPrOH)_4$ compound. This oxohydroxocluster contains 6 pentacoordinated and 6 hexacoordinated tin atoms, and the metal-oxygen core is surrounded by 12 Bu^n groups that prevent the further condensation [528] (Fig. 11.2). An analogous oxohydroxocluster is formed on the hydrolysis of $(Butenyl)Sn(OC_5H_{11}{}^t)_3$ at h > 3.

The subsequent polymerization of the butenyl groups in the presence of azobisisobutyronitrile (AIBN) at 80°C leads to opalescence in solutions. The reaction results in formation of a composite containing the nets, where the tin oxohydroxoclusters are connected by polybutane chains (Fig. 11.3 *a*)

The introduction of the transition metals into the covalent hybrid materials usually requires a different strategy because of the more ionic character of the M–C bonds and its consequently lower stability to hydrolysis. There are 2 ways to solve this problem: the metal-oxygen core can be connected with the organic components via M–O–Si–C bonds or via the complex-forming ligands containing the organic functional groups that can be polymerized. The first approach was realized by Judeinstein [860], who obtained the polyoxometallates modified by organic groups — $[SiW_{11}O_{40}(SiR)_2]^{4-}$, which contained two unsaturated monomeric groups (R = vinyl, allyl, metacryl, styryl). Their radical polymerization in the presence of azobisisobutyronitrile (AIBN) provided hybrid composites, where the polyoxometallate clusters were connected by polymethacrylate or polystyrene chains.

The other approach can be illustrated by the structures of heteroleptic oxoalkoxide clusters of transition metals containing the polymerizable ligands — $Nb_4(\mu\text{-}OMc)_4(\mu\text{-}O)_4(OPr^i)_8$, $Ti_6O_4(OEt)_8(OMc)_8$ (OMc–methacrylate), and $Zr_{10}(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_4(\mu\text{-}OPr^n)_{10}X_6$ (X = allylacetoacetate) [780, 1439, 1392]. These clusters were produced by controlled hydrolysis of metal alkoxides in the presence of complexing ligands (metacrylic acid, allylacetoacetate). Like the oxohydroxocomplexes of tin, these clusters contain on their periphery the ligands, which polymerization leads to the formation ofhybrid materials, where the nano-blocks of oxoclusters are connected by organic chains. The low size and low h value for these clusters makes them hydrolysis-sensitive and therefore the polymerization should be carried out in anhydrous conditions. This problem can be avoided if larger metal-oxygen cores — for example, the colloid particles — are applied. Thus Caris has carried out the polymerization of methylmetacrylate on the surface of submicron $TiO_2 \cdot xH_2O$ particles, which have been modified with $Ti(OPr^i)_2(OCOCH_2C_6H_{13})(OCO\text{-methacrylate})$ via interaction of the latter with the OH groups on the surface of the $TiO_2 \cdot xH_2O$ particles. These modified species were dispersed in the water solution of sodium dodecyl sulfate, thus creating the micellar systems with the metal-oxygen nuclei. The subsequent polymerization of the metacrylate has led to a hazelnut-like structure, where the TiO_2 nucleus was imbedded in a polymethylmetacrylate shell [295] (Fig. 11.4).

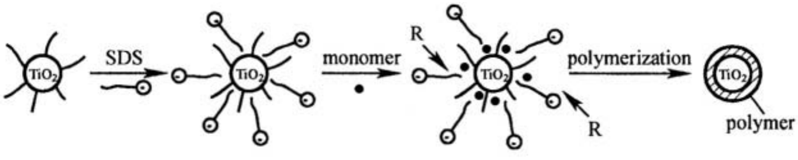


Fig. 11.4. Emulsion polymerization at the surface of TiO_2 particles [295].

The most successful example of formation of hybrid materials with simultaneous formation of inorganic and organic networks is considered to be the approach applied by Sanchez [1392], who applied the interaction of $Zr(OR)_4$ with strongly chelating agents — methacrylamidoalysilate (MASA), acetoacetoxyethylmethacrylate (AAEM) — containing the reactive methacrylate groups. The simultaneous organic and inorganic polymerizations were carried out at 60°C and h = 2 in neutral or basic media in the presence of AIBN as catalyst. The AAEM/Zr ratio varied in 0.25 to 0.75 interval. The study of the milky sols produced (X-ray absorption, IR, NMR) showed that the organic polymerization was carried out with a good yield and the bonds of Zr with the complexing agents were preserved. The experiments with other ligands carried out according to the same scheme — the synthesis of heteroleptic precursors via the addition of the polymerizable ligands to $M(OR)_4$, M = Ti, Zr, their controlled hydrolysis to form oxoclusters or polymers, subsequent polymerization of the unsaturated groups of the organic component in the presence of a catalyst followed by thermal treatment — all turned out to be less successful. Application of the unsaturated carboxylic acids like C_6H_5–CH=CHCOOH was shown to be accompanied by a partial loss of the ligands due to the low stability of the carboxylates to hydrolysis. Application of the allyl acetylacetone for the modification of $Ti(OBu^n)_4$ led to very slow polymerization with extremely low yields. The chelating ligands in combination with $Zr(OR)_4$ turned out to be optimal for the preparation of the hybrid composites, the structure and the texture of the latter being dependent on h and, in particular, on the complexation ratio x = L : Zr. Thus at x = 0.25 the nanosized and at x = 0.75 the submicronsized materials were obtained. In the second case the zirconium oxoclusters were bound by long polymethacrylate chains, while in the first case the short organic chains are connecting the bigger oxoparticles (Fig. 11.3 *b*).

In addition to the examples discussed above, where the hybrid materials were derived from the alkoxides of the transition metals, it is necessary to mention that $M(OR)_n$ (M = Ti, Zr) are the typical inorganic chain-forming reagents often added to the silicon alkoxides to play the cross-linking role between the organosilicon units, which increases the hardness and the refractive index of the hybrid materials. $M(OR)_n$ were also found to catalyze the condensation of siloxanes.

Among the most perspective applications of the organic-inorganic hybrid materials one should mention the preparation of materials with good mechanical properties (the main problem being the study of the influence of polymers on glass fibers and tissues), optical properties (doping by dyes, preparation of waveguides, gel glasses with dispersed liquid crystals), preparation of coatings and membranes (control of porosity, balance of hydrophilic and hydrophobic properties), preparation of photo- and electroactive materials (insertion of redox aims into hybrid matrices), and creation of new biomaterials (improvement of natural systems, synthesis of new microstructural composites).

Chapter 12

THE OVERVIEW OF METAL ALKOXIDE DERIVATIVES ALONG THE GROUPS OF THE PERIODIC TABLE

This chapter considers the alkoxides of *metals* (and therefore does not provide data on the alkoxide derivatives of such nonmetals or semimetals as B, C, Si, P, As, Sb, Se, and Te).

The tables here are organized as follows: first come the derivatives of aliphatic alcohols (n-, i-, s-, t-, c-R for each homologue), then phenols (positioned according to the increase in the number of substituents in the cycle), naphtols, unsaturated, fluorinated, chlorinated alcohols, silanols, polyatomic alcohols (glycols, pinacols, glycerin, pyrocatechol).

Next are placed the classes of alkoxide halides, hydrides, and bimetallic alkoxides. The latter are considered in the chapters devoted to more electronegative metal (in those devoted to the other metal they are mentioned only in the footnotes after the table).

The following data are provided for the distinct compounds: composition, molecular structure, synthetic approach (according to the numeration in the Chapter 2), and main properties (such as physical state, color, m.p., b.p., sublimation temperature (°C/mm Hg), solubility, molecular complexity, magnetic moment *etc.*). Then are mentioned the investigation techniques and given references. The data provided in the tables are shortly discussed for each element (or group of elements) in short reviews accompanying each table.

Unfortunately, length restrictions did not permit us to consider in detail the tremendous amount of information available on heteroleptic complexes, which are briefly reviewed in Chapter 7. The reviews do not consider a broad group of autocomplexes — derivatives of nitro-, aminophenols, ketoenols, and also chloro-, bromo-, and iodophenols that are stable to hydrolysis and are only formal analogs of alkoxides and phenoxides.

The alkoxides are considered in the order corresponding to increasing group number in the Periodic Table — first the derivatives of the main group and then the derivatives of the bigroup.

12.1. Alkaline, alkaline earth, and magnesium alkoxides

This group of derivatives has been known for more than 160 years. The interaction of K and Na with alcohols was first observed by Liebig in 1837. The alkaline alkoxides have been long and broadly used as reactants and catalysts in the organic synthesis; they are described in an enormous number of works, where they usually have not been isolated in the pure form. The paradox with them is that at present their properties appear to be much less studied than those of the derivatives of multivalent metals. The literature reviews on the application of MOR in the organic synthesis are provided in [1420] and [286]. A rather thorough review by Turova and Novoselova from 1965 [1644] has also been devoted to the chemistry of the alkoxides of this group. The interest to the alkoxides of alkaline and especially alkaline earth metals has strongly increased recently in connection with the search for volatile and soluble “precursors” in the preparation of complex oxide materials — high-temperature superconductors, ferroelectrics, and so on. The major success in this area has been achieved by the groups of Caulton and Chisholm on the preparation of the alkoxides and phenoxides with sterically demanding radicals — the compounds that are oligomeric in contrast to polymeric MOAlk and $M(OAlk)_2$. This new generation of alkoxide derivatives has been investigated in a much more detailed manner with the aid of a number of modern methods and the X-ray single crystal study.

12.1.1. Synthesis

In principle, all the methods described in Chapter 2 have been applied for the preparation of the alkoxides of this group. The direct reaction of metals with alcohols (method 1) can be carried out only for the first members of the homologous series and also the phenols. The techniques differ in reaction conditions (the catalysts and solvents applied) and also in the separation conditions for $\mathbf{M(OR)_n}$. For the preparation of unsolvated MOR (being of special interest for the organic synthesis) it was proposed that the highly disperse (“molecular”) metals be taken in steichiometric amounts and that the reactions be observed in hydrocarbon, $\mathbf{Et_2O}$, or THF media [258, 9, 1147, 567, 1023].

Of practically universal character is the technique based on carrying out the metal interaction with alcohol in liquid ammonia proposed by Chablay [313] at the beginning of the twentieth century, which has not received any broad application because of inconveniences connected with this solvent [1740]. The activation of the alkaline earth metals by gaseous ammonia noted by Chablay is used now in the preparation of the derivatives of barium and the “least acidic” alcohols — that is, $\mathbf{[Ba(OR)_2]_2{\bullet}nTHF}$, $\mathbf{R = CPh_3}$, $\mathbf{C_6H_3Bu^t{}_2\text{-}2,6}$, $\mathbf{OC_6H_3Bu^t{}_2\text{-}3,5}$, $\mathbf{Bu^t{}_3Si}$, $\mathbf{Ph_3Si}$, where the usual activation approaches. Catalysis with $\mathbf{HgCl_2}$ or $\mathbf{I_2}$, ultrasound treatment proved to be unsuccessful. THF (at 20°C) and toluene (at –40°C) were applied as solvents in these reactions. The use of hexane for this purpose gave only $\mathbf{[Ba(NH_3)_6]}$ as the product. The mechanism proposed for the metal activation with ammonia includes the formation of an amide intermediate — $\mathbf{M(OR)_x(NH_2)_{2\text{-}x}}$ [497, 303, 1150, 1484].

The alcoholysis of oxides or hydroxides of alkaline or alkaline earth metals (method 3) is used mainly in the industrial preparation of the alkoxides [1644, 1499]. This method has become the major route to the hydrolysis-insensitive phenoxides, even in laboratory practice. The alcohols, benzene, and water have been used as reaction medias.

Concerning the application of hydrides in the preparation of alkali alkoxides (method 4), see Chapter 2 [467, 1716, 246, 628, 1361]. $\mathbf{LiBu^n}$ was found to be a useful initial reagent in the synthesis of LiOR [864, 792], and $\mathbf{MgR_2}$ or ether-free Grignard reagents — in the preparation of magnesium derivatives of s- and t- alcohols [400, 1582]. Sylilamides have been also used in certain cases. Thus $\mathbf{Ba(OBu^t)_2({}^tBuOH)_2}$ could be obtained only on alcoholysis of $\mathbf{Ba[N(SiMe_2)_3]_2}$ [174].

Application of the alcohol interchange reaction (method 6) is limited by certain phenols and also di and trisubstituted glyoxides (while the reaction of metals with glycols gives only monosubstituted derivatives) [745, 621, 575, 1584, 1369]. As redox processes (method 7) can be considered the Grignard-type reactions — the interaction of metal alkyls with carbonyl compounds, which provide access to $[LiOC_5H_7^c(THF)]_4$ [37], $LiOCH{=}CH_2$ [1206], ROMgBr[1210].

12.1.2. Properties

The alkoxides of alkaline or alkaline earth metals are colorless solids very sensitive to moisture and carbon dioxide. A very important detail, which should be taken into consideration in handling MOR and $Ba(OR)_2$ (except methoxides and derivatives of ${}^tROH$) is their trend to oxidation in the presence of the traces of oxygen present in the atmosphere and in solvents (see below).

The derivatives of *n*-alcohols are insoluble in nonpolar solvents, liquid NH_3, SO_2, and so on. The ramification of the radical and decrease in the polarity of the M-O bond decreases the solubility of corresponding alkoxides in alcohols and increases the solubility in nonpolar solvents. The first members of the homologous series (including t-butoxides) form solvates with alcohols, which usually easily lose the first molecules of solvating alcohols, but the complete desolvation is very difficult to achieve. The latter is nearly always associated with partial solvolysis (with formation of oxoalkoxides). The considerable difficulties appear then in the isolation of individual compounds. The exact composition of a number of solvates has been determined by a number of physicochemical techniques (thermogravimetry [498] and tensimetry [1643]). The available structural data indicate their oligomeric nature (even when the desolvation gives polymeric products). All these compounds are therefore well soluble in alcohols, THF, hydrocarbons, and liquid ammonia.

In the solubility polytherms in the $M(OR)_n$–ROH (M = Li, Mg, Ca, Sr, Ba; R = Me, Et) systems, the shape of the liquidus lines has usually a specific character: the solubility of solvates increases with temperature up to their partial or complete desolvation in contact with the solvent. The sign of the ΔH for dissolution changes at this point, and the solubility of the $M(OR)_n$ or less solvated forms decreases drastically with temperature (see solubility polytherms for LiOMe, LiOEt in the Fig. 3.1). The polarity of the M-O bonds in MOR and $Ba(OR)_2$ — the first members of the homologous series — causes their ability to electrolytic dissolciation and noticeable conductivity for their solutions in polar solvents (its value in alcohols is only several times lower than that of such strong electrolytes as NaOH and KOH) [112].

According to the observed desolvation temperatures, the stability of $M(OR)_n{\cdot}mROH$ increases from Li to K and then decreases to Cs (the analogous picture is observed in the Mg–Ca–Ba series); in the homologous series the stability of solvates increases noticeably from 20°C for the methoxides of Ba and Cs to 100°C for propoxides and t-butoxides (see Table 12.1).

Practically all the LiOR, starting with the ethoxide, are transferred into the gas phase without decomposition, while among the Na–Cs alkoxides the volatility is observed only for $MOBu^t$, derivatives of fluorinated alkoxides, and syloxides (whose tetrameric molecules display the cubane-type cores). In the high vacuum (10^{-6}) the sublimation is observed also for $MOPr^i$ (M = K, Rb, Cs) that form a polymeric crystal structure of the same type as LiOMe. The phenoxides with very branched radicals — e.g., $C_6H_3Bu^t_2$–2,6, $C_6H_2Bu^t_2$–2,6-Me–4) and $M(OR^t_F)_2$ — can be sublimed only in high vacuum $(10^{-5}$mm Hg) [1089,757,1321]. Much higher volatility (sublimation at 10^{-1} to 10^{-2} mm Hg) is characteristic of syloxides and alkoxyalkoxides (containing chelate cycles) — $[Ba_6O(OC_2H_4OMe)_{10}(MeOC_2H_4OH)_4]$ and $\{[Ba[OC(CH_2OR)_2Bu^t]_2\}_2$ [1702]. 497, 304, 739]. The alkoxyalkoxides $Ba[O(C_2H_4O)_nMe]_2$, n = 2, 3, reported by Rees [1345], are liquids and display unlimited solubility in nonpolar solvents (in their monomeric molecules the Ba-atoms are surrounded by 6 or 8 oxygen atoms like in the crown-ethers complexes).

It is difficult to trace the general regularities in the thermal stability of the alkoxides following the data of single publications, in spite of the differential thermal analyses being made in some cases. It is well known that the start of the thermal decomposition can be dependent on the purity of the samples, the particle size, thermal prehistory, and so on. It can only be concluded that the pyrolysis of MOR commences at 250 to 330°C independently of the nature of M and R. In the $M(OR)_2$ series the derivatives of barium decompose at 250 to 360°C, at much higher temperatures than those of magnesium (120 to 140°C). The products of thermal decomposition are M_2CO_3 or MOH, H_2, C_nH_{2n}, carbon, and, in case of methoxides of K–Cs the free metals [1578].

The unsolvated MOMe and $M(OMe)_2$ possess polymeric layered structures analogous to that of LiOH [1737, 507, 1729,1728] and $Mg(OH)_2$ respectively [1646; 1517] (see Section 4.8.2). The increase in the size of R in the n-series decreases the order in packing of the layers and leads finally to complete amorphization [1646]. The iso-derivatives (especially those of t-R) are usually oligomeric. The most widely spread and most stable among the MOR are supposedly the cubane-like molecules described for $[LiOR(THF)]_4$ ($R = C_5H_7^c$, Ph

$[C(=CH_2)Bu^t]$, $[C{=}CH(CH_2)_3]^c$ [37,1303]), **$[MOBu^t]_4$** (M = K, Rb, Cs) [1728, 352], **$[MOSiMe_3]_4$**(M = Li, Rb, Cs) [1730], **$[K_4(OSiPh_3)_4]_2Dme_3]$** [592], **$[NaOC(CF_3)_nMe_{3-n}]_4$** [1386], **$[Na(OC_6H_4Me{-}4)Dme]_4$** [548]. The cordination number for the metal atoms in the **$[M(\mu_3\text{-}OR)]_4$** molecules is equal to 3 and increases to 4 or 5 in the presence of solvating ligands. The dimeric **$[LiOCBu^t_3]_2$** molecule contains the 4-member cycles [128], while the solvated **$[LiOR{\cdot}L]_2$ (R = CBu^t_3, $C_6H_3Bu^t_2$-2,6, $C_6H_2Bu^t_2$-2,6-Me-4,** L = THF, **Et_2O)** are pairs of triangles sharing a common edge [795, 934, 792, 311]. In the structure of **$[KOBu^t{\bullet}{}^tBuOH]_2$,** where the alcohol molecules are bidentate, the dimers form a polymer chain [352]). Another type of oligomers known for the alkali alkoxides is a hexagonal prism with a **$[M_6(\mu_3\text{-}OR)_6]$** core. It is represented by **$[LiOR]_6$ [R= $CMe(CHC_2H_4)^c{}_2$, CMe_2Ph, Ph(THF)] [656,** 352,810], and **$[NaOBu^t]_6$** [675]. The structure of the latter contains also the nanomeric **$[NaOBu^t]_9$,** which can be described as hexagonal bipyrmids with 2 cut vertexes. The structure of Li-OBu^t is unknown (in spite of repeated attempts to solve it); however, the mass-spectrometry data indicate the existence of nona- and hexameric molecules in the gas phase [657] and thus permit the analogy with that of **$NaOBu^t$.**

The molecular structures of the alkoxides and phenoxides of divalent metals are more diversified. Monomeric are the phenoxides with rather branched radicals formed in the presence of solvating molecules, — for example, **$\{Mg[OC_6H_2(CF_3)_3\text{-}2,4,6]_2THF_3\}$,** a tetragonal pyramid [1361]; **$[M(OAr)_2THF_3]$** (M = Ca, Sr, Ba, **R = $C_6H_2Bu^t_2$-2,6-Me-4, $C_6H_2Bu^t_3$-2,4,6),** trigonal bipyramids [757,495]; **$[Ca(OC_6H_3Me_2\text{-}2,6)_2(\eta^2\text{-}Dme)_2]$,** an octahedron [551].

Not solvated molecules form dimers of two triangles sharing a common edge, like **$[Mg(OAr)_2]_2$ (Ar = $C_6H_3Bu^t_2$–2,6, $C_6H_2Bu^t_2$–2,6-Me-4)** [288]. The addition of 0.5 mol of solvating ligand per mol of $M(OR)_2$ leads to a combination of 2 tetrahedra with a common face, **$[Ba_2(OSiBu^t_3)_4THF]$** [305]; 1 mol of L produces 2 tetrahedra with a common edge, **$\{Ca[OCPh_2(CH_2C_6H_4Cl\text{-}4)]_2(THF)\}_2$** [1572]; 1.5 mol L, 2 trigonal bipyramids with a common face - **$[Ba_2(OCPh_3)_4(THF)_3]$** [497]; and finally, 2 mol of L, an octahedron and a trigonal bipyramid with a common face, **$[Ca(OSiPh_3)_2(NH_3)_2]_2$** [449]. The trinuclear molecules **($[Sr_3(OPh)_6(Hmpa)_5]$, $[Ba_3(OSiPh_3)_6THF]$,** and **$[KBa_2(OSiPh_3)_5(Dme)_2]$)** contain **$[M_3]$** triangles centered with **$2\mu_3$-OR-groups** [304, 398]. The cubane-type cores are observed in the structures of solvates such as $Mg(OMe)_2{\cdot}3.5MeOH$ [1524] and $Ba(OBu^t)_2(Bu^tOH)_2$ [174], where a half of the OR-groups are terminal and the metal atoms are octahedrally coordinated. Nonamers are represented by $Ca_9(OC_2H_4OMe)_{18}{\cdot}2MeOC_2H_4OH$, which core is a fragment of CdI_2-type packed planar layer, containing 3 octahedra in the center and six 7-vertex polyhedra on the periphery [654].

The change in the ionic contribution in the M–O bonding in $M(OMe)_2$ and $M(OEt)_2$ series for the Group II elements is clearly illustrated by the comparison of their IR spectra. It is to be noted that these are the C-H stretching frequencies and not the C–O ones, as one might suppose, that appear to be most sensitive to the electronegativity of metal. Thus from Be to Ba the v(E) Me decrease with nearly $200\ cm^{-1}$, supposedly due to the induction effect along the M-O-C-H chain [681].

Among the chemical reactions of this group of alkoxides, special attention should be paid to oxidation (in particular the uncontrolled one) with the oxygen gas. A thorough investigation of this process was carried out by LeBerr [999]. The primary products of this reaction contain peroxide groups such as -OOR and -OOH [241], which decompose by a radical pathway producing water and oxo- and carboxylic groups in the coordination sphere of the metal atoms. This process is accompanied by the appearance of yellowish brown color, whose intensity increases noticeably on storage of the samples or on reflux (in the solutions in alcohols). Thus from the yellow solutions of $Ca(OEt)_2$, obtained on long-term reflux, there was observed crystallization of an oxocomplex — $Ca_6O_2(OEt)_8 14ROH$ (whose molecular structure is composed of two cubic cores with a common edge $[Ca_2(oxo)_2]$, Fig. 4.11 *c*) [1653]. The color is supposedly due to free radicals present in trace amounts, which was confirmed by the data of an ESR study of the colored $Ba(OR)_2$ samples). Appearing the IR spectra of such samples are the new bands corresponding to v(OH) of the alcohol molecules and also v(COO) and $\delta(OCO)$ of a formate group formed on decomposition of peroxides independently on the nature of the original radical [1654]). The trend of alkoxides to oxidation increases in the series Li << Cs, Mg << Ba and $Et < Bu^n << Pr^i << C_2H_4OMe$ [1654], which corresponds to the rate of the radical formation (which has been determined by ESR in particular for LiOR) [70]. It appears thus natural that the barium reaction with 2-methoxyethanol inspite of extraordinary precautions leads to an oxoalkoxide,

$[Ba_6O(OC_2H_4OMe)_{10}(HOC_2H_4OMe)_4]$ [1304], while the corresponding calcium complex **$Ca(OC_2H_4OMe)_2$** is quite stable to oxidation [654].

The samples obtained in hydrocarbon media with steichiometric amount of alcohol turn to be much more stable compared to those obtained from alcohol solutions or by desolvation of **$M(OR)_n{\cdot}xROH$.** The oxidation ofthe alkoxides on their synthesis in hydrocarbons is hindered supposedly by their precipitation and also by much lower solubility of **O_2** in hydrocarbons in comparison with alcohols. The microhydrolysis promotes apparently the oxidation via introduction of the alcohols into the systems. Concerning the difference in the properties of the samples containing oxo- microadmixtures and those of the pure **$M(OR)_n$**, see Chapter 5.

Due to the obstacles described above, the products of interaction of the metals with alcohols turn out usually to be polynuclear oxocomplexes especially characteristic of barium. Their molecules can be considered to be the products of the condensation of metal atoms around polydentate oxo- or hydroxogroups.Thus them olecules of **$[Ba_5(\mu_5\text{-}O)(OPh)_8(PhOH)(THF)_8]$** [303], **$[Ba_5(\mu_5\text{-}OH)(OC_6H_3Bu^t_2\text{-}3,5)_9THF_5]{\bullet}PhMe$ [1150], $[Ba_5(\mu_5\text{-}OH)[OCH(CF_3)_2]_9THF_4(H_2O)]{\cdot}THF$** [1702], and **$[LiMg_4(\mu_5\text{-}O)(\text{-}OC_6H_3Me\text{-}2)_7THF_4]$** [727],contain the tetragonal pyramidal $[M_5O]$ cores. The molecule of **$[Ba_8(\mu_5\text{-}O)_2(OPh)_{12}(PhOH)_2(Hmpa)_6]{\bullet}2PhMe$** can be described as 2 **$[Ba_5O]$** tetragonal pyramids with a common **$[Ba_2]$** edge [304]. In the molecule of the abovementioned 2-methoxyethoxide, **$[Ba_6(\mu_6\text{-}O)(OC_2H_4OMe)_{10}(MeOC_2H_4OH)_4]$**, the 6 barium atoms form an octahedron around the hexadentate oxygen atom [304].

The appearance of the oxogroups in the molecular structures of these compounds is not connected with microhydrolysis (as was usually supposed). This is testified by high yields of the products and good reproducibility of the experiments carried out by different researchers and under different conditions. Caulton *et al.* [174] supposed that this phenomenon is caused by the redox processes that proceed with the participation of the metal. The preparation of the pure **$Ba(OR)_2$** should apparently be based on alcoholysis of organometallic compounds, silylamides, and so on.

Alkaline and alkaline earth alkoxides form numerous bimetallic complexes with the alkoxides of the Groups III to VIII. The information available about those is presented in the chapters devoted to multivalent metals. The Tables 12.1 and 12.2 list only the few compounds where both atoms belong to the title groups, such as $KBa_2(OSiPh_3)_5(Dme)$ [398], $KSr(OPr^i)_3$ [1690]; $Li_2Mg(\mu\text{-}OC_6H_4Me\text{-}2)_4(Tmeda)_2$ [727], and $H_2Sr_6Ba_2O_2(OPh)_{14}(Hmpa)_6$ (a structural analog of the barium phenoxide) [304]. Among the complexes of the alkaline atoms it is necessary to note $LiOR{\bullet}LiR'$ [102], and $MOR{\bullet}LiR'$ — the intermediates in the metalalkyls preparation via metathesis of MOR (M = Na–Cs) with LiR [1023].

The metathesis reactions, where MOR or $M(OR)_2$ are used as alkaline agents in nonaqueous medias, provide efficient approaches to high-purity samples of MHal [1000], M_2S, and M_2S_n [805, 806, 1009, 1036], MHSe [1566], silicates [1593], peroxides, oxides [77], and so on. The most important, however, is played by the metathesis of M^1OR with $MHal_n$, which is one of the major routes to the alkoxides of multivalent metals (see Section 2.5).

Among the heteroleptic derivatives of the considered metals, major attention is paid to to magnesium alkoxide halides — the intermediates in many reactions of organic synthesis and also catalysts of Meerwein-Schmidt reaction, aldol condensation, and so on. Their formation was postulated in a tremendous number of reactions such as Grignard syntheses, alcoholysis and oxidation of RMgHal,* and complex formation of alkoxides and halides. The individual $HalMgOR{\bullet}nEt_2O$ (R = Me, Et, Pr^n, Bu^t, Hal = Cl, I, n = 0 – 1) — possessing the characteristic X-ray powder patterns and IR spectra — were obtained on alcoholysis of Grignard reactants in ether media and also on thermal decomposition of "cements" formed on interaction of alkoxides with halides in alcohols. Shearer *et al.* have carried out an X-ray single crystal study of $[MgBr(OBu^t)(Et_2O)]_2$, whose molecule is built up of 2 tetrahedra sharing a common edge [138]. Magnesium alkoxide halides are quite stable in the presence of ether or hydrocarbons, but on action of polar solvents they decompose — in contradiction to the earlier literature data giving the individual components. The speed of this decomposition increases in the series $THF < Me_2CO < ROH$ [1650]. The physicochemical investigation of the interaction in the $Mg(OR)_2$–$MgHal_2$–ROH (R = Me, Et, Hal = Cl, I) systems has indicated the formation of a crystalline complex — $[Mg_4(OMe)_6(MeOH)_{10}]^{2+}Cl^-{}_2$ (which cation demonstrates a cubane core analogous to that of $Mg(OMe)_2 3.5MeOH$ but

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* The alkoxide nature of these products was ultimately proved by Nesmeyanov and Sazonova in 1941. They were initially considered to be adducts of RMgX with oxoderivatives [1210].

Table 12.1. Alkaline alkoxides

Chemical composition. Structure	Synt. route	Properties	Investig. methods	Ref.
Li				
[Li(μ_4-OMe)]$_\infty$ *anti*-PbO struct. type with alternating [ROLiOR] layers,[$LiO_{4/4}$]-tetrah., [OLi_4]-tetragon. pyr.	1	powd., 310 (dec.), s. in ROH (polytherm), in liq. NH_3, hc., invol.	IR, X-r powd., conduct.	112, 212, 313, 507, 852, 871, 1460, 1489, 1557, 1643, 1737
·2MeOH = $Li_4(\mu\text{-}OR)_4(\mu\text{-}ROH)_2(ROH)_4]$ ·2ROH, square [Li_4], 2 cycles [$Li_2(\mu\text{-}OR)_2$], 4 cycles [$Li_2(\mu\text{-}OR)_2(\mu\text{-}ROH)$]		cr., 28 (dec. under s.), s. in ROH 12%, p_{diss} (polytherm)	X-r	1521, 1643
LiOEt ↑100°/vac.	1, 4, 5	powd., 150/10^{-2} (subl.), 325 (dec.), ins. in hc., α= 6, 4 (m-s), ΔH_{form}= -108.6	IR, ^1H, m-s, DTA, thermochem., conduct.	112, 159, 184, 342, 864, 871, 1489, 1557
·2ROH		cr., 62 (m.), s. in ROH 16.4%, s. in liq. NH_3, 55 (dec. under s.), p_{diss} (polytherm)	tensim.	184, 313, 1643

$LiOPr^n$	1	sld., s. in ROH 23, in C_5H_{12} 1%	IR	871, 1489, 1557
$LiOPr^i$	1, 4	sld., 170/0.1 (subl.), v. s. in C_5H_{12}- 3.78 M/l , ins. in ROH, α=11.5 ($C_6H_{12}^c$), 4 (THF), 6, 4 (m-s)	IR, ^1H, m-s, cryosc., ebul.	697,864, 871, 1489, 1557, 1562
$LiOBu^n$	1, 4	sld., ins. in ROH, hc., α=6, 4 (m-s),	IR, ^1H, ^7Li, m-s	313, 657, 864, 871, 1267, 1489, 1557, 1562
$LiOBu^i$ $\cdot$nROH	1, 4	sld.,100/10^{-2} (subl.), s. in ROH 1.3, in C_5H_{12} 45.3%, α=3-5	IR, ^1H	313, 871, 1489
$LiOBu^s$	1	sld., s. in ROH 2.8%, in C_5H_{12} 81%, α=9 (bz.)	IR	313, 871, 1489, 1489, 1557
$LiOBu^t$	1, 4, 7	sld.,170-205(m.), 110/0.1 (subl.), 250 (dec.), s. in hc., eth., in THF 22%, in b. ROH 8%; α=9 (bz.),6 (m-s, tol, eth., CCl_4), 5-4 (C_6H_{12}, Py, R_2O, ROH); μ=0.74	IR, ^1H, ^{13}C, ^7Li, ^6Li, m-s, cryosc., ebul., X-r (parameters)	352, 657, 675, 697, 713, 871, 1023, 864, 949, 1289, 1489, 1557
$[Li_8(OH)_3(OBu^t)_5]_2$= $[Li_8(\mu_4\text{-}OH)(\mu\text{-}OH)_2(\mu_3\text{-}OR)_5]_2$, CN Li 3, 2	hyd-rol.	sld., s. in hex.	X-r	986

$LiOC_5H_{11}{}^i$	1, 1a	powd., $100/10^{-2}$ (subl.), s. in liq. NH_3 lower layer, $\alpha=3\text{-}5$ (bz.)	IR	313, 810, 1489
$LiOC_5H_{11}{}^{neo}$	4	sld.,220 (m.), $135/10^{-4}$ (subl.), s. in hc.	IR, ^1H, $^{13}C\{^1H\}$	652
$LiOCHEt_2$	1, 4	sld.,$100/10^{-2}$ (subl.), $\alpha=9$ (bz.); 6, 4 (m-s)	m-s., ebul., cryosc.,	864, 1489, 1557
$LiOCHMePr^i$	1	sld., v. s. in hc., Diox, ins. in ROH, $\alpha=9$ (bz.)	cryosc., ebul.	1557
$LiOC_5H_{11}{}^t$	1	cr., s .in hc., Diox, ins. in ROH, $\alpha=9$ (bz.)	cryosc., ebul.	1557
$[Li(\mu_3\text{-}OC_5H_7{}^c)THF]_4$, cube $[M_4O_4]$, CN Li 4	7	cr., s. in THF	X-r	37
$LiOCEt_2Me$, $LiOCEt_3$	4	cr., s. in bz., eth.	-	39
$LiOCHBu^t{}_2$	4	-	-	167
$[LiOCBu^t{}_3]_2$, cycle **$[Li(OCBu^t{}_3)(THF)]_2$** 2 trian. sharing a $(\mu\text{-}OR)_2$ side	4	cr., 140(m., dec.) cr., 116 (m.), s. in hex., THF	^1H, ^7Li, X-r X-r	128, 1030 795
$\{Li[\mu_3\text{-}OCMe(CHCH_2CH_2)^c{}_2]\}_6$ hexagon. prism $[M_6O_6]$, $[LiO_3C_3]$	4	cr., s. in hex., $\alpha=3$	^1H, $^{13}C\{^1H\}$, m-s, X-r	656
$[Li(\mu_3\text{-}OCMe_2Ph)]_6$ hexagon. prism $[M_6O_6]$, CN Li 3	1	cr., 170 (m.), $120/10^{-1}$ (subl.), 250 (dec.)	IR, ^1H, ^{13}C, ^7Li, m-s, X-r	352
$LiOC_{10}H_{19}$ (menthoxyd)	1	cr., s. in THF	-	1023

LiOPh	3	sld., 476 (m., dec.), s. in system LiOPh-PhOH-H_2O, v. s. in H_2O, EtOH, Me_2CO, α =1 (PhOH)	IR, electr. sp., DTG, X-r powd.	145, 565, 1672
·$2H_2O$	1, 3	cr., s. in H_2O 12.5%	-	1672
[Li(μ_3-OPh)THF]$_4$·PhOH, cube	1	cr., s. in hex., THF	X-r	1303
[Li(μ_3-OPh)THF]$_6$ hexagon prism [M_6O_6], CN Li 4	4	cr., α=4-6 ($C_2H_6O_2$)^c, 4 (THF)	^1H, ^7Li, X-r	810, 1483
[Li$_2$(μ-OPh)$_2$ (18-crown-6)]$_2$, linear chains, the center a cycle [M_2(μOR)$_2$]		cr., 143 (m.), ins. in eth., hex.	IR, ^1H, ^{13}C, electr. sp., X-r	1720, 1184
[Li$_2$(μ-OPh)$_2$(15-crown-5)]$_\infty$		cr., 196(m.)		
LiOAr, Ar=C_6H_4Me-2,C_6H_4Et-2,$C_6H_4Pr^n$-2, $C_6H_4Pr^i$-2, $C_6H_4Bu^t$-2, $C_6H_3Me_2$-3.5, $C_6H_3Me_2$-2.6, C_6HMe_4-2,3,5,6		wh. powd., $\alpha=2\leftrightarrow 4$	^1H, ^{13}C, ^7Li, η, tensim.	810, 1594
[LiOC$_6$H$_3$Me$_2$-2,6] ∞, **[LiOC$_6$H$_3$Me$_2$-2,6(Et$_2$O)$_2$]$_2$**	1	powd., α=2 (THF), s. in hc.	IR, ^1H, X-r	759, 810, 1473
[Li(OC$_6$H$_3$Pr$^i_2$-2,6)(Et$_2$O)]$_n$	4	powd., 120-170 (dec.)	^1H, ^{13}C	504, 617
Li(OC$_6$H$_3$Bu$^t_2$-2,6)				810
[Li(OC$_6$H$_3$Bu$^t_2$-2,6)L]$_2$, L=Et_2O, THF, Dmso 2 trian. sharing a (μ-OR)$_2$ side, CN Li 3	1, 4	cr., 170(m., dec.)-**THF;** 296(m.), α=2 **Et_2O;** s. in hex.-tol.	^1H, X-r	312, 504, 792, 934, 1078, 1473
[Li(OAr)(Et$_2$O)]$_n$, Ar = $C_6H_3Bu^t_2$-2,4, 3,5		cr., 211 (dec.), >300 (m.)	^1H, ^{13}C	

$[Li(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)L]_2$, L=$Et_2O$, THF, 2 trian. sharing a (μ-OR)$_2$ side, CN Li 3	4	172 (m.) - **Et_2O,** s. in hex-eth., α=2	IR, ^1H, X-r	
$[Li(OC_6H_2Bu^t_3\text{-}2,4,6)(Et_2O)]$	4	cr., 294(m.), s. in eth., α=2	^1H	312, 1372
$[Li_3(\mu\text{-}OC_6HPh_2\text{-}2,6\text{-}Bu^t_2\text{-}3,5)_3]$ trian. $[Li_3]$, CN Li 2	4	cr., s. in tol., ins. in hex.	^1H, X-r	1700
$LiOC_{10}H_7\text{-}\beta$	1	sld., s. in ArH	-	1806
$LiOCH{=}CH_2$	7	sld., s. in eth., bz., $+H_2O \rightarrow MeCHO$	IR	1206
$LiOC({=}CH_2)Bu^t$ $=[Li(\mu_3\text{-}OR)]_6$ hexagon. prism $[Li_6O_6]$, π- bonds Li...C=C	4	cr., s. in hc.	X-r	1023, 1748
·THF, cube $[M_4O_4]$, CN Li 4	7	sld.		37
$\{LiO[C{=}CH(CH_2)_3]^c\ THF\}_4$ struct. analog of the previous one	F	sld.	X-r	37
$Li_{33}H_{17}(OBu^t)_{16}$, the core of condensed $[Li_4H_4O]$ cubanes **$Li_{10}H(OBu^t)_9$, $Li_{12}H(OBu^t)_{11}$**	com-plex	cr., dec. in $C_5H_{10}{}^c$ in a few week	X-r	761
$LiOCH(CF_3)_2$	4	sld.,194(m.), 50/0.05(subl.)	-	467
$LiOC(CF_3)_3$	1, 4	142 (m.), 218 (b.), v. s. in eth., Me_2CO, α=1.4	IR	467
$LiOC_6H_2(CF_3)_3\text{-}2,4,6 \cdot 0.75Et_2O$	4	102 (dec.)	IR, ^1H, ^{19}F	1361

$LiOCH_2SiMe_3$	4	sld., 222 (m.), 140/10^{-4} (subl.), s. in bz.	IR, ^1H, $^{13}C\{^1H\}$	652
$[LiOSiMe_3]_4$, cube $[M_4(\mu_3\text{-}OR)_4]$	1, 4	cr., 120(m.,dec.), 115/1 (subl.), s. in hc.,eth., α=4, 6 (m-s), 7(s)	IR, ^1H, m-s, ebul.,cryosc.	1419, 1558, 1730
$[Li(OSiPh_3)]_n$↓ **$[Li(OSiPh_3)(\eta^2\text{-}Dme)]_2$** 2 tetrah. sharing a $(\mu\text{-}OR)_2$ edge	4	wh. powd. cr., s. in Dme, ins. in hex.	IR, ^1H, ^{13}C, X-r	1093
$LiOC_2H_4OEt$	1	-	-	1243
$[LiOCMe_2CH_2OMe]_6$		110/10^{-3} (subl.)	m-s	732
$LiOC_6H_4OMe$-2, **$LiOC_6H_4(CH_2OMe)$-2**	4	sld., s. in Py, eth., α=2, 4	^{13}C	810
$LiOC(CF_3)_2C_2F_4OCF(CF_3)_2$	F	visc.liq., 155/0.3 (b.), α=1	IR, m-s	1544
$LiOC_2H_4OH$, **$[Li_2(\eta^2,\mu\text{-}OCH_2\text{-})_2{\cdot}H_2O]_\infty$**, layered struc. with cycles $[LiO_2C_2]$	1	200° → $(LiO)_2R+R(OH)_2$	IR, X-r	313, 407, 621
$Li_2[(CF_3)_2CO]_2{\cdot}THF$	4	-	-	515
$LiOCH_2(CHOH)_2CH_2OLi$ **$LiOCH_2(CHOH)_4CH_2OLi$** (derivative of mannit)	1	-	-	313
$LiOC{\equiv}COLi$	1, 7	yel. powd, ins. in liq.NH_3, pyrophor	IR, X-r powd.	266
Na				

[NaOMe] $_{\infty}$ struct. analog of LiOMe, $[Na(\mu_4\text{-}O_{4/4})]$ -tetrah. ↑170°		powd., **d=1.28,** 300° → Na_2C_2+ Na_2CO_3 +H_2+C; system NaOR - ROH (polytherm), s. in ROH, ins. in THF, ΔH^{o}_{form}=-89	IR, ^{1}H, thermochem DTA, conduct., X-r powd.	112, 258, 313, 498, 567, 677, 852, 959, 998, 1023, 1270, 1489, 1460, 1578, 1729, 1737
·2MeOH **·nMeOH,** n=3, 4, 5 ↓ H_2O(trace)	1, 4	cr., $p_{dec.}$ (polytherm) n,m.:(**3**,-3),(**4**,+6), (**5**,+30);s. in ROH 32.1%	X-r powd.	498, 576, 887, 892, 1262, 1737
$[Na(\mu_5\text{-}OMe)_{0.67}(\mu\text{-}OH)_{0.33}]_{\infty}$ struct. analog of KOMe, 1/3 OR substituted statistically with OH, $[NaO_{5/4}]$- tetragon. pyr.		powd., **d=1.63**	X-r powd.	1729
NaOEt ↑90°/vac.	1, 4	powd.,320°→NaOH+ H_2 +C_2H_4+C; ins. in liq. NH_3, THF, ΔH^{o}_{form}= -98.5	IR, DTA,TGA, thermochem	9, 159, 258, 313, 567, 998 1023, 1147, 1460, 1489, 1578, 1276
·2ROH		cr., s. in liq. NH_3, ROH - 21.8% (20°)	tensim., thermochem	184, 342, 576, 887, 1740
NaOPr^n **·2ROH,**	1	320 (dec.), ΔH^{o}_{form} = -99 cr., 220 (dec.)	IR, thermochem	567, 576, 1460
NaOPr^i **·3, 2(?) ROH**	1	220 (dec.); s. in THF; ΔH^{o}_{form} = -110	IR, ^{1}H, thermochem	567, 1023, 1460
NaOBu^n **·2ROH**	1, 6	powd., s. in liq. NH_3,THF, ΔH^{o}_{form} = -111	thermochem.	313, 567, 959, 998, 1023, 1270

NaOBu^i , ·2ROH	1	powd., s. in $C_6H_4Me_2$; cr., $\Delta H^o_{form} = -115.6$	-	313, 567, 576
NaOBu^s , ·3ROH	1	cr., 200(dec.), s. in THF D	IR	567, 576, 1023, 1460, 1277
NaOC$_4$H$_9$^{t} =$[Na(\mu_3\text{-}OR)]_6[Na(\mu_3\text{-}OR)]_9$, trig. prism [$M_6$] and doubly truncated hexagon. bipyr. [M_9] with alternating pyr. [NaO_3] and μ_3-O, **·L, L=ROH, THF**	1	cr., 140/10^{-3} (subl.); 186 (dec.); s. in THF 16%, in b. ROH 7.8%, hex., α=8 (bz.),4 (THF,Py), 1(ROH); $\Delta H^o_{form} = -114.$	IR, TGA, thermochem X-r X-r powd.	452, 675, 697, 949, 998, 1023, 1289, 1075 1386, 1276
NaOC$_5$H$_{11}$^{n}	1	s. in liq. NH_3	-	258, 313
NaOC$_5$H$_{11}$^{i}	1, 3	amor. powd., 270(dec.), $\Delta H^o_{form} = -124.6$	thermochem.	313, 258, 576
NaOCHMePr^n	1	$\Delta H^o_{form} = -116.$	thermochem	998
NaOC$_5$H$_{11}$^{t} , NaOC$_8$H$_{17}$^{n}	1, 6	powd.		1023, 1499, 1270
NaOC$_{12}$H$_{25}$^{n}, NaOCH$_2$Ph, NaOCHPh$_2$	1, 4	powd., ins. in THF	-	1023, 959
NaOCPh$_3$	1	cr., ins. in ROH, α=1, μ=1.62 (Diox)	cryosc.	161, 1198
NaOC$_{10}$H$_{19}$ (menthoxyd)	1	amor. powd., s. in THF	-	258, 1023
[NaOPh]$_\infty$, polymer chain $[Na_2(OPh)_2]_\infty$, CN Na 3	1, 3, 6	powd.,385(m.),450(dec),v. s. in H_2O, liq.NH_3, ins. org. solv., α=0.86(PhOH), $\Delta H^o_{form} = -78$	IR, electr. sp., cryosc., TGA, X-r , thermochem	145, 482, 567, 579, 998, 1740

$[NaOPh \cdot 2PhOH]_\infty$ 2 mol. linked into chains of cylces by either Na...O or Na... π-Ph interaction		cr., 150 (m.), NaOPh - PhOH (polytherm)	X-r	145, 858 482,
$\cdot xPhOH \cdot yH_2O$, x, y = (0, 3), (1, 3.5), (1, 7), (1,8)		cr., s. in system NaOPh - $PhOH$-H_2O; m: 52; 34.7; 19(dec.); 21	-	1012, 1672
$\cdot NaOH \cdot 2.5H_2O$		cr.		
$\cdot nH_2O$, n=1 and 3 (layered struct., tetrah. $[Na(\mu\text{-}H_2O)(\mu\text{-}OPh)]\infty$ and tetrah. pyr. $[Na(\mu\text{-}H_2O)_5]$, OPh....H_2O) ; 5; **$\cdot 0.5C_4H_8O_2$**		cr., 52(m.)	thermochem X-r	579, 1483
$\{[Na(MeOH)_4]^+(OPh)\}_\infty$, linear chains of oct. $[Na(\mu\text{-}ROH)_4(ROH)_2]$-*trans*			X-r	974
$[Na_2(\mu\text{-}OPh)_2L]_2$, L=15-crown-5, $C_6H_{11}{}^c$-15-crown-5, 18-crown-6 etc., isostr. with its Li- analog		cr., ins. in eth., hex., m: 151 (15-C-5), 136 ($C_6H_{11}{}^c$-15-C-5)	IR, ^1H, ^{13}C, electr. sp., X-r	1184,1720
$NaOC_6H_4Me$-2, $3ArOH$, **$\cdot nArOH \cdot 6H_2O$,** n=1, 2, **$\cdot H_2O$,** **$\cdot 3NaOH \cdot 6H_2O$**	3, 5	cr., s. in system NaOAr – ArOH -H_2O (0-50°)	-	1012
$NaOC_6H_4Me$-3	1,3, 6	sld., 94(m.), 450(dec.)	-	1740

$[NaOC_6H_4Me\text{-}4]_\infty$, linear chains of tetrah. $[Na_4]$, bitetrah. $[Na_6]$, **·Dme=** $[Na(\eta^2\text{-}Dme)(\mu_3OAr)]_4$, cube $[M_4O_4]$, CN Na 5	1, 3, 6	cr., 125(m.), 450(dec.)	X-r	548
NaOAr, $Ar=C_6H_3Me_2$-2,4,-2,5,-3,4; C_6H_3Me-5-Pr^i-2	3, 6	sld., 43-83 (m.)	-	152, 590
$[Na(OC_6H_3Bu^t{}_2\text{-}2,6)]$ **$[Na(OC_6H_3Bu^t{}_2\text{-}2,6)Dmso_2]_2$** 2 tetrah. sharing a $(\mu\text{-}Dmso)_2$ edge	1	cr.,s. in tol., THF, Dmso	X-r	1078, 1079
$NaOC_6H_3Ph_2\text{-}2,6$	3	sld., s. in THF, tol.	^1H	460
$[Na(OC_6H_2Bu^t{}_3\text{-}2,4,6)L]_n$, L= Et_2O, THF	1 (I_2)	cr., s. in bz., THF	-	312; 1148
$NaOC_{10}H_7\text{-}\alpha$, $NaOC_{10}H_7\text{-}\beta$	3, 6	sld., 45 (m.), 120 (m.), s. in hc., NH_3	-	152, 1583, 1740, 1806
$NaOCH=CH_2$, **$NaOCH_2CH=CH_2$**	1, 7	sld., ins. in eth., bz., $+H_2O \rightarrow MeCHO$	IR	1206, 313
$[NaOC(CF_3)_3]_4$, cube $[M_4(\mu_3\text{-}O)_4]$	1, 4	cr., 143 (m.), 30/10^{-2} (subl.), 119 (dec.), s. in eth.	^1H, ^{19}F, m-s, TGA, X-r	467, 1386
$[NaOCH(CF_3)_2]_4$, cube $[M_4(\mu_3\text{-}O)_4]$	1, 4	cr., 114 (m.), 80/10^{-2} (subl.),140 (dec.),s. in eth.	IR, ^1H, ^{19}F , TGA, X-r	467, 1386, 1387
$NaOCMe(CF_3)_2$	4	cr., 100/10^{-2}(subl.),162 (dec.), s. in eth., C_6F_6	IR, ^1H, ^{19}F TGA, X-r	1386

$[NaOCMe_2CF_3]_4$, cube $[M_4(\mu_3\text{-}O)_4]$, 9 intra and intermol. Na...F contacts	4	cr., $120/10^{-2}$ (subl.), 177 (dec.), s. in eth.	^1H, ^{19}F, TGA, X-r	1386
$NaOC(CF_3)_2C_2F_4OCF(CF_3)_2$	F	visc.liq.,155/0.1(b.),α=1	IR, m-s	1544
$NaOC(CF_3)_2(CF_2Cl)$	4	sld., 122(m.), 80/1(subl.), 250(dec.),s. in eth., MeCN	-	467
$NaOC(CF_3)_2(CCl_3)$	4	cr.,170/0.1(subl.),210 (dec.), s. in eth., Me_2CO	-	467
$[Na[OC_6H_2(CF_3)_3\text{-}2,4,6](THF)_2]_2$ 2 tetrah. sharing a $(\mu\text{-}OR)_2$ edge, **·1.5THF**	4	cr., 126 (dec.)	IR, ^1H, ^{19}F, m-s, X-r	246, 1361
$[NaOSiMe_3]_4$, cube $[M_4(\mu_3\text{-}OR)_4]$ **$NaOSiPh_3$, $NaOSiMe_2Ph$** **$NaOSi(OMe)_3$**	1, 4 1	cr.,147 (m.,dec.), 140/ 10^{-3} (subl.), s.in hc., α=10 (bz.), 87 (m.), s. in hex. sld., s. in THF	IR,^1H, m-s, ebul.,cryosc. X-r powd. IR, ^1H	797, 1419, 1558, 1730 1097, 1419
$NaOC_2H_4OMe$	1	sld., s. in hex.	IR	1652
$NaOC_2H_4OEt \cdot 0.5\ ROH$	1	-	-	1243
$[NaOC(CH_2OPr^i)_2Bu^t]$		$155/10^{-3}$ (subl.)	-	732
$NaOC_6H_4OMe\text{-}2$, $\cdot 5ArOH$, $2.5ArOH \cdot 2H_2O$	3, 6	cr., m.:120, 172, 139		152, 1149
$(NaOCH_2\text{-})_2$ ↑190° **$NaOC_2H_4OH$, $\cdot L$**, L=$R(OH)_2$,EtOH	1, 3, 6	sld. cr., s. in ROH, ins. in hc., ΔH_{form}=-150	IR, X-r powd., thermochem	313, 575, 579, 621, 1413, 1584
$Na(OC_2H_4)_nOH \cdot R(OH)_2$	1, 6	cr.	-	745
$NaOCH_2CH(OH)CH_2OH$, $\cdot AlkOH$	1, 3, 6	sld., 245(dec.), s. in EtOH(t), RCOOR'	thermochem.	428, 577, 1022, 1413

$NaOCH_2CH(OH)CH_2ONa$ **$NaOCH_2CH(ONa)CH_2ONa$**	1, 6 6	sld., 220 (m., dec.) -	 -	
$NaOC_6H_7O_2(OH)_2$ (derivatives of starch, inulin, glycogen, lichenin) **$(NaO)_3C_6H_7O_2$** (-cellulose)	1, 6			1413, 1477
$NaOCH_2(CHOH)_2CH_2OH$, $\cdot$L, L=H_2O, MeOH, AlkOH **$(NaO)_2R(OH)_2$, $\cdot xH_2O$, $\cdot 2NaOH$, $\cdot 2NaOH \cdot xH_2O$**	1, 3, 6 3	sld., ΔH^o_{form} = - 258. sld., 140 (dec.)	thermochem.	313, 578
$NaOCH_2(CHOH)_4CH_2OH$ (derivative of mannit)	1, 6	-	-	313, 578, 1413
$NaOCH_2(CHOH)_4CHO$ (derivatives of fructose, glucose)	1	-	-	1413
$(NaO)_2C_6H_4$-1,2, -1,3, -1,4 **$NaOC_6H_4OH \cdot n\ Ar(OH)_2$**	6 1, 3		thermochem.	579, 1149
$C_6H_3(ONa)_3$-1,2,3, $(NaO)_2C_6H_3OH$ **$NaOC_6H_3(OH)_2$**	6		thermochem.	578
NaOC≡CONa ("carbonyl") struct. type CaC_2, $[ONa_5]$	7	yel. powd, ins. in liq.NH_3, pyrophor.	IR,X-r powd.	266, 1729
$(NaO)_2[OC(CF_3)_2]_2$	F	cr., v. s. in THF	« NMR	26
K				

[K(μ_5-OMe)]$_\infty$, struct. type of *anti*-PbO with alternating [ROMOR] layers, [$MO_{5/4}$]-tetragon. pyr., [OM_5C]-oct. $\uparrow 150^\circ/10^{-2}$	1, 5	sld., 330°$\rightarrow K+H_2+C+$ $+K_2CO_3$; system MaOR-ROH (polytherm), $\Delta H^\circ_{form} = -100$	IR, thermo-chem.,DTA , X-r powd.	313, 258, 576, 1489, 1578, 1728, 1737
·nMeOH, n=1, 3, 5		cr.,(n,m.):**(3,**-19),**(5,**+30); $p_{dec.}$ **3** (polytherm)	tensim., X-r (parametr)	498, 1737
KOEt	1, 5	sld., s. in ROH 27.3%(20°); $\Delta H^\circ_{form} = -98$	DTA, TGA, thermochem	184, 258, 1365, 1578, 1277
·EtOH		cr.,250°$\rightarrow KOH+H_2+C_2H_4$		
KOPr^n	1, 5	250°$\rightarrow KOC_3H_5 + H_2$; $\Delta H^\circ_{form} = -106$	thermochem thermolysis	576, 1578
[K(μ_4-OPr^i)]$_\infty$, struct. analog of LiOMe	1, 3	$210/10^{-6}$(subl.),s.inhc., $\alpha=1$	m-s, X-r	675, 1277
KOBu^n	1, 5	-	-	313
KOBu^i	1	$\Delta H^\circ_{form} = -117$	thermochem	313, 576
[KOBu^t]$_4$, cubane [$K_4(\mu_3$-OR$)_4$]	1	170-190 (m.), $140/10^{-3}$ (subl.), s. in THF, b. ROH 17%, hc., $\alpha=4$ (m-s,tol.,THF), 1 (ROH)	^1H, ^{13}C, m-s, X-r	352, 672,697, 1023, 1289, 1728, 1728
[K(μ-OBu^t)(μ-^{t}BuOH)]$_\infty$ linear chains of tetrah. sharing a edge	1	cr., s. in THF-C_5H_{12}, hc., t$\rightarrow$KOR$\uparrow$+ROH,α=3(in s)	IR, ^1H, ^{13}C, X-r	352
KOC$_5$H$_{11}$^{i}	1	amor. sld., 250 (dec.), $\Delta H^\circ_{form} = -126$	thermochem.	258, 313, 576
KOCHEt$_2$	3	-	-	1277
KOC$_5$H$_{11}$^{t}	1	sld., v. s. in C_7H_{16}	-	1023

$KOCH_2Ph$	3	-	-	1277
$KOCPh_3 \cdot PhMe$	1	cr., 220/2 (dec.)	-	161
KOPh polymer chain $[K_3(OPh)_3]_\infty$, CN K 6 and 3	1 ,3, 6	sld., 290(m.); KOPh-PhOH (polytherm), v. s. in H_2O, NH_3,, ins. in eth., hc., α=0.86	IR,electr. sp.,cryosc., TGA, X-r powd.	145, 145, 482, 534
$\cdot nPhOH$, n=2, 3 polymeric zigzag chains $[(\pi\text{-}PhOH)K(\mu\text{-}OPh)_{5-n}(\mu\text{-}HOPh)_{n-1}(OPh)]_\infty$		cr., m.:142, 135 (dec.); system KOPh-PhOH-H_2O, s. in H_2O 80%	IR, thermochem	145, 145, 482, 579, 1672
$\cdot 2H_2O$		cr., s. in H_2O 57%	thermochem	579, 1672
$2KOPh \cdot L$, L= 15-crown-5, $C_6H_{11}{}^c$-15-crown-5		cr., ins. in eth., hex., m.: 169 and 83	IR, ^1H, electr. sp.	1184
$KOC_6H_4Me\text{-}4 \cdot 3ArOH$	3	cr., 148 (m.)	-	1149
$KOC_6H_3Me_2$-2,6				385
$KOC_6H_3Bu^t{}_2$-2.6	4	cr., s. in THF	^1H	628
$KOC_{10}H_7\text{-}\alpha$, $\cdot 4ArOH \cdot 5H_2O$	3	cr., s. in ArH, liq. NH_3	-	1149, 1740
$KOC_{10}H_7\text{-}\beta$, $\cdot 2ArOH \cdot 5H_2O$	3	cr.,40(m.),s.inArH, liq.NH_3	-	1149, 1740, 1806
$KOCF_3$	F	powd., 80°→KF+COF_2	X-r powd.	1344, 238
KOC_2F_5	F	↔KF+CF_3COF (20°)	IR, NMR	1344
$KOC_3F_7{}^i$	F	instab. cr.	IR, NMR	1344
$KOCMe(CF_3)_2$, $KOCMe_2(CF_3)$	1	powd., t→ROH	thermolysis	930
$KOC(CF_3)_3$	4	powd., 140/0.2 (subl.), 220 (dec.), v. s. in eth., Me_2CO, MeCN	IR, m-s	467, 1716

$[K[OC_6H_2(CF_3)_3\text{-}2,4,6](THF)_3]_2$ 2 oct. sharing a $(\mu\text{-}OR)_2$ edge, $(\mu\text{-}THF)_2$	4	cr., s. in THF	X-r	246
$[KOSiMe_3]_4$ cube $[M_4(\mu_3\text{-}OR)_4]$	4	cr.,135(m.,dec.), $70/10^{-6}$ (subl.),s.in hc.<NaOR	IR, m-s, X-r powd.	797, 1419 1558, 1730
$KOSiBu^t{}_3$, $KOSi(OBu^t)_3$	4	cr., s. in eth.	IR	735, 1571
$[K(\mu_3\text{-}OSiMe_2Ph)]_n$, **$[K(PhH)(\mu_3OSiMe_2Ph)]_4$**	4	cr. powd., s. in bz., hex.	^1H, ^{29}Si, X-r; X-r-powd.	797, 592, 1093
$[K_4(\mu_3\text{-}OSiPh_3)_4]_2Dme_3]$, cube$[M_4O_4]$ **$[K_4(\mu_3\text{-}OSiPh_3)_3(\mu\text{-}OSiPh_2)(\eta\text{-}Ph)(\eta^2\text{-}Dme)]_2(\eta\text{-}Dme)$**, 2 cubans		cr., s. in Dme, ins. in hex	IR, ^1H, ^{13}C, X-r	
$KOC_2H_4OEt \cdot ROH$	1	cr., 61 (m.)	-	1243
$KOC_6H_4OMe\text{-}2$, $\cdot 3ArOH$, $\cdot ArOH \cdot 1.5H_2O$	3	cr., m.:168, - , 188	-	695, 1149
$(KOCH_2\text{-})_2$ **KOC_2H_4OH**	1	cr., s. in ROH, $R(OH)_2$ >20 (dec.)	IR, X-r powd.	313, 621
$KOCH_2CHMeOK$, $(KOCHMe)_2$	6	cr.	-	1584
$KOC_6H_4OH\text{-}1,2$, $\text{-}1,3$, $\text{-}1,4$, $\cdot n\ Ar(OH)_2 \cdot mH_2O$	3, 6	cr., s. in $H_2O \approx 60\%$	-	695, 754, 1149, 1672
$KOCH_2CH(OH)CH_2OK$	3, 6	-		428, 577, 578
$KOCH_2CH(OH)CH_2OH$, $\cdot AlkOH$		cr., 120 (dec.), s. in EtOH (t), ins. in eth., hc.	thermochem.	
$KOC_6H_7O_2(OH)_2$, (derivatives of starch, inulin, glycogen, lichenin)	1	powd. -		313, 578, 1413
$KOCH_2(CHOH)_2CH_2OH$, $\cdot H_2O$	1,3,6	powd., $\Delta H^o{}_{form} = -264$	thermochem.	

$KOCH_2(CHOH)_4CH_2OH$ (derivative of mannit)	1, 6	-	-	
$[K_2(OC{\equiv}CO)]_\infty$ ("carbonyl") struct. type of CaC_2, linear mol., $[OK_4]$-tetragon. pyr.	7	light yel. powd., ins. in liq. NH_3, expl. in the air	IR, X-r-powd.	266,1382, 1728, 1728
$KOC(CF_3)_2C(CF_3)_2OH$	3	cr., v. s. in THF	IR, NMR, X-r powd	26
Rb, Cs				
$[M(\mu_5\text{-}OMe)]_\infty$ isostr. with its K-analog $\uparrow > 20°$		powd., 330° → $K+H_2+C+K_2CO_3$; system MOR-ROH (polytherm)	X-r powd.	498, 1728
·nMeOH, n= 1 (?), 2, 5, 7	1	cr., m: 67,-37,-72 **(Rb)**; 76, -45, -77 **(Cs)**	therm. analysis	498, 1578
MOEt, ↑ 50/vac.(dec.) **·EtOH**	1, 4, 5	powd., 200 (m., dec.), → $CsOH+H_2+C_2H_4$; $\Delta H°_{form.}$=-96.5 **(Rb)**,-96.6 **(Cs)**	DTA, TGA, thermochem.	184, 313, 1578
$CsOPr^n$, **$\cdot Pr^nOH$**	1, 3	powd., 250 (m., dec.) cr., 100 (dec., vac.)	thermolysis	1578
$[MOPr^i]_\infty$ isostr. with its K-analog	1	powd., subl.:200/10^{-6} **(Rb)**, 170/10^{-6} **(Cs)**, s. in hc., α=1	m-s, X-r powd.	675
$[MOBu^t]_4$ isostr. with its K-analog	1	powd., **Rb**:185-200/10^{-2} (m., subl.),282(dec.); **Cs:** 350(dec.); s. in THF-C_5H_{12}, hc., α=3 (in s.), 4 (m-s)	^1H, ^{13}C, m-s, cryosc., X-r	352, 1728

$[M(\mu\text{-}OBu^t)(\mu\text{-}Bu^tOH)]_\infty$, isostr. with its K-analog		cr., s. in THF-C_5H_{12}, t→KOR+ROH, α=3 (in s.)	IR, ^1H, ^{13}C, X-r	
MOPh isostr. with its K-analog	3	sld., m: 304 (Rb), 154 (Cs), s. in H_2O, NH_3	IR, electr. sp., X-r powd.	145, 482, 1732
$CsOC_6H_3Pr^i_2$-2,6, layered struc. with chains $[(\mu\text{-}O)Cs(\eta^6\text{-}Ar)(C\text{-}1)_2]$	1	cr., s. in THF	^1H, X-r	379
$MOCF_3$	F	sld., 120°→$CsF+CF_2O$, s. in eth.,Me_2CO,ins. in MeCN	IR, Raman, X-r powd.	238, 375, 486, 1344
MOC_2F_5 (+MF-admixture)	F	stab.<<$MOCF_3$, 20°→$MF+CF_3COF$	IR, NMR	1344, 1447
$MOC_3F_7{}^n$, $MOC_3F_7{}^i$, $MOC_4F_9{}^n$	F	sld., 125°→$CsF+CF_2O$	IR, NMR	486, 1344
$[MOSiMe_3]_4$, isostr. with its Li-analog	4	cr., m.,dec.:140 (Rb), 200 (Cs), 80/10^{-6} (subl.), α=4	m-s, X-r	1419, 1730
$[M_2(OC{\equiv}CO)]_\infty$ ("carbonyl") isostr. with its K-analog	7	yel.(Rb), colrl.(Cs) powd., ins. in liq. NH_3, bz., expl.in the air; $+H_2SO_4$ →$(CHO)_2$	IR, X-r-powd.	266, 694, 1728

Table 12.2. Magnesium and alkaline earth metal alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
Mg				
[Mg(μ_3-OMe)$_2$]$_\infty$, Mg(OH)$_2$ struct. type with alternating [ROMOR] layers, [MgO$_{6/3}$]-oct., [OMg$_3$]- trig. pyr. **·0.75ROH** (=" 1ROH")		120-400 (dec.), ins. in NH$_3$, hc.	IR, TGA, X-r powd., photolysis	155, 681, 1036, 1201, 1237, 1582, 1646
·3.5MeOH ("4ROH")= [Mg$_4$(μ_3-OR)$_4$(OR)$_2$(ROH)$_{10}$]$^{2+}$ [(RO)$_2$H]$^-_2$ [Mg$_4$(μ_3-OR)$_4$(OR)$_4$(ROH)$_8$] 8ROH, cubane-like cations and molecules connected into a 3-dimensional network by H-bonds	1, 4	s. in bz., ROH (polytherm), 10.5%(20°), 39° (dec. under s.), p_{diss} (polytherm)	tensim., X-r	1524, 1646
Mg(OMe)$_n$(OH)$_{2-n}$, n=0.7; 1.5 struct. type of Mg(OH)$_2$	3	360 (dec.)	IR, TGA, X-r powd.	965, 1582
Mg(OEt)$_2$↓ struct. type of Mg(OH)$_2$	1, 2	wh. powd., ins. in org. solv., 130°→ C$_2$H$_4$ + Mg(OH)(OR)	IR, TGA, X-r powd.	494,681,1036 1098, 1507, 1582, 1646
Mg(OPr^n)$_2$↓ struct. type of Mg(OH)$_2$	1	powd., 138-485(dec.)	IR, TGA, X-r powd.	310, 1582, 1641
Mg(OPr^i)$_2$↓	4	visc. gel→powd., 440 (dec.)	IR, TGA	263, 807, 1582

$Mg(OBu^n)_2$↓, struct. type of $Mg(OH)_2$	1	gel→powd., 122 (dec.)	IR, X-r powd.	310, 1641
$Mg(OBu^t)_2$↓	4	powd., 440°→MgO	IR, TGA	400, 1582
$Mg(OC_5H_{11}^i)_2$↓	1	ins. in ROH	-	310
$Mg(OC_6H_{11}^c)_2$↓	1	ins. in ROH	IR, ^1H,DTA	71, 310
$Mg[OCHMe(C_6H_{13})]_2$↓	4	powd., 450°→MgO, s. in hex.	IR, TGA	310, 1582
$Mg(OCH_2Ph)_2$↓	1, 6	ins. in ROH	-	310, 1099
$Mg(OC_2H_4Ph)_2$	4	-	IR	71
$Mg(OR)_2 \cdot 2THF$, R=$CMePh_2$, CPh_3	4	cr., s. in THF, bz., α=1	IR, ^1H, ebul., X-r powd.	71, 648
$Mg(OPh)_2$, $Mg(OC_6H_3Me_2-2,6)_2$	4	-	IR	71
$Mg(OC_6H_3Pr^i_2-2,6)_2 \cdot 2THF$	4	cr., s. in THF, bz., α=1	IR, ^1H, ebul., X-r powd.	71, 648
$[Mg(OC_6H_3Bu^t_2-2,6)_2]_2 \cdot 1.5\ PhMe$ 2 trian. sharing a $(\mu\text{-}OR)_2$ side	4	cr., s. in THF, tol., α=2	IR, ^1H, X-r	288
$[Mg(OC_6H_2Bu^t_2-2,6\text{-}Me\text{-}4)_2]$, 2 trian. sharing a $(\mu\text{-}OR)_2$ side $\cdot$**L**, L=Et_2O, PhCOOMe	4	cr., s. in THF, bz., α=2 cr., α=1	IR, ^1H, ebul., X-r	288, 503, 648
$Mg(OC_6F_5)_2 \cdot Py$	4	-	^1H, X-r (?)	1333
$\{Mg[OC_6H_2(CF_3)_3-2,4,6]_2THF_3\}$ tetragon. pyr.	6	cr., 107(m.), s. in THF, α=1	IR, ^1H, ^{19}F, m-s, X-r	1361
$Mg(OC_2H_4OMe)_2$ **$[Mg_4(OC_2H_4OMe)_6\ Dme_2]^{2+}$** **$[Hg(SiMe_2Ph_3)_3]^-_2$**, cation – struct. type of $Ti_4(OMe)_{16}$	1	visc. sld. .yel.→ red cr., s. in Dme	IR ^1H, ^{13}C, X-r	1652 1380

$Mg(OCH_2\text{-})_2$ **$\cdot nR(OH)_2$**	6	amor. sld., 330(dec.),ins. in liq. NH_3, org. solv.; α=1; 160° → $Mg(O_2R)+R(OH)_2$	IR, TGA, DTA,m-s, X-r (parametr)	621, 1051
$Mg(OCH_2)_2CH_2$, $\cdot nR(OH)_2$	6	sld.,330(dec.), 92(dec.)	IR,X-r powd.	1051
$Mg(OCH_2CHMeO)$ **$\cdot nROH$**	6	sld., 330(dec.) cr., 110(dec.)	IR,TGA, DTA, X-r (parametr)	1051

$3Mg(OMe)_2 \cdot MgCl_2 \cdot 10MeOH$= $[Mg_4(\mu_3\text{-}OR)_4(OR)_2(ROH)_{10}]^{2+}Cl^-_2$ cation - cube	methastab. phase in system $Mg(OR)_2$-$MgCl_2$ -ROH	X-r	165, 1650
$[MgHal(OR)L]_2$, Hal=Br, I, L=Et_2O, THF R=Me, Et, Pr^n, Bu^t, CEt_3, CEt_2Me, CMe_2Pr^n; **$[MgBr(OBu^t)(Et_2O)]_2$** 2 tetrah. sharing a $(\mu\text{-}OR)_2$ edge	cr., ins. in eth.(R=Me-Bu^t), others - s. in eth., bz., α=2, dec.in ROH, R_2CO, THF, α=2	IR, ^1H, ebul., X-r powd. X-r	400, 1650 138
$MgBr(OC_{10}H_7\text{-}\beta) \cdot Et_2O$	-	-	1806
MgH(OR), R=Me↓, Et↓, Pr^i↓, Bu^t↓, $C_6H_{11}^c$, CPh_2Me, CPh_3, Ph, PhC_2H_4, $C_6H_4R_2$-2,6,	sld. or visc. liq, s. in THF, α=2; 300° → M + $MO+H_2+C_2H_n$+ROH	IR, ^1H, , ebul., X-r powd.	71, 123
$[Li(MgTHF)_4(\mu_5\text{-}O)(\mu\text{-}OC_6H_3Me\text{-}2)_7]$ = trig. bipyr. $[M_5]$, 2 at. Mg –ax., CN Mg 5, Li 3 **$[Li_2Mg(\mu\text{-}OC_6H_4Me\text{-}2)_4(Tmeda)_2]$,** linear chain, centr. $[MgO_4]$ tetrah. sharing edges with 2 tetrahs. $[LiO_2N_2]$	s. in THF	^1H, X-r	727

Ca				
$[Ca(OMe)_2]_\infty$ ↓, struct. type of $Mg(OMe)_2$	1, 3, 4, 5	vh. powd., 150 (dec.), ins. in NH_3, hc., ROH	IR, TGA, X-r powd..	313, 494, 681, 1036, 1201, 1517, 1646
$[Ca(\mu_3\text{-}OMe)_n(\mu_3\text{-}OH)_{2-n}]_\infty$, n=0.5-1.7, isostr. with $Ca(OMe)_2$	4	cr.	X-r powd..	59
$[Ca(OEt)_2]$ ∞↓ ↑80°		wh. sld., 220°→ C_2H_4+ $Ca(OH)(OR)$+ROH; ins. in NH_3,hc.,$\Delta H_{form.}$= -229	IR, X-r powd., thermochem	313, 681, 1036
·**nROH**, n=2, 4 ↓ t (ROH)	1,4, 5	cr., s. in ROH (polytherm), 2.3%(20°), 60° (n=4, dec. under s.), p_{diss} (polytherm)	tensim.	1646
$Ca_6O_2(OEt)_8\cdot 14ROH$ **(="$Ca(OEt)_2\cdot 2EtOH$)** =$[Ca_6(\mu_4\text{-}O)_2(\mu_3\text{-}OR)_4(OR)_4]$ 14ROH 2 cubes sharing a $[Ca_2(oxo)_2]$ face		cr., v. s. in ROH, THF, tol., hc.	X-r	1653
$Ca(OBu^i)_2$, $Ca(OC_5H_{11}{}^n)_2$, **$Ca(OC_5H_{11}{}^i)_2$**	1, 5	wh. powd.	-	313
$Ca(OCH_2Ph)_2$	1, 6	"	-	1099
$[Ca(CHBu^t{}_2)_2]_3$		$185/10^{-3}$ (subl., dec.)	-	732
$[Ca(CBu^t{}_3)_2]_2$		t→$Ca(CHBu^t{}_2)_2$+ CH_2=CMe_2	-	732

$Ca(OPh)_2$ **$\cdot nPhOH\cdot 2H_2O$**, n=2, 4 **$\cdot nH_2O$**, n=5.5 (<0°); 3; 2/3	3	wh.powd., 110°→H_2O + $PhOH$→H_2+MeH+CO; s. in system $Ca(OPh)_2$-$PhOH$-H_2O, 14.5% (20°)	thermolysis	565, 1457, 1672
$[Ca_3(OPh)_5Hmpa_6]^+$ $[OPh(PhOH)_2]^- \cdot PhMe$, cation - $[Ca_3(\mu_3\text{-}OR)_2(\mu\text{-}OR)_3)(Hmpa)_6]^+$ - trian. $[M_3]$, $[CaO_6]$ -oct.	1, 4	cr., 78 (m.), 130 (dec.), s. in tol., C_5H_{12}	IR, TGA, X-r	304
$[Ca(OC_6H_3Me_2\text{-}2,6)_2(Dme)_2]$-*cis*, oct.	1	cr., s. in liq. NH_3, Dme	X-r	551
$Ca(OC_6H_3Bu^t_2\text{-}2,6)_2 \cdot 2THF$	1	cr., 90(subl., dec.),s. in hc.		1089
$Ca(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2$, 2THF **$[Ca(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2THF_3] \cdot THF$**, trig. bipyr., 2 THF -ax.	1, 5	cr., 90 (subl.,dec.), s. in hc.	IR, ^1H, ^{13}C, X-r	1572 757
$[Ca(OC_6H_2Bu^t_3\text{-}2,4,6)_2]_2$, **$\cdot 3THF \cdot PhMe$**	1	cr., 110 (m.), 250/10^{-4} (subl., dec.), s. in tol., C_5H_{12}, α=1 cr., 133(m.), s. in THF	IR, IR, ^1H, ^{13}C, cryosc.	495, 732
$Ca[OC(CF_3)_3]_2$	1	yel.-wh.powd.,140/10^{-5} (subl.), 260 (dec.), s. in THF	^{19}F	1321
$Ca[OC_6H_2(CF_3)_3\text{-}2,4,6]_2THF_3$	4	cr.,118 (dec.), s. in THF, α=1	IR, ^1H, ^{13}C, m-s	1361

$[Ca[OCPh_2(CH_2C_6H_4Cl\text{-}4)]_2(THF)_3]\cdot THF$ **$[Ca[OCPh_2(CH_2C_6H_4Cl\text{-}4)]_2(THF)]_2\cdot 2PhMe$** 2 tetrah. sharing a $(\mu\text{-}OR)_2$ edge **$\{CaI[OCPh_2(CH_2C_6H_4Cl\text{-}4)]THF_4\}$-*trans*,** oct.	5	cr., s. in THF, α=1 colrl. cr., s. in tol.	!R, ^1H, ^{13}C X-r	1572
$[Ca(OSiPh_3)_2(NH_3)_2]_2\cdot 0.5PhMe$, oct., $[CaO_3N_2]$ and trig. bipyr. sharing a $(\mu\text{-}OR)_3$ face	1	cr., s. in tol., hex., t→NH_3	X-r	449
$Ca_9(OC_2H_4OMe)_{18}\cdot 2MeOC_2H_4OH$= $[Ca_9(\eta^2,\mu_3\text{-}OR)_8(\eta^2,\mu\text{-}OR)_8(\eta^1\text{-}OR)_2(\eta^1\text{-}ROH)_2]$, 9 Ca at. form a planar layer of CdI_2 type, 3 oct. in the center, 6 peripheral 7-vertex polyhedra	1	cr., s. in hex., α=1	IR, cryosc., X-r	654, 1652
$\{[Ca[OC(CH_2OPr^i)_2Bu^t]_2\}_2$ $_{,\ oct}$. and 5-vertex polyhedron sharing common $(\mu\text{-}OR)_3$ face	4	cr., 150/10^{-2} (subl.), s. in THF	X-r	732
$Ca(OCH_2\text{-})_2$ **$Ca(OC_2H_4OH)_2$**	1 6	amor.sld., ins. in liq. NH_3, org. solv.	-	313, 621
$Ca(OCH_2)_2CHOH$, $Ca[OR(OH)_2]_2$ **$Ca_3[OR(OH)_2]_6\cdot nR(OH)_3$**, n=4, 6	3	sld., 350(dec.),$n_D\approx$ 1.51, polytherm s. in $R(OH)_3$	IR, TGA, X-r powd.	593, 1593
$Ca[OC_6H_4(OH)\text{-}1,2]_2$	3	-	-	176
$Ca(OCH\equiv)_2$	7	-	-	1288, 267

$CaCl(OR)\cdot THF$, R=Me, Et, Bu^n, Ph **$CaCl(OEt)$ ↓**		s. in THF, ins. in hex. amor. powd., system $Ca(OR)_2$-$CaCl_2$-ROH	IR	1071, 1628
$[CaI[OCPh_2(CH_2C_6H_4Cl\text{-}4)THF_4]$-*cis* , oct.		s. in THF	IR, ^1H, ^{13}C, X-r	1572
Sr				
$[Sr(OMe)_2]_\infty$, struct. type of $Mg(OH)_2$	1,3, 4, 5	powd.., 230 (dec.); s. in ROH (polytherm),5% (20°), ins. in liq. NH_3	IR, X-r powder	313, 681, 1036, 1201, 1517, 1646
$[Sr(OEt)_2]_\infty$↓, struct. type of $Mg(OH)_2$	1, 5	sld., 230 (dec.); ins. in liq. NH_3,, hc.	IR, X-r powd.	313, 681, 1036, 1646
$\cdot nROH$, n=2, 4	1, 5	cr., s. in liq.NH_3,, ROH (polytherm), 4% (20°), **n=4:**10° (dec. under s.), p_{diss} (polytherm)	X-r powd., tensim.	1646
$[Sr(OPr^i)_2]_n$	1, 4	-	-	1690
$[Sr_5O(OC_5H_9{}^{neo})_8({}^{neo}C_5H_9OH)THF_4]$ tetragon. pyr. $[Sr_5(\mu_4\text{-}O)(\mu_3\text{-}OR)_4(\mu\text{-}OR)_4L_5]$	1	cr., s. in THF (t)	X-r	191
$Sr(OPh)_2\cdot 4H_2O$	3	cr., s. in H_2O - 33%	-	1672
$[Sr_3(OPh)_6(Hmpa)_5]\cdot PhMe\cdot C_5H_{12}$ = $[Sr_3(\mu_3\text{-}OR)_2(\mu\text{-}OR)_3(OR)(Hmpa)_5]$; trian. $[M_3]$	1	cr., 127 (m.), s. in tol.	IR, ^1H, ^{13}C, ^{31}P, TGA, X-r	304
$[Sr_4(OPh)_8(PhOH)_2(THF)_6]$= $[Sr_4(\mu_3\text{-}OPh)_2(\mu\text{-}OPh)_4(OPh)_2(PhOH)_2THF_6]$, struct. type of $Ti_4(OMe)_{16}$	1	cr., 96 (m.), s. in THF	IR, ^1H, ^{13}C, X-r	496

$[Sr_6Ba_2O_2(OPh)_{12}(PhOH)_2(Hmpa)_6]\cdot 2PhMe$, isostr. with its Ba-analog	1	cr., 311 (m.), s. in tol.	IR, ^1H, ^{13}C, TGA, X-r	304
$[Sr(OC_6H_2Bu^t_2-2,6\text{-}Me\text{-}4)_2THF_4]$	1	cr.	^1H	394
$[Sr(OC_6H_2Bu^t_3-2,4,6)_2]_2$ **$[Sr(OC_6H_2Bu^t_3-2,4,6)_2THF_3]\cdot 0.5THF$**, trig. bipyr., 2 THF - ax.	1	cr., 142 (m.), 250/10^{-4} (subl.,dec.), s. in tol., THF,ins. in C_5H_{12}, α=2 cr., 210 (dec.), s. in THF	IR, ^1H, ^{13}C, cryosc., X-r	495, 732
$Sr[OC(CF_3)_3]_2$	1	wh.sld., 230/10^{-5}(subl.), 320 (dec.), v. s. in THF	^{19}F	1321
$Sr(OC_2H_4OMe)_2$	1	wh. sld., s. in ROH	IR	1652
$\{[Sr[OC(CH_2OPr^i)_2Bu^t]_2\}_2$	4	cr., 170/10^{-2} (subl.), s in THF	X-r	732
$Sr(OCH_2\text{-})_2\downarrow$	1, 5	wh. sld.	X-r powd.	313, 621
$Sr(OCH\equiv)_2\downarrow$	7	wh.sld.,turns yel.	-	267, 1288, 1360
$KSr(OPr^i)_3$		sld., s. in bz.	^1H, $^{13}C\{^1H\}$	1690
Ba				
$[Ba(OMe)_2]_\infty\downarrow$, struct. type of $Mg(OH)_2$		powd., 250 (dec.); ins. in liq. NH_3, ROH, hc.	IR, X-r powd.	681, 1036, 1201, 1517, 1646,1654
$\cdot nROH$, n=1, 4	1, 3, 5	cr., s. in liq. NH_3, ROH (polytherm), **n=4:** 36.1% (20°), 20° (dec. under s.), p_{diss} (polytherm)	X-r powd., tensim.	313, 1646, 1654

$[Ba(OEt)_2]_\infty\downarrow$, struct. type of $Mg(OH)_2$ $\uparrow 40°$		powd., 270 (dec.), ins. in liq. NH_3, ROH, hc., ΔH_{form}= -229	IR, X-r powd., thermochem	681, 1036, 1646, 1654
·nROH, n=2, 4	1, 5	cr., s. in liq. NH_3, ROH (polytherm), 30.2% (20°), **n=4:** 40° (dec. under s.), p_{diss} (polytherm)	X-r powd.; tensim.	313, 1646
$Ba(OPr^i)_2$	1	wh. powd., turns dark, s. in ROH 5-10%	IR	1654, 1687
$BaO_n(OPr^i)_{2-2n}·x^iPrOH$		colrl. cr., s. in bz.		1654
$Ba(OBu^n)_2$	1	powd., s. in ROH, decre-ases with increasing t	IR	1654
$[Ba(OBu^t)_2]_n$ $\uparrow 100°$; C_5H_{12}	1	wh.sld., $270/10^{-5}$(subl.), 320 (dec), s. in THF	^1H, ^{13}C $\{^1H\}$, X-r	174, 1321, 1689
$[Ba(OBu^t)_2(Bu^tOH)_2]_4$ = $[Ba(\mu_3\text{-}OR)(OR)(ROH)_2]_4$, cube, oct. Ba	4	cr., s. in THF		
$[H_3Ba_6O(OBu^t)_{11}(OCEt_2CH_2O)THF_3]$= $[Ba_5(\mu_5\text{-}O)(\mu_3\text{-}OR)_4(\mu\text{-}OR)_3(OR)\ THF_3]$ $(\mu_3\text{-}OR)(\mu\text{-}OR)_2\ Ba(\eta^2\text{-}RO_2)$, tetragon. pyr. $[Ba_5(\mu_5\text{-}O)]$	1	cr., >340 (m.), s. in THF, tol.-C_5H_{12}	^1H, ^{13}C, X-r	303
$[Ba_4(OC_5H_9{}^{neo})_8({}^{neo}C_5H_9OH)_6Py_2]$ struct. type of $Ti_4(OMe)_{16}$, mols. Py – Ba(1)	1	cr., s. in Py, ROH	X-r	191
$Ba(OCEt_3)_2$, $Ba(OCMeEtPr^i)_2$, $Ba(OCHBu^t{}_2)_2$	1, 4	sld., 240-265/10^{-5} (subl.), 350 (dec), s. in THF	^1H, ^{13}C, m-s	1321
$[Ba_2(OCPh_3)_4(THF)_3]·PhMe·THF$ 2 trig. bipyr. sharing a $(\mu\text{-}OR)_3$ face	1	cr., 250 (dec.), s. in THF	^1H, ^{13}C, X-r	497

$Ba(OPh)_2$, $\cdot 4H_2O$	3	cr., 450 (dec.); s. in H_2O 23%	thermo-lysis	565, 1672
$[Ba_5O(OPh)_8(PhOH)(THF)_8]$= $[Ba_5H(\mu_5\text{-}O)(\mu_3\text{-}OR)_4(\mu\text{-}OR)_4(OR)\ THF_8]$ tetragon. pyr. $[M_5]$	1	cr., 226 (m.), s. in THF, C_5H_{12}	IR, X-r	303
$[Ba_6(OPh)_{12}(Tmeda)_4]\cdot 4PhMe$= $[Ba_6(\mu_3\text{-}OR)_6(\mu\text{-}OR)_6(\eta^2\text{-}L)_4]$, 2 trian. $[Ba_3]$, connected via $2\mu_3$-, 2 μ, CN Ba 6, 7	1	cr., 96 (m.), s. in tol.	IR, ^1H, $^{13}C\{^1H\}$, ^{31}P, X-r	304
$[Ba_8O_2(OPh)_{12}(PhOH)_2(Hmpa)_6]$ 2PhMe $=[Ba_8H_2(\mu_5\text{-}O)_2(\mu_3\text{-}OR)_8(\mu\text{-}OR)_6\ L_6]$, 2 tetra -gon. pyr. $[M_5(\mu_5\text{-}O)]$ sharing a $[M_2]$ edge	1	cr., 217 (m.), s. in tol.	IR, ^1H, $^{13}C\{^1H\}$, X-r	304
$[(Ba_5(OH)(OC_6H_3Bu^t{}_2\text{-}3,5)_9THF_5$= $[(BaTHF)_5(\mu_5\text{-}OH)(\mu_3\text{-}OR)_4(\mu\text{-}OR)_4(OR)]$, 4 faces of pyr. $[M_5]$-centered by μ_3-OR, 4 (μ-OR), OR, Ba-ax.	1	cr., $100/10^{-1}$(dec.), s. in THF, $CHCl_3$, CH_2Cl_2, low - in hc., α=2	IR, ^1H, m-s, X-r	1150
$[Ba(OC_6H_3Bu^t{}_2\text{-}3,5)_2(18\text{-}crown\text{-}6)]$	1	cr., α=1		
$[Ba(OC_6H_3Bu^t{}_2\text{-}2,6)_2(\eta^2\text{-}Me_2NC_2H_4OH)_4]\cdot 2PhMe$, dodecahedron $[BaL_4]$, ArO...H (L)	1	cr., 94 (m.), s. in THF, bzl., tol., CH_2Cl_2	IR, ^1H, ^{13}C, X-r	303
$[Ba(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2THF_2]$ **$[Ba(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2THF_3]\cdot THF$** isostr. with its Ca-analog	1, 5	wh.cr., s. in THF, hc.	IR, ^1H, ^{13}C X-r	1572, 757
$[Ba(OC_6H_2Bu^t{}_3\text{-}2,4,6)_2]_2$	1	cr., 180 (m.), $250/10^{-4}$ (subl.,dec.), s. in THF, s. in tol., ins. in C_5H_{12}, α=2	IR, ^1H, ^{13}C, cryosc.	495, 732
$[Ba(OC_6H_2Bu^t{}_3\text{-}2,4,6)_2Dme_2]\cdot PhMe$		cr., 307 (m.)		

$[Ba(OC_6H_2Bu^t_3\text{-}2,4,6)_2THF_3]\cdot THF$ **$[Ba(OC_6H_2Bu^t_3\text{-}2,4,6)_2(Hmpa)_3]$**		cr., 152 (m.) cr., 72 (m.), s. in C_5H_{12}		
$Ba[OCH(CF_3)_2]_2$	1	sld., $230/10^{-5}$ (subl.), 260 (dec.), v. s. in THF	^{19}F	1321
$Ba[OC(CF_3)_3]_2$	1	sld.,$280/10^{-5}$ (subl.), 320 (dec.), v. s. in THF	^{19}F	1321
$[Ba_5THF_4(H_2O)(OH)[OCH(CF_3)_2]_9]$ **THF**= $[(BaL)_4Ba(H_2O)(\mu_5\text{-}OH)(\mu_3\text{-}OR)_4(\mu\text{-}OR)_4(OR)]\cdot L$, tetragon. pyr. $[M_5]$, 4 μ_3-OR - cap the side faces	1, 6	cr., $200/10^{-3}$ (subl.), s. in THF	^1H, ^{19}F, X-r	1702
$Ba[OC_6H_2(CF_3)_3\text{-}2,4,6]_2THF$	4	cr., 205 (dec.), $\alpha=1$	IR, ^1H, ^{13}C	1361
$[Ba_2(OSiBu^t_3)_4THF]$ 2 tetrah. sharing a $(\mu\text{-}OR)_3$ face	1	cr., 80/1 (subl.), s. in THF, C_5H_{12}	^1H, ^{13}C, X-r	497
$[Ba(OSiPh_3)_2]_n\downarrow$ **$[Ba_3(OSiPh_3)_6THF]\cdot 0.5THF$** = $[Ba_3(\mu_3\text{-}OR)_2(\mu\text{-}OR)_3(OR)(THF)]$, trian. $[M_3]$, 1 gr. $[BaO_4]$, 2 gr.$[BaO_5]$	 1	powd., 250 (dec.) cr., $225/10^{-2}$ (subl., -THF), s. in tol.- C_5H_{12}	 ^1H, ^{13}C, ^{29}Si, X-r	1484 305
$[Ba_6O(OC_2H_4OMe)_{10}(MeOC_2H_4OH)_4]$= $Ba_6(\mu_6\text{-}O)(\mu_3,\eta^2\text{-}OR)_8(\eta^2\text{-}ROH)_4(\eta\text{-}OR)_2]$, oct. $[M_6]$, 8 faces capped by - μ_3-OR-gr., CN Ba 8 -ax., 9 - equ..	1	cr., $160/10^{-1}$ (subl.), s. in tol., C_5H_{12}, $\alpha=1$	IR, ^1H, ^{13}C, cryosc., X-r	304
$\{[Ba[OC(CH_2OEt)_2Bu^t]_2\}_2$ **$\{[Ba[OC(CH_2OPr^i)_2Bu^t]_2\}_2$** isostr. to its Ca-analog	4, 5 4	cr., $150/10^{-2}$ cr., $185/10^{-2}$ (subl.), s. in THF	X-r	732
$Ba[O(C_2H_4O)_nMe]_2$, n=2, 3	1	liq., s. in eth., bz., $\alpha=1$	IR, ^1H, m-s	1345
$Ba(OCH_2\text{-})_2$ $\downarrow$	1, 5	sld.	X-r powd.	313, 621

$BaO_2C_6H_4$-1,2, ·3.5H_2O	3	cr., ins. in H_2O	-	530, 1285
$BaO_2C_6H_4$-1,3 ·2H_2O **$Ba(OC_6H_4OH)_2$**	3	cr., s. in system $Ba(OAr)_2$ - ArOH - H_2O, s. in H_2O-53.5%	-	1672
$Ba(OCH\equiv)_2$	7	sld., ins. in liq. NH_3	-	267
ClBaOMe		cr.,160(dec.); system $Ba(OR)_2$-$BaCl_2$ - ROH +ROH→$Ba(OR)_2$·ROH	IR	1628
$[BaI(OC_6H_2Bu^t_2$-2,6-Me-4)$THF_3]_2$, ·2THF 2 oct. sharing a $(\mu\text{-}I)_2$ edge tol.↓↑THF **$[BaI(OAr)]_n$·PhMe↓**		cr., s. in THF, hc. sld., ins. in org. solv.	IR, ^1H, ^{13}C, X-r	1572
$KBa(OPr^i)_3$		powd., s. in bz.	^1H, ^{13}C	1687
$[KBa_2(\mu_3\text{-}OSiPh_3)_2(\mu\text{-}OSiPh_3)_3(Dme)_2]$·$C_6H_{14}$ trian. $[M_3]$, $[KO_4]$, $[BaO_4(\eta^1\text{-}Dme)]$, CN Ba 5, 6		cr., s. in Dme, bz.	^1H, ^{29}Si, X-r	398

with a statistical distribution of OR and ROH groups) [165,1524] in only one case. This phase is metastable and decomposes on action of alcohol giving a precipitate of $\mathbf{Mg(OMe)_2MeOH}$. The stability of polymeric MCl(OR) (R = Me, Et) to alcoholysis increases from Mg to Ba [1628]. The metathesis reactions of $\mathbf{MI_2}$ with KOR (in 1:1 ratio) in THF gave oligomeric alkoxoiodides — $\mathbf{CaI[OCPh_2(CH_2C_6H_4Cl\text{-}4)]THF_4}$-***trans*** **and** $\mathbf{[BaI(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)THF_3]_2}$ with octahedral coordination of the metal atoms. The reversible desolvation of the latter in toluene provided insoluble polymeric $\mathbf{[BaI(OAr)]_n{\bullet}PhMe}$ **[1572].** Hydrolysis of MOR is always complete, even in the presence of only traces of water. At the same time the $\mathbf{M(OAlk)_2}$ form a number of crystalline products containing OR, OH, ROH — groups in common [1644], whose nature remains still unknown. The only exclusions are the above-mentioned $\mathbf{Ca_6O_2(OEt)_8{\bullet}14ROH}$ [1653] and also $\mathbf{M(OH)_n(OMe)_{2\text{-}n}}$ (M = Mg, n = 1.3; Ca, 0.3; 1) — the phases of steichiometrical composition obtained on intercalation of MeOH into the layered structures of hydroxides under high pressure [965, 59].

12.1.3. Phenoxides

Phenoxides of the elements of this group are typical salts: they are insoluble in organic solvents except for LiOPh and are transferred even into EtOH media only in the presence of water. Their aqueous solutions are highly basic, but the hydrolysis equilibrium can be shifted only by prolonged reflux (pK of PhOH is 6 orders of magnitude higher than that of $\mathbf{H_2O}$). In contrast to the alkoxides they are easily soluble in liquid ammonia, and their solutions display a considerable conductivity. The phenoxides are usually obtained initially from the syntheses as $\mathbf{MOAr{\bullet}\mathit{x}ArOH{\bullet}\mathit{y}H_2O}$ adducts that melt without decomposition. The unsolvated MOAr usually also have distinct melting points; their thermal decomposition occurs at 450 to 500°C independently of the nature of the metal. The known structures of NaOAr contain linear chains with OAr-bridging groups and H-bonds [858, 482, 548], only $\mathbf{[LiOPh(THF)]_n}$ are oligomeric (cubane and hexagonal prismatic cores) [810, 1303, 1483].

12.1.4. Fluoroalkoxides

Among the derivatives of halide-substituted alcohols the fluoroalkoxides are of special interest. The presence of "peripheral" fluorine atoms enables the secondary M...F interaction and filling of the coordination sphere of the metal, which leads to an unusually high volatility. These compounds are described in the review by Willis [1749].

The preparation of the trifluoromethoxides was achieved by Bradley, Redwood and Willis *et al.* [238, 1344] by a principally new technique (denoted as "F" in the Table 12.1, in addition to the specification provided in Chapter 2) based on interaction of alkaline fluorides with carbonylfluoride:

$MF + COF_2 \leftrightarrow MOCF_3$ (M=K, Rb, Cs; no react. for Li, Na, Ba)

In the acetonitrile media the equilibrium is shifted due to formation of insoluble alkoxides. The other perfluorohomologs for Rb and Cs were obtained on application of fluoroanhydrides of acids and ketones in this reaction:

$MF + C_nF_{2n+1}COF \leftrightarrow MOCF_2C_nF_{2n+1}$ (n=1–3)
$MF + (CF_3)_2CO \leftrightarrow MOCF(CF_3)_2$ [1344]

The synthesis of fluorinated butoxides was carried out by interaction of metal hydrides with corresponding alcohols in ether media [467, 947]. The interaction of fluorinated ketones with sodium in THF or aqueous alkali led to the derivatives of perfluoropinacol:

$2\,Na + 2\,(CF_3)_2C{=}O \rightarrow Na^+_2[OC(CF)_2C(CF_3)_2O]^{2-}$ [26]

The primary perfluoroalkoxides are rather unstable. They dissociate: methoxides on heating in vacuo and ethoxides already at room temperature according to the reaction opposite to that of their formation. The stability decreases in the following series:

$CsOCF_3 > RbOCF_3 > KOCF_3$,
$CsOC_3F_7^n > CsOC_3F_7^i > CsOC_2F_5 >> RbOC_3F_7^n > RbOC_3F_7^i$ [238, 1344].

The most stable turned out to be the derivatives of carbinols $(CF_3)_nH_mMe_{3-n-m}COH$ and fluorinated phenols. They are described for Li, Na, and Ba and are formed on interaction of metals, hydrides, or alkyls, MR_n, with alcohols. The cubane-shaped $NaOR_F$ molecules of this kind are present not only in the solid state but even in gas. The temperatures of their sublimation decrease on substitution for Me and H with CF_3-groups. The stability of the Na...F bonds is so high that the gas-phase decomposition of these compounds (~300°C) yields NaF [1386]. The observed frequency corresponding to the vibration of the C–O bonds in the IR spectra of $MOCF_3$ is very high, indicating its increased order [375]. The fluorinated alkoxides of alkaline earth metals are transferred into the gas phase only in a rather high vacuum (10^{-5} mm Hg) at t > 200°C (i.e., under the conditions very close to those of pyrolysis). Of considerable interest is a volatile and hydrolysis-insensitive $[Ba_5(\mu_5\text{-OH})[OCH(CF_3)_2]_9(THF)_4(H_2O)]$ complex, which contains the solvating O-donor molecules in addition to the pentadentate OH-group [1702]. All these derivatives of alkali metals are well soluble in organic solvents, while those of alkaline earth ones are soluble only in THF. $CsOCF_3$ was proposed as a reagent in the preparation of the active samples of CsF [486] and also in the synthesis of the fluorinated esters [1716].

In conclusion we mention only the major areas of the application of the alkoxides of this group in organic chemistry. These are the ester condensation (NaOR, Kleisen); reduction of the carbonyl compounds into alcohols ($Mg(OR)_2$, ClMgOEt (Meerwein), BrMgOEt, IMgOEt (Gomberg), NaOR (Verley), HMgOEt (Bauer) [123], Ashby [71]); alkoxylation of RHal in the synthesis of ethers (NaOR, $M(OR)_2$ (Masada) [1067]; MOR•LiR' M = Na–Cs (Lochmann) [1023]); polymerization of unsaturated compounds (acrylates, methacrylates, vinyl ethers, *etc.)* ($MOBu^t$ [87], ROMgHal [809, 1023]).

Concerning the application of these compounds in the sol-gel technology of complex oxide materials, see Chapter 10.

12.2. Copper, silver, and gold alkoxides

The intensive development of the chemistry of homo- and heterometallic alkoxides of copper started more than 10 years ago in connection with the prospects of their application in the preparation of materials and initially in high temperature superconductors. In the search for the appropriate precursors in sol-gel and MOCVD techniques, attention was focused on the alkoxides of copper (I) and the fluorinated alkoxides of copper (II) — oligomeric derivatives soluble in non-polar solvents and existing not only in condensed but also in the gas phase. The derivatives of copper (II) and aliphatic alcohols, even rather branched or functional ones (such as alkoxyalkoxides) turned out to be polymeric substances uninteresting for further application.

12.2.1. Synthesis

The preparation of CuOR is usually achieved by the exchange reaction of CuCl with LiOR in THF (method 5) and also by alcoholysis of CuR (method

4). The insoluble $Cu(OR)_2$ were prepared mainly by methathesis of $CuCl_2$ and LiOR (LiCl remains in this case in solution, method 5). The difficulties in carrying out these syntheses are connected with rather the high stability of the insoluble CuCl(OR) intermediates that in order to be destroyed have to be washed repeatedly with alcohols, which increases the risk of partial hydrolysis [1614]. A much easier and more efficient approach is provided by the anodic oxidation of metal in alcohols in the presence of electrolyte and sometimes even Dmfa, which forms stable complexes with $Cu(OR)_2$ (method 2). The direct interaction of metal with alcohols can be achieved only in the presence of amine ligands (Section 2.1). In a number of cases the alcohol interchange reactions (method 6) and oxidation of CuOR by alkylperoxides $(RO\text{-})_2$ (method 7) were used.

12.2.2. Properties

The alkoxides of Cu(I) are colorless or yellowish crystalline substances. The data on the thermal behavior are accessible only for a limited number of derivatives, but it can be supposed that all of them except the polymeric CuOMe can exist in the gas phase. At high temperatures they undergo pyrolysis with formation of copper metal or Cu_2O (which is applied in the preparation of thin films from the gas phase [841]). The X-ray single crystal data show CuOR to be tetrameric; their molecules are square planar with the O-atoms in the corners of the square and the Cu ones (in *sp*-hybrid state) in the middle of the edges. They are structural analogs of the $[Cu_4O_4]^{4-}$ anions. The attachment of additional ligands (usually PR_3) or complexation with the alkoxides of other metals leads to the increase in the CN to 3 or 4 (sp^2 or sp^3 hybridization, respectively) and formation of binuclear molecules, where the metal polyhedra share a common edge as in $[Cu(\mu\text{-}OR)(PR_3)]_2$, $[CuY(\mu\text{-}OSiPh_3)_2(OSiPh_3)_3(Me_2PhP)]$ or cubane-like $[Cu(\mu_3\text{-}OPh)(PPh_3)]_4{\cdot}2PhMe$. The alkoxides of Cu(I) are rather sensitive to oxidation in the presence of traces of oxygen and immediately achieve the blue color. These substances have a rather broad spectrum of applications in organic and inorganic synthesis — in the reactions of metallation and condensation of unsaturated hydrocarbons [1241, 1602], as alkoxylating agents for CCl_4 [711],reactants for CO and CO_2 [1769] and nitrile [1602] fixation, in the synthesis of soluble hydride complexes such as $[HCuPR_3]_6$ [647], and so on.

$Cu(OR)_2$ are blue or green nonmelting solids insoluble in organic solvents (methoxide is slightly soluble in liquid NH_3). They can be transferred into solutions via complexation with amines or aminoalcohols [1445, 1614] or by partial substitution of OR-groups with other ligands, such as, for example, acac [1286]. The inaccessibility of the single crystals of $Cu(OR)_2$ limits our knowledge on their structures. The conclusions concerning the coordination of copper atoms made by different authors on the base of electron spectroscopy and magnetic measurements data were quite different. Thus the structure of the methoxide was supposed to be built up of tetrahedra [6] or tetragonally distorted $[CuO_6]$ octahedra in a chain structure analogous to that of $CuCl_2$ [254]. The single crystal data have been obtained only for the amine complexes, derivatives of fluorinated alcohols and bimetallic complexes. The coordination of the Cu(II) centers in them may be quite different, such as, triangular, square planar, tetrahedral, or trigonal bipyramidal; the molecular complexity varies from monomeric structures to the polymer ones.

$Cu(OR)_2$ were proposed as catalysts for the Et_2S oxidation in oil [1068], for the oxidative polymerization [60], for the reversible fixation of CO and CO_2 with formation of alkylcarbonates [1381, 1602], and also as alkoxylating agents in the reactions with RHal for the synthesis of ethers [1741]. Reduction of the copper glycerate with metallic Al was used for the preparation of high-purity copper powders with 0.01 to 0.05 m particle size, which is a highly active catalyst [715].

The alkoxides of copper(II) were successfully applied in the preparation of HTSC ($YBa_2Cu_3O_{7-\delta}$, and Bi- and Pb-containing ones). It is covered by a great number of publications (especially in patent literature), but the chemical principles of the preparation of these materials remained unchanged since the very first ones [958, 755, 1614, 1620, 1633] (see also Section 10.5).

12.2.3. Derivatives of gold (I)

Derivatives of gold containing the Au–O–C bond are derivatives of fluorinated alcohols and appear to be always stabilized by PR_3 ligands. They all are therefore stable to hydrolysis and soluble in chlorinated organic solvents. Of special interest are derivatives of a dibasic alcohol $C(CF_3)_2(OH)_2$, where both hydroxyl groups are attached to the same carbon atom. The analogous derivatives have also been described for Cu(I).

Table 12.3. Copper, silver and gold alkoxodes

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
Cu(I)				
CuOMe↓	4	yel. powd., 20(dec.), t→ $Cu + Cu_2O$(expl.)	IR	413, 1741
Cu(OR)(PPh$_3$)$_n$, n=1, 2 R=Me, Et, Pr^n, Pr^i,C_3H_5, CH_2Ph; **Cu(OCHPh$_2$)(PPh$_3$)$_n$**, n=2, 3	4	clrl. cr.,α=1 (bz) 200°→Ph_2CO+...	IR, ^1H,TGA	966, 1241
CuOBu^n	4	yel. powd., by 20°	-	1741
CuOBu^s	4	stab.		1741
[CuOBu^t]$_4$, square [O_4], Cu-at. in the mid-points of the edges	5	yel. cr., 260 (m., dec),170/1 (subl.); 400°/10^{-5} →$Cu + Cu_2O$	m-s, tensim., X-r	676, 841, 1008, 1602,1741
[Cu(OBu^t)(PR$_3$)]$_2$,R= Pr^i,$C_6H_{11}{}^c$, Ph - 2 trian. with a common side (μ-OR)$_2$		pale yel., s. in bz., hex.	IR, ^1H, ^{31}P, X-r	1670
CuOR, R=$C_4H_7{}^c$,CHMePr, $CHEt_2$, $C_5H_9{}^c$, $C_6H_{11}{}^c$, $CHPh_2$	4	yel.sld., s. in eth.; t→ $CuO + Cu + RCH_2OH$ +...	-	1741
[CuOCEt$_3$]$_n$	5	visc. liq.,110/10^{-5} (subl.), 135 (dec.), s. in org. solv., α=3.6	^1H, ^{13}C, cryosc.	1196
CuOCHBu$^t_2$	5	pale yel. cr., 150 (dec.), s. in eth., α=4 (bz.)	IR, electr. sp., cryosc.	167

CuOPh	4, 5	colrl. cr., ins. in eth.	-	1196, 1588
[Cu(OPh)(PPh$_3$)$_2$]$_2$, 2 tetrah. with a common (μ-OR)$_2$- edge	4, 6		IR, ^{1}H, X-r	1241, 1027, 1263
[Cu$_2$(OPh)$_2$(PPh$_3$)$_3$], trian. and tetrah. with a common edge	3, 4, 6		X-r	
[Cu(μ$_3$-OPh)(PPh$_3$)]$_4$·2PhMe cubane-like core			X-r	
[Cu(OPh)(4-MeC$_6$H$_4$NC)$_2$]$_2$ 2 oct. sharing a (μ-OR)$_2$ edge, Cu...C	5		-	
[Cu(μ-OAr)(Et$_3$N)$_2$]$_2$, Ar =Ph, C$_6$H$_4$Me-4, C$_6$H$_4$Bu^t-4, C$_6$H$_4$Me-3, C$_6$H$_3$Me$_2$-3,5, C$_6$H$_4$OMe-4, naphthols	5	-	-	1196
[Cu(OC$_6$H$_3$Ph$_2$ -2.6)]$_4$, square [O$_4$], Cu-atoms in the mid-points of the edges	4	wt., 20 (dec.)	IR, ^{1}H, ^{13}C, X-r	1027
Cu(OBu^t)$_n$(OR^F)$_{1-n}$, R^F=C$_4$F$_9$^{t}, C(CH$_2$F)$_3$, CMe(CF$_3$)$_2$, CMe$_2$(CF$_3$)		wh. sld., 70/10^{-3}, 95/10^{-3} (subl.)	-	683
[Cu[OCH(CF$_3$)$_2$](PPh$_3$)$_n$], n=3 (tetrah.) , 2	4	clrl. cr., 90/10^{-3} (subl.)	IR, ^{1}H, X-r	683, 1241
[CuOSiR$_3$]$_4$, R=Me,Et; R$_3$=Me$_2$Bu^t square	4, 5	sld, oil (Et), wt, α=4, diamagn.	IR, ^{1}H, ^{13}C, ^{29}Si, X-r	1416, 1094
[CuOSiPh$_3$]$_4$, square [O$_4$], Cu-at. in the mid-points of the edges <O-Cu-O 176, <Cu-O-Cu 93-95, **·PhMe**	4	yel.cr., s. in hc.	IR, ^{1}H, ^{13}C, ^{29}Si, X-r	1094
[Cu(OSiPh$_3$)L]$_2$, L=PMe$_2$Ph, **PEt$_3$** 2 trian. with a common edge (μ-OR)$_2$]		colrl. cr., α=2	IR, ^{1}H, ^{13}C, ^{29}Si, m-s, X-r	

$CuOC_2H_4OEt$	5		$^1H, ^{13}C$	1425
$[Cu_2(\mu\text{-}OAr)(\mu\text{-}Cl)(Et_3N)_4]$, Ar=Ph, C_6H_4Me-4, $C_6H_4Bu^t$-4, C_6H_4Me-3, $C_6H_3Me_2$-3,5		-	-	1196
$[Li_4Cu_4(\mu_3\text{-}OBu^t)_4(\mu\text{-}OBu^t)_4]$, two 8-membered cycles $[Li_2Cu_2(\mu_3\text{-}OR)_2(\mu\text{-}OR)_2]$ with common $[Li_2O_2]$-gr.; [OCuO]-linear, $[LiO_3]$ -trian.		poorly yel. cr., 150/vac. (subl.)	$^1H, ^{13}C$, ESP, electr. sp., m-s	1321
$NaCu(OBu^t)_2$ **$Ba[Cu(OBu^t)_2]_2$** **$[LnCu_2(OBu^t)_5]_2$**, Ln=La,Pr,Nd, Sm,Lu oct. *trans*-$[Sm_2Cu_4]$, 8 (μ_3-OR), 2 (OR) term.		wh.,180/10^{-5} (subl.), 240(dec.) invol., 240 (dec.) cr., bl. (Nd), yel. (Sm), 210/10^{-2} (subl.), μ_{eff}=1.51 (Nd, Sm), s. in org. solv.	$^1H, ^{13}C$, electr. sp., ESP, m-s IR, ^1H, X-r	1321 1213
$NaCu(OCEt_3)_2$		wh., 185/10^{-5} (subl.), 220(dec.)	-	1321
$[Ba_2Cu_4(OCEt_3)_8]$ **$[BaCu_6(OCEt_3)_8]$** 2 cycles $[BaCu_3(\mu\text{-}OR)_4]$, tetrah. $[BaO_4]$, gr. $[Cu(OR)_2]$ - linear, $[Cu_3(OR)_4]$ -plane **$[Ba_4Cu_6O(OCEt_3)_{12}]$**, the edges of $[(\mu_4\text{-}O)Ba_4]$ tetrah. are capped with 6 linear $[Cu(\mu\text{-}OR)_2]$, $[BaO_4]$ -tetrah.		colrl. cr., 170/vac. (dec.), poorly s. in THF colrl. cr., s. in C_7H_{16} -	$^1H, ^{13}C$, ESP, electr. sp., m-s $^1H, ^{13}C$, X-r X-r	1321

***trans*-[BaL]$_2$[Cu$_4$(OR)$_8$],** R=Bu^t, CMe$_2$CF$_3$, L= Me$_3$NO, Et$_3$PO, [M$_6$]-oct., 2 Ba-ax., all μ-OR - along non-equ. edges, gr. [OCuO]-linear, L -ax.		-	^{1}H, ^{19}F, X-r	173
[BaTHF(μ-OR)]$_2$[Cu$_2$(μ-OR)$_4$], R= CMe(CF$_3$)$_2$, [O$_4$]-square with Ba and Cu in the mid-points of the edges, 2 Ba (trig. bipyr.) bind 2 μ-OR, Ba...F, CN Ba 11		-	^{1}H, ^{19}F, X-r	173
Na$_x$Cu(OAr)Cl$_x$, Ar=Ph, C$_6$H$_4$Me-4, C$_6$H$_4$Bu^t-4, C$_6$H$_4$Me-3, C$_6$H$_3$Me$_2$-3,5		-	-	1196
[K(crown)]$^+$[Cu(OSiPh$_3$)$_2$]$^-$·1/2PhMe		-	IR, ^{1}H, ^{13}C, ^{29}Si, m-s	1094
[YCu(OSiPh$_3$)$_4$(Me$_2$PhP)], tetrah. [YO$_4$], trian. [CuO$_2$P] with a common (μ-OR)$_2$ edge		-	IR, ^{1}H, ^{29}Si, ^{89}Y, X-r	396
[Cu$^I_2$Zr$_2$(OPr^i)$_{10}$] [1664, 1385]; **[Cu$^I_4$Zr$_4$O$_3$(OPr^i)$_{18}$]** [1385]				
Cu(II)				
Cu(OMe)$_2$↓	2, 5, 6, 7	bl. sld., s. in liq.NH$_3$, 188 (dec.→Cu), $\mu_{eff.}$= 1.12-1.24, antiferr.	IR, electr. sp., magn. prop.	7, 6, 97, 254, 413, 1108, 1410, 1493, 1614, 1602
Cu(OMe)$_2$·L·nMeOH L=En, Dipy,Phen, n=1, 2	1, 3, 4	bl. sld., $\mu_{eff.}$=1.64, 400° →CuO	IR, electr. sp., ESR,magn.prop.	936
Cu(OEt)$_2$↓	2, 5, 6	bl.sld.,$\mu_{eff.}$=1.20; t→MeCHO+Cu	IR, electr. sp., magn. prop.	97, 958,1102, 1108, 1410, 1493

$Cu(OEt)_2 \cdot L \cdot nEtOH$ L=En, Dipy, Phen, n=1, 2	1, 3, 4	bl.sld., $\mu_{eff}=1.43$	IR, electr. sp., ESR, magn. prop.	936
$Cu(OPr^n)_2$↓	2	grn. sld.	IR	97, 1614
$Cu(OPr^i)_2$↓	5, 6	bl. sld., $\mu_{eff}=1.50$	IR, magn. prop.	1108, 1493
$Cu(OBu^n)_2$↓	2	grn. sld., $\mu_{eff}=1.18$	IR	97, 1493, 1614
$Cu(OBu^s)_2$↓	6	grn. sld.	IR, magn. prop.	1493
$Cu(OBu^t)_2$ ↓	5, 6, 7	yel.-grn. sld., 150° → $CuOBu^t$↑	IR, electr.sp., magn. prop.	1108, 1493, 1602
$Cu(OC_5H_{11}^t)_2$↓	6	grn. sl d., $\mu_{eff}=1.83$	IR, magn. prop.	1493
$Cu(OC_6H_{11}^c)_2 \cdot 1/4Dmfa$↓	2	-	-	1410
$Cu[O(CH_2)_6Me]_2$↓	6	bl. sld.	IR	653
$Cu(OCEt_3)_2$	5	or.-brn. lig.,	^1H, electr. sp., ESP	1321
$Cu(OPh)_2$↓	2	grn. sld.	IR, electr. sp., ESR,. magn. prop.	97
$[Cu(OPh)_2Dipy]$	5	brn. cr., s. in THF, $\alpha=1$, $\mu_{eff}=1.69$	X-r	289
$[Cu(OPh)_2En]_2 \cdot 2PhOH$↓ 2 tetragon. pyr. with a common $(\mu\text{-}OR)_2$ edge	5	grn. cr, $\mu_{eff}=1.78$		
$Cu(OCH_2CF_3)_2$ **$Cu(OCH_2CCl_3)(OMe)$**	5, 6	-	IR, ^1H, ^{19}F, electr. sp., m-s, magn.. prop.	316

$[Cu[OCH(CF_3)_2]_2Am]$, Am=Tmeda, Dipy, 2Py, square	5, 6	purple cr., 60-150 (m.), vol.,300°→Cu	ESR,electr. sp., X-r,	841
$[Cu[OCMe(CF_3)_2]_2Am]$, Am= Tmeda, Dipy, 2Py, square	5, 6	bl.- purple, cr., 70-138 (m.), vol.	IR, ESR, electr. sp., X-r	841
$[Cu_4(\mu\text{-}OBu^t)_6[OC(CF_3)_3]_2]]$ (1), linear chain, in the center - 2 tetrah. with a common $(\mu\text{-}OR)_2$ edge, each shares a $(\mu\text{-}OR)_2$ with a trian.	6	155 (m.,dec.), subl.→ $Cu(OR)_2$, in s.→ **2**+$Cu(OR)_2$, antiferr., J=-131.6	IR, ESR, ^1H, ^{19}F, magn. prop., X-r	1321
$[Cu_3(OBu^t)_4[OC(CF_3)_3]_2]$ (2)	6	yel., t,vac.→ $Cu(OBu^t)_2$ +**1**; antiferr., J=-114.4		
$[Cu(OBu^t)[OC(CF_3)_3]]_n$	6	157 (m.),110/vac.(subl.)		
$[Cu^{1.75+}{}_4[OC(CF_3)_3]_7]_n \cdot nEt_2O$, n=0-4	4	<20 ° subl.vac.	-	1321
$Cu[OC(CF_3)_2]_2 \cdot$ Tmeda,	4	purple sld., 191(m.,dec.), s. in $Me_2CO\text{-}H_2O$, μ_{eff} =1.87	magn. prop.	427
$Cu[OC(CF_3)_2]_2O$ Am, Am=Phen, Dipy, En, Tmeda $[CuN_2O_2]$ square with 2 chelate cycle	5	pink cr., 150(m.), s. in CH_2Cl_2	X-r	195, 427, 798
$Cu[OC(CF_3)(C_6F_5)]_2 \cdot (\text{-}CH_2NMe_2)_2$	4	opt. isomers	^{19}F, electr.sp.	
$\{Cu[OSi(OMe)_3]_2Py_2\}$, tetrah.	5	grn.cr., s. in THF, hc.	IR, ^1H, X-r	1097
$Cu(OC_2H_4OMe)_2\downarrow$ **$\cdot 4$ Dmfa**	1, 2, 6	bl. cr.	IR	653, 1614, 1652

$Cu(OC_2H_4OEt)_2$↓	5	bl.cr., $\mu_{eff}=1.28$, 600°→CuO	^{13}C, magn. prop., electr. sp.	1425, 834
$Cu(OC_2H_4OBu^n)_2$	-	s. in org. solv.		1321
$[Cu(OC_2H_4OC_2H_4OMe)_2]_n$, $n\geq5$	6	bl.cr., s. in bz., $\mu_{eff}=1.18$	IR, ^1H, magn. prop.	653
$Cu(OC_2H_4O)$↓	2	-	IR	97
Cu(OR)Cl↓, R=Me, Et, Bu^n, Bu^t, **$CuCl(OCH_2CHal_3)_2$,** Hal=F, Cl		grn. powd., $\mu_{eff}=1.67$ (Me), 1.40 (Et)	IR, magn. prop.,electr. sp.	5, 254, 316, 1603
$[Cu_2(OMe)_2Cl_2Py]_\infty$, linear chains of dimers - tetragon. pyr. with a common $(\mu\text{-}OR)_2$-edge, sharing a $(\mu\text{-}Cl)_2$ edge		grn. .cr., antiferr.	ESP, magn. prop., X-r	1747
Cu(OMe)Br↓		brn., paramagn.	IR, electr. sp.	5
$Na_2Cu(OPr^i)_4$		gray-grn. sld.,, invol., 75 (dec.), v. s. in THF	H, ^{13}C, ESP, electr. sp.	1321
$NaCu(OBu^t)_3$,		170 (m., dec.), $70/10^{-5}$ (subl.), 170 , α=2, 3; hν→$NaCu^I(OR)_2$	^1H, ^{13}C, ESP, electr. sp., m-s	1321
$NaCu(OCEt_3)_3$		grn. powd., 125 (dec.), v. s. in THF; hν→ $NaCu^I(OR)_2$	^1H, ESP, electr. sp.,	1321
$Ba[Cu(OBu^t)_3]_2$		yel.-grn. sld., $160/10^{-5}$ (subl.), 170(dec.); hν→$Ba[Cu^I(OR)_2]_2$	^1H, ESP, electr. sp.,	1321
$[Na_2Cu[OCH(CF_3)_2]_4]_\infty$ chains of cycles $[Na_2Cu_2O_4]$; $[NaO_{4/2}F_{5/2}]$-get 2 F atoms from OR at one Cu, 3 – from the other, **·4THF**		bl. cr., 140 (m.), $90/10^{-5}$ (subl.), 200 (dec.), s. in org. solv.	^{19}F, electr. sp., ESP, X-r	982, 1321

$[Ph_4P]_2\{Cu[OC(OH)(CF_3)_2]_4\}$, anion – a square in a 1 6-membered cycle	-	IR, electr. sp., X-r	798
$BaCu[OCH(CF_3)_2)]_4$	bl.cr., 220/10^{-5} (subl.),s.inTHF	^{13}C, ^{19}F, ESP	1321
$Ba[Cu(OCMe(CF_3)_2)_3]_2$, angular mol., central $[BaO_4]$-gr. is bound to $[CuO_3]$ - trian via common $(\mu\text{-}OR)_2$- edge, 9 Ba...F	grn. .cr., 70-90 (subl.)	IR, ESR, ^1H, ^{19}F, magn. prop., X-r	1321
$M_2Cu[(\text{-}CH_2O)_2]_2$↓, M=Na, K($\cdot 6H_2O$) **$Na_2Cu[(\text{-}CMe_2O)_2]_2$**	bl. or vlt. cr., 186(dec.)	-	1298
$[BaCu(\eta^2,\mu\text{-}ORO)_2[\eta^2\text{-}R(OH)_2]_3]$, $R=C_2H_4$, cubic $[Ba(OH)_6O_2]$ and square planar $[CuO_4]$ share a common $(\mu\text{-}OR)_2$ - edge **$\{Ba[\eta^2\text{-}R(OH)_2]_3[\eta^1\text{-}R(OH)_2]_3\}^{2+}$ $[Cu(\eta^2\text{-}RO_2)]_2^{2-}$**, cations - tricapped trig. $[BaO_9]$ prisms, anions - squares	bl.cr. -	X-r X-r	1028
$M_2Cu\{[OC(CF_3)_2]_2\}_2$, M=K, Cs	s. in H_2O, $\mu_{eff}=2.0$	magn. prop.	26
$M_2[Cu(C_6Br_4O_2\text{-}1,2)_2]$↓, M=K, $[H_2Tmeda]/2$	grey-grn. powd..	IR, ^{19}F, electr.sp.	1044
$BaCu_4[C_6H_8O_5(OH)]_2$↓ (derivative of mannit)	bl. cr.	-	1596
$Ba_2(CuO)_3Y(OC_2H_4OMe)_7$	-	-	1321
$[Cu_4Zr_4O_3(OPr^i)_{18}]$ [1385]; **$[CuClM^{IV}{}_2(OPr^i)_9]$**, M^{IV}= Ti, Zr, Hf [1664, 1686, 1690]; **$CuLa_6O(OBu^t)_{18}THF_3$** [442]			

Ag *

AgOPh↓	3	wh. powd., pyroph.	-	1806
$Ag_2(C_2H_4O_2)$ ↓ (?)	2	s. in NH_4OH	-	1280
$[Ag(OSiMe_3)(PMe_3)_n]$, n=1-3	5	$\alpha=1$ (bz), vol.	^1H, cryosc.,m-s	1416

Au*				
[Au(OBu^t)(PPh$_3$)]	5	wh.	IR, ^{1}H	1546, 940
[Au(OPh)(PPh$_3$)]	4	98 (m.)	IR, ^{1}H	1293
[Au(OR)(PPh$_3$)], R= CH(CF$_3$)$_2$, CH$_2$CF$_3$,	5	118 (m.), 184 (m.)	IR, ^{1}H	940
AuOSiMe$_3$(PMe$_3$)		subl. (?)		1416
[(PPh$_3$)Au]$_2$(C$_6$H$_4$O$_2$-1,2), gr. [OAuP] -linear	5	157(m.)	X-r	979
[(PPh$_3$)AuO]$_2$C(CF$_3$)$_2$], **·H$_2$O**	4	wt., yel cr., 125, 135 (dec.)	IR	1160

*All marked complexes are stable in ambient atmosphere

12.3. Beryllium alkoxides

Beryllium belongs to those few elements whose alkoxides are much less studied than the derivatives of other elements and definitely less than those of the other Group II metals and especially of those of its diagonal analog aluminium. The first attempts at $Be(OEt)_2$ preparation were attempted by Schmidt [1426] in 1929 via the action of metal on EtOH (in the presence of $AlCl_3$ or $BeCl_2$) and also on the chloride metathesis with NaOEt. It turned out that $Be(OEt)_2$ was insoluble in alcohol and not volatile, which hindered its separation from NaCl. The data of Meerwein [1101] on the existence of a bimetallic $K_2Be(OEt)_4$ complex were not confirmed later [1645], but a large number of bimetallic complexes with 1:1 composition were subsequently described 1:1 (see Table 12.4). A great contribution to the chemistry of beryllium alkoxides was made by Coates and his collegues, who carried out the preparation of oligomeric $Be(OR)_2$, alkoxide halids and alkoxoberyllates with branched radicals — volatile and soluble in nonpolar solvents.

12.3.1. Synthesis

The interaction of metal with alcohol (on catalytic action of $BeCl_2$, $HgCl_2$ or I_2) is used only for the synthesis of the ethoxide, which precipitates on reflux (method 1). In the case of MeOH or ^iPrOH, the stable viscous liquid alkoxide halids are formed [1645, 1624, 1120]. The electrochemical approach (method 2) was applied only for the preparation of $Be(OC_2H_4OMe)_2$ [1652].

The reaction of berylliumorganic compounds with alcohols (method 4) or ketones (method 7) yields RBeOR', which usually are stable to further alcoholysis, but the action of the excess of alcohols on BeR_2 ($R = Me, Et, Pr^i$) at low temperatures gave $Be(OR)_2$ ($R = Me, Bu^t, CEt_3$) [399]. The dimeric MeBeOMe easily disproportionates with the formation of $BeMe_2$ and insoluble $Be(OMe)_2$ [399]. The metathesis of $BeCl_2$ with lithium alkoxides (method 5) was proposed for the preparation of polymeric $Be(OR_n)_2$ and $Be(OPr^i)_2$ [65]; however, the IR spectra of the products presented in this publication indicate the presence of considerable amounts of admixtures.

A heterogeneous alcohol interchange interaction between solid $Be(OMe)_2$ and higher alcohols in refluxing benzene provided $Be(OR_n)_2$ ($R= C_6H_{11}, C_8H_{17}$) [65], while the prolonged refluxing of $Be(OEt)_2$ with methanol gives the methoxide [681] (method 6).

12.2.2. Properties

All the derivatives of the alcohols with *n*-structure —$Be(OPr^i)_2$ and quite unexpectedly $Be(OC_2H_4OMe)_2$— are amorphous polymers, insoluble, and not volatile. The same is true for the phenoxides with nonbranched Ar-groups.

$Be(OR^t)_2$, $Be(OSiR_3)_2$, and $Be(OArR_2\text{-}2,6)_2$ are oligomeric compounds easily soluble in organic solvents and volatile in vacuo **(10^{-2} mm Hg)**. It is worth mentioning especially the perfluoro-*t*-butoxide $Be[OC(CF_3)_3]_2$, which sublimes at room temperature [39]. The majority of the molecules of this class are trimers. According to the Proton NMR data for $Be(OBu^t)_2$, their structure is analogous to that of $[Be_3Cl_2(\mu\text{-}OBu^t)_4]$ (see below). On transition from $Be(OCEt_2Me)_2$ **to** $Be(OCEt_3)_2$ (i.e., on substitution for the third Me-group with the Et one), the molecular complexity decreases to 2; the molecule of $Be[OC(CF_3)_3]_2$ was also found to be dimeric [39]. In both of these the Be atoms do apparently have a triangular coordination. The molecules of 2,6-**Bu^t_2-substituted phenoxides** are already monomeric, and the Be atoms in them should posses a linear coordination (which has been otherwise known only for $BeHal_2$ in the gas phase). The lower molecular complexity and increased CN for Be can also be achieved by the solvation of the oligomeric molecules. Thus $Be(OBu^t)_2 \cdot 4\text{-}Me_2NC_5H_4N$ is a monomer, in which the bidentate ligand causes the formation of a tetrahedral chelate (it is interesting to note that NH_3, amines, Py, and Dipy are unable to form complexes with trimeric $Be(OBu^t)_2$). Complexation of Et_2O with dimeric $Be[OC(CF_3)_3]_2$ or monomeric $Be(OC_6H_2Bu^t_3\text{-}2,4,6)_2$ leads to formation of monomers with tricoordinated Be atoms [39, 1372].

Rather stable alkoxide halids of variable composition are formed on alcoholysis of $BeCl_2$ with primary or secondary alcohols and also on interaction of $BeHal_2$ with $Be(OR)_2$. These are viscous liquids, which leads to suspection of the presence of oxo-ligands in their composition. The interaction of the solid ethoxide with the solution of $BeCl_2$ in ethanol for several months has produced a solid crystalline $BeCl(OEt) \cdot 2EtOH$ **[1624]**. The alkoxide halids with R^t of 2:2 and 3:2 compositions are easily crystallized from the nonpolar solvents. The dimeric $[BeBr(\mu\text{-}OBu^t)(Et_2O)]_2$ molecule consists of two tetrahedra sharing a common edge. The linear $[Be_3Cl_2(\mu\text{-}OBu^t)_4]$ molecule contains a $[BeO_4]$ tetrahedron in its centrum, which shares two opposite edges with the $[BeO_2Cl]$ triangles [137].

Table 12.4. Beryllium alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
$Be(OMe)_2$↓	4, 5, 6, 7	wh. sld., >360 (?-dec.)	IR	65, 399, 681, 1072, 1201
$Be(OEt)_2$↓	1, 5	wh. amor. sld., ins. in org. solv.	IR	65, 681, 1426, 1624, 1645
$Be(OPr^i)_2$↓ (?), $Be(OBu^n)_2$↓	5	wh. powd.	IR	65
$Be(OBu^t)_2$	4, 5	cr.,112 (m.), $100/10^{-3}$ (subl.), s. in hex., bz., α=3	IR, cryosc.	39, 137, 399
· 4-$Me_2NC_5H_4N$		cr., 157 (m.), s. in hex., α=1		
$[Be(OBu^t)L]_2O$, L=THF, Py		cr., s. in L		39
$Be(OC_5H_{11}{}^t)_2$	5	wh. sld., s. in eth., 48(m.); $100/10^{-3}$ (b.), α=3	cryosc.	39
$Be(OC_6H_{13}{}^n)_2$↓	6	yel. sld.	IR	65
$Be(OCEt_2Me)_2$	5 ,7	wh. sld.; 38 (m.); $120/10^{-3}$ (b.); s. in eth., α=3	IR, ^1H, cryosc.	39
$Be(OCEt_3)_2$	4, 5	wh. sld., 36(m.), $50/10^{-3}$ (subl.); v. s. in bz., eth., **α=2**	IR, ^1H, cryosc.	39, 399
$Be(OC_8H_{17}{}^n)_2$↓	6	yel. sld.	IR	65
$Be(OCHBu^t{}_2)_2$	4, 7	wh. sld.,390(dec.),low s. in bz.	IR	39
$Be(OAr)_2$↓ Ar=C_6H_5, C_6H_4Me-3, -4, α-$C_{10}H_7$ (?), β-$C_{10}H_7$	4	wh. sld., ins. in org. solv., 300-350 (dec.)	X-r powd.	589, 599, 1315, 1485, 1645

$Be(OC_6H_3Bu^t_2\text{-}2,6)_2$	4	cr.,174(m.);120/10^{-2} (subl.);α=1	^1H, cryosc.	39
$Be(OC_6H_2Bu^t_3\text{-}2,4,6)_2$, **·$Et_2O$,** trian.	4	152 (dec.) ,s. in eth.; 120 (m.,dec.)	IR, ^1H, X-r	1372
$Be[OC(CF_3)_3]_2$, **·Et_2O** · **2L,** L=NH_3, Py	4 5	cr.,85 (m.),20/10^{-2} (subl.),α=2, s.in C_6F_6, $PhNO_2$, ins. in bz. cr., 43/10^{-3} (subl.);s.in bz.,α=1 cr., m.: 94, 128	IR, ^1H, ^{19}F	39
$Be(OSiMe_3)_2$	5	pale yel. sld., 69 (m.), 80/10^{-2} (subl.); s. in eth., α=3	IR, ^1H, ^9Be, cryosc.	39
$Be(OC_2H_4OMe)_2$↓	2	wh. powd., ins. in org. solv.	IR, X-r powd.	1652
$BeO_2C_6H_4$-1,2, -1,3, -1,4↓	4	colored sld., ins. in org. solv.	-	1315
BeCl(OEt)· L, **L=2 EtOH,** **·0.7 AcOEt**		cr.,106 (m., dec.), s. in ROH 26%, system .$BeCl_2$-$Be(OR)_2$-ROH (20°); visc. liq.	IR, cryst.-opt.	1120, 1624
$BeHal(OBu^t)$, Hal=Cl, Br, I; **·L,** L=Et_2O, THF		130(dec.**Cl**),s.in eth., bz., α=4 cr., 85 (m., Cl, Et_2O), 175 (m., dec., Cl ,THF), 160 (dec., I, Et_2O), s. in eth., bz., α=2	IR, ^1H, cryosc.	39 137

$[BeBr(OBu^t)(Et_2O)]_2$, 2 tetrah. sharing a (μ-OR)$_2$ edge	cr.,130 (dec.), s. in eth., bz., α=2	IR, ^1H, X-r	39, 137·
$BeCl(OC_5H_{11}^t)\cdot THF$	cr., 149 (m.), s. in eth., hex., α=2	cryosc.	39
$BeCl(OCEt_2Me)$	126 (m.); s. in eth., α=2	cryosc.	39
$BeCl(OCEt_3)\cdot THF$	63 (m.); α=2	cryosc.	39
$BeCl(OCHBu^t_2)$	190 (dec.), α=2	cryosc.	39
$BeCl(OCH_2Bu^t)\downarrow$, $\cdot Et_2O$	250(dec.); 162(m.), α=1-2	cryosc.	39
$[Be_3Cl_2(\mu\text{-}OBu^t)_4]$, linear chain, central tetrah. $[BeO_4]$ sharing a (μ-OR)$_2$ edge 2 trian. $[BeO_2Cl]$	cr., 330 (dec.)	X-r	39, 137
$Be_3Hal_2(OBu^t)_4$, X = Br, I, **$Be_3(Me_2N)_2(OBu^t)_4$**,	cr.,s. in bz.-hex.,180 (dec.,Br), 155 (dec.I), α=1 cr.,93 (m.), 70/10^{-3} (subl.), s. in bz., ins. in hex.	IR, ^1H, cryosc.	39
$Be_3Cl_2(OC_5H_{11}^t)_4$	cr.,85(m.); s. in eth., hex., α=1		39
$BeCl[OCH(CH_2Cl)_2]\cdot Et_2O$ **$BeCl(OCH_2CH_2Cl)\cdot Et_2O$**	cr., 114 (m., dec.), s in CCl_4 cr., 199 (m.)		1100
$NaBe(OMe)_3\cdot MeOH$	cr.,40(dec.),s.inROH, ins. in bz.	IR, tensimetr.	137
$MBe(OPr^i)_3$, M=Li, Na	sld., Li: α=2; Na: α=1 (ROH)	ebul.	65

$MBe(OBu^t)_3$, M=Li, Na, K, Rb, Cs	cr., Li, Rb - s. in bz;. **Li**: 212 (dec.); **Na**:215 (dec.); **K**:162(m.), s. in THF; **Rb**:145 (dec.), s. in bz., **Cs**: 179(m.)	IR, ^1H, ^9Be	39
$MBe(OBu^t)_3 \cdot Dig$, M=Li, Na	cr., s. in hex., bz., 69 (m., Li), 82 (m., Na), α=1		
$LiBe(OBu^t)_2(OC_5H_{11}{}^t)$	sld., 138 (m.), $75/10^{-2}$ (subl.), s. in eth., α=2	cryosc.	39
$LiBe(OC_5H_{11})^t{}_3$	cr., 56 (m.), $100/10^{-2}$(subl.), s. in eth., α=2	IR, ^1H, ^9Be	39
$LiBe(OCEt_3)_3$	cr., α=1-2	cryosc.	39
$LiBe(OSiMe_3)_3$	cr.,172(m),110/vac.(subl), α=2	IR, ^1H, ^9Be, ebul	39

$Be[Ta(\mu\text{-}OEt)_2(OEt)_4]_2$ [1519]; **$BeAl_2(OR)_8$, $BeAl_2(OPr^i)_2(OR)_6$, $BeAl(OPr^i)_5$(?)** [15, 1117]

A number of heteroleptic alkoxide complexes with analogous composition — $Be_3X_2(OBu^t)_4$, X=R, N_3, CN, NO_3, RS, Me_2N, and so on — were found to possess a considerable thermal stability [39]. They are supposedly structural analogs of alkoxide halids, which is confirmed by the data of an X-ray single-crystal study of $Be_3(BH_4)_2(\mu\text{-}OBu^t)_4$ [1174]. The cubane-like structure (analogous to that of $[RZnOR']_4$) was proposed for numerous products of partial alkaholysis of $BeMe_2$ — tetrameric MeBeOR [399]. The dimeric Bu^tBeOR molecules do obviously contain the $[Be_2O_2]$ cycles [39].

$Be(OBu^t)_2$ reacts with alkali alkoxides forming the complexes of $MBe(OCMe_3)_3$ (M = Li, Na, K, Rb, Cs) composition, which are easily soluble in nonpolar solvents and dimeric in solution. They are also formed on alcoholysis of Na_2BeH_4 or organometallic compounds [39]. The known alkoxoberyllates with less branched radicals (Me, Pr^i) have the same composition, but due supposedly to the higher polarity of the M–O bonds they are soluble only in alcohols [137, 65]. The question concerning the individuality of the liquid alkoxoberyllates of aluminium [1117, 15] should be so far considered as open in the view of the absence of the mass-spectral confirmation. Concerning the existence of trimetallic $BeAlM^V(OPr^i)_{10}$ [14], see Section 12.16.

12.4. Zinc, cadmium, and mercury alkoxides

The derivatives of Zn were among the first derivatives studied. The methanolysis of ZnR_2 was described first by Butlerov [1591] and Beilstein [1354] in 1863. Its products were found to be RZnOMe or $Zn(OMe)_2$, depending on the ratio of the reactants. The detailed study of this process was carried out in the 1900s by Tishchenkos pupil Tolkachev [1591]. At the same time, even now the alkoxides of Zn, Cd, and Hg remain much less studied than the intermediate alcoholysis products derived from metalorganic derivatives — RMOR'. The volatile and soluble zinc alkoxides useful as precursors of the ZnO-derived oxide materials were obtained only during the last decade. Hg(OR)2 are very unstable and decompose even on short-term storage.

12.4.1.Synthesis

The alcoholysis reaction starting from dimethyl- or diethylzinc remains the major approach to $Zn(OR)_2$. The latter can contain admixtures $R_nZn(OR')_{2-n}$, which can be separated by destination in vacuum [255]. The alkyl-alkoxoderivatives are usually very stable. Thus EtZnOR, R = Pr^i, Bu^t, and $C_6H_3Bu^t_2$-2,6 are not decomposed even on reflux with an excess of the corresponding alcohol or phenol [731, 255, 628], while the alcoholysis of Ph_2Zn can easily be completed [255]. The considerable stability of alkyl-alkoxides like $[RZnOR']_4$ and $Zn_7R_6(OR)_8$, existing in equilibrium with ZnR_2 [525], is supposedly provided by their structures. The former are built up of cubane-like molecules with alternating Zn and O-atoms in the vertexes, while the latter are "dicubanes" — the pairs of two such cubes sharing a common Zn-vertex (the corresponding Zn atom being octahedrally coordinated, see Section 4.4).The better but less accessible starting reagent for the alcoholysis reaction appears to be $Zn[N(SiMe_3)_2]_2$ (used recently for the preparation of $Zn(OR)_2$— derivatives of rather branched alcohols). Zn and Cd phenoxides can be prepared by alcoholysis of the corresponding acetates [1095] (method 4). The derivatives of mercury form under the same conditions as the mercuroorganic phenols or are reduced, giving the metallic mercury [1070].

The metatheis of acetates with the alkali alkoxides (method 5) can be used for the preparation of the methoxides and ethoxides of all three elements and is the only reaction leading to $Hg(OR)_2$ [1623]. The trans-esterification of $Zn(OMe)_2$ (method 6), according to [1121], can be carried out only in the presence of LiOR (forming soluble bimetallic complexes). The direct electrochemical synthesis on the anodic oxidation of metals in alcohols has been described for $Zn(OEt)_2$ and a series of cadmium derivatives ($Cd(OR)_2$ — obtained in the presence of such donor ligands as Dipy, Phen, and Dmso [98]) (method 2).

12.4.2. Properties

The derivatives of the title metals are white (Zn, Cd) or yellow (Hg) solids, usually insoluble in organic solvents, not melting and not volatile. It is interesting to note at the same time that the polymeric methoxides and ethoxides of Zn and Cd (as well as the corresponding hydroxides) undergo "aging." Thus after the prolonged reflux in alcohols they lose the ability to dissolve in acids and even in *aqua regia.* Their X-ray patterns display sharp, intense lines demonstrating the formation of the crystalline structure instead of the halo, characteristic of the fresh samples [1623, 1649]. The pyrolysis temperature for the samples of $Cd(OMe)_2$ increases from 289 to 421 on storage during 6 months [823].

The trend to aggregation is so strong for $Zn(OR)_2$ that the separate molecules can be formed only with such sterically crowded radicals as CEt_2Me,

CEt_3, $C_6H_3Bu^t_2$-2,6, and $C_6H_2Bu^t_3$-2,4,6. The first of these derivatives is insoluble in organic solvents but can be sublimed in a high vacuum; the second is soluble even in hexane and is rather volatile. Its tetrameric nature in solution suggests a cubane-like structure. The phenoxides coming next are soluble in hydrocarbons but not volatile. Their dimeric nature suggests that their molecules are triangles sharing a common edge. The comparison of these molecules with the corresponding derivatives of beryllium ($Be(OBu^t)_2$ — trimer, $Zn(OBu^t)_2$ — polymer, $Be(OCEt_3)_2$ — dimer, and $Be(OC_6H_3Bu^t_2\text{-}2,6)_2$ — monomer [198]) illustrates the increase in the coordination numbers with the increase in the atomic radius. The alkoxides of cadmium form apparently less stable aggregates than their Zn analogs. This conclusion can be made using the comparison of the properties of the t-butoxides or 2-methoxyethoxides (see Table 12.5). The Zn atoms usually are tetrahedrally coordinated in the oligo- and polymeric structures (the CN = 5 was observed for Zn only in the structure of its monoglycerate).

Cadmium methoxide and ethoxide crystallize formed a layered polymeric structure of CdI_2 type as well as $Cd(OH)_2$. The nonanuclear molecule of cadmium 2-methoxyethoxide contains 7 octahedra and 2 5-vertex polyhedron; while the metal atom in the structure of $[Cd(OC_6H_4Bu^t_2\text{-}2,6)_2THF_2]$ has a square planar coordination.

The major application of $Zn(OR)_2$ is connected with their catalytical activity in the polymerization of olefine oxides. It is rather interesting that the activity of the freshly prepared amorphous samples of the zinc methoxide, ethoxide, or $Zn(OMe)_n(OEt)_{2-n}$ as heterogeneous catalysts in these reactions is noticeably higher than for soluble $R'ZnOR > ZnR_2$ as homogeneous catalysts [808, 1604].

The layered structure and hydrophobic properties of zinc monoglycerate prepared by high-temperature alcoholysis of acetate (in contrast to the properties of the samples obtained from the water solutions at room temperatures) permit it to be applied as a lubricant and alternative to graphite and talc [700]. The alkoxides of mercury were used in the 1970s as fungicides [715, 819] but were found to be too poisonous and were forbidden as they caused the death of birds and small animals in several places in Europe ("The dead spring").

Table 12.5. Zinc, cadmium, and mercury alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
$Zn(OMe)_2\downarrow$	4, 5	wh. sld.., 130 (dec.)	IR , X-r powd.	7, 27, 255, 808, 1591, 1623, 1649
$Zn(OEt)_2\downarrow$	2, 4, 6	wh. sld.	IR	255, 943, 1121, 1591
$Zn(OPr^n)_2\downarrow$, $Zn(OPr^i)_2\downarrow$	4, 6	wh. sld.	IR	255, 1121
$Zn(OBu^n)_2\downarrow$	6	wh. sld..	-	1121
$Zn(OBu^i)_2\downarrow$	4	280° $\rightarrow H_2+C_4H_8+ROH+C_4H_{10}+\ldots$	-	1591, 1585
$Zn(OBu^t)_2\downarrow$	4	sld.	IR	255, 401
$Zn(OCEt_2Me)_2\downarrow$	4	sld.., 250(m.), $180/10^{-4}$ (subl.)	IR, ^1H	650
$Zn(OCEt_3)_2$	4	sld.., 90 (m.), $220/10^{-4}$ (b.), s. in hex., $\alpha=4$	IR, ^1H, $^{13}C\{^1H\}$	650
$Zn(OC_8H_{17}{}^n)_2\downarrow$	6	yel. sld..	-	1121
$Zn(OCH_2Ph)_2$	6	-	-	1099
$Zn(OPh)_2\downarrow$	4	wh. sld..	-	1095, 978
$Zn(OC_6H_4Me\text{-}4)_2\downarrow$, $Zn(OC_6H_4C_8H_{17}\text{-}4)_2\downarrow$	4	wh. sld..	-	1095
$Zn(OC_6H_3Bu^t{}_2\text{-}2,6)_2$ $[Zn(OC_6H_3Bu^t{}_2\text{-}2,6)_2THF_2]$	4	wh. cr., $\alpha=2$, s. in bz., hex-THF colrl. cr.	^1H, cryosc.	628
$Zn(OC_6H_2Bu^t{}_3\text{-}2,4,6)_2$	4	colrl. cr., $\alpha=2$	^1H, cryosc.	628

$[Zn(OC_6H_2Bu^t_3\text{-}2,4,6)_2THF_n]$, n=1, 2, tetrah.		s. in hex., 1:2 +bz →1:1	X-r	
$Zn(OC_2H_4OMe)_2$	4	wh. sld.,s. in ROH, Py, sparingly - in bz, THF, 130(dec.)	IR, ^1H	255, 650, 539
$Zn(OC_2H_4OEt)_2$ $(RO)ZnO(CH_2)_nOR'$, $R,R'=C_1\text{-}C_{20}$	4	wh. sld., s. in tol. 10%, in ROH-25%	-	
$Zn(OC_2H_4OC_2H_4OMe)_2$	4	gl, s. in ROH, Py, 125 (dec.)	IR, ^1H	650
$Zn(OC_6H_4OMe\text{-}2)_2\downarrow$	4	wh. sld.	-	1095
$Zn(C_6H_4O_2\text{-}1,2)\downarrow$, $[Zn(\eta^2C_6H_4O_21,2)Phen_2]\cdot 2R(OH)_2$, $[ZnO_2N_4]$ - oct. $Zn(C_6H_4\text{-}C_6H_4O_2\text{-}2,2')\downarrow$ $Zn(C_{10}H_6\text{-}C_{10}H_6O_2\text{-}2,2')\downarrow$, ·Dipy	2, 4	colrl. sld., not melting stab. to H_2O, dec. by acids and bases 300 (dec.)	TGA, X-r	45, 1042
$[ZnC_3H_5O_2(OH)]\infty\downarrow$ polymer layers of 5-membered cycles $[ZnO_2C_2]$, $[ZnO_5]$ - trig. bipyr.	4	cryst. plates, ins. in org. solv., dec. by H_2O (t)	IR, X-r, X-r-powder	700, 1329, 1501
$3Zn(OR)_2\cdot ZnCl_2\downarrow$, R=Me, Et		wh. sld.	-	688, 1623
$M[Zn(OMe)_3(MeOH)]$ $M_2[Zn(OR)_4]$, M=Li, Na, K, R=Me, Pr^i		colrl. cr.	IR, ebul.	1101, 1121, 1471
$[M_2Zn_2(\mu_3\text{-}OBu^t)_2(\mu\text{-}OBu^t)_4]$, M=Na,K $Ti_4(OMe)_{16}$ type, 2 trig. pyr. $[M^2O_3]$, 2 tetrah. $[Zn^1O_4]$		colrl.cr., s. in eth., hc.,subl.:, 240, 216 (m.); 100/, 140/10^{-5} **(Na, K)**	^1H, X-r	1322
$KZn(OC_6H_3Bu^t_2\text{-}2,6)_2Br$		colrl. cr., s. in THF	^1H, cryosc.	628
$K_2Zn\{[OC(CF_3)_3]_2\}_2$		-	-	26

$Na_2Zn_2Cl_2(OMe)_4$		colrl. cr., s. in MeOH	ebul., conduct.	1471
$ZnM^{II}{}_2(OBu^t)_6$, M^{II}=Ge, Pb [1683]; **$ZnAl_2O_2(OR)_4$, R=** Bu^n, Bu^s [1244]				
Cd				
$Cd(OMe)_2\downarrow$ $Mg(OH)_2$ type with alternating [ROMOR]... layers, oct. $[MO_{6/3}]$, trig. pyr. $[OM_3]$	2, 4, 5	wh. sld., dec.:289→ 421 (6 months)	IR, NMR (calc.abinitio) X-r powder	98, 823, 995, 1191, 1623, 1649
$Cd(OEt)_2\downarrow$, isostr. with $Cd(OMe)_2$ with dist. orientation of layers	2, 5, 6	wh. sld., dec.: 228→257	IR, X-r powder	98, 823, 1623, 1649
$Cd(OPr^n)_2$, $Cd(OBu^n)_2$ **$Cd(OBu^t)_2$**	2 4	- wh..sld., s. in tol., THF, MeCN	IR IR	98 183
$Cd(OCH_2Ph)_2$	7	yel. cr.	-	1340
$Cd(OPh)_2\downarrow$, $Cd(OC_6H_4Me\text{-}4)_2\downarrow$	2, 4	greyish amor. sld..	-	98, 1095
$[Cd(OC_6H_4Bu^t{}_2\text{-}2,6)_2THF_2]$-*trans* square planar	4	yel. cr.	X-r	651
$Cd[OC_6H_2(CF_3)_3\text{-}2,4,6]_2THF_2$	4	145(dec.), s. in THF, hex., α=1	IR, ^1H, ^{19}F, m-s	1361
$Cd_9(OC_2H_4OMe)_{18}\cdot 2MeOC_2H_4OMe$, centrosym. planar arrangement of Cd - 7 oct. and 2 dist. oct.	4	colrl. cr., s. in hex., tol., THF, CH_2Cl_2	IR, ^1H, $^{13}C\{^1H\}$, ^{113}Cd, X-r	183
$Cd(C_6H_4O_2\text{ -1,2})\downarrow$ **$[Cd(C_6H_4O_2\text{-1,2})Phen_2]\cdot 2R(OH)_2$,** **$Cd(C_6H_4\text{-}C_6H_4O_2\text{-2,2'})\downarrow$** **$Cd(C_{10}H_6\text{-}C_{10}H_6O_2\text{-2,2'})\downarrow$, $\cdot$Dipy**	4	colrl. sld., not m., stab. to H_2O >300 (dec.)	TGA	45

$3Cd(OR)_2{\cdot}CdI_2\downarrow$, R=Me, Et	5	wh..sld.	-	1623
$CdM^{II}_2(OBu^t)_6$, M^{II}=Ge, Sn, Pb [1681]; **$[CdZr_2(OPr^i)_9Cl]_2$** [1508]; **$[CdM^{IV}I(OPr^i)_9]$, $[CdM^{II}M^{IV}_2(OPr^i)_{12}]_2$,** M^{II}= Ca, Sr, Ba , M^{IV} =Ti, Zr, Hf , Sn [1686, 1687, 1688, 1690, 1691]				
Hg				
$Hg(OMe)_2\downarrow$	5	yel. sld., turns blk. on staorage under ROH, 90 (dec.)	IR, X-r powd.	1623, 1649
$Hg(OEt)_2\downarrow$	5	yel. sld., ~20 (dec.)	IR, X-r powd.	1623, 1649
$Hg(OSiMe_3)_2$	5	colrl.cr.,90/vac. (subl.), 160 (dec.); s. in eth., $+H_2O$ (traces)$\rightarrow$ $HgO+R_2O$	IR, ^{199}Hg, cryosc.	1417, 1558

12.5. Aluminium alkoxides

$Al(OR)_3$ were first prepared by Gladston and Tribe in 1876 on the action of metal on anhydrous alcohols in presence of I_2, HI or AlI_3. Wislizenus and Kaufman, studying the reductive properties of the aluminium amalgam, proposed useing it for obtaining water-free alcohols. They found, however, that after all water has reacted, the alcohols themselves start to react with aluminium. In 1897 Hillyer and Crooker reported the preparation of $Al(OR)_3$ on the action of alcohols on the metal in the presence of Al, Sn, Pt, and Fe chlorides [1301].

The classic study of $Al(OR)_3$ was carried out by Tishchenko [1585] at the end of nineteenth century. His dissertation, entitled "On the Action of Amalgamated Aluminum on Alcohols (Aluminum Alkoxides, Their Properties and Reactions)," became a great resonance for the chemistry of alkoxides (see also Chapter1). The synthetic approaches, that he developed are still in use; the purity of the samples obtained by Tishchenko, taking into account the data he reported, was definitely not worse than that of those described at present. In 1929 Meerwein and Bersin [1101], performing the acidimetric titration of $Al(OR)_3$ solutions by solutions of alkali alkoxides, discovered the existence of bimetallic alkoxides (Meerwein salts), which play an important role in the modern chemistry of metal alkoxides.

Compared with the tremendous number of publications on the application of $Al(OR)_3$ in organic and polymer chemistry as reducing or condensation agents (Cannizzaro-Tishchenko-Meerwein-Ponndorf-Verley-Oppenauer reactions), components of catalytical systems for polymerization processes, alkylating agents, and so on. [1420], the studies of the alkoxides themselves appear very limited. The most important among them were those devoted to the peculiarities of the physicochemical behavior of $Al(OR)_3$ in connection to the nonuniformity of their molecular complexity, carried out during the last 30 years, and also the synthesis and structure studies of the bimetallic complexes. The synthetic approaches and physicochemical properties of a broad variety of aluminium alkoxides are summarized in [1301].

12.5.1. Synthesis

The most widespread synthetic approach to $Al(OR)_3$ remains even at present the reaction of the aluminium amalgam with anhydrous alcohols proposed by Tishchenko and then described in detail by Adkins [10]. The most attractive and widely used derivative is the isopropoxide, which is soluble in boiling alcohol under the reaction conditions (compare Chapter 2). As catalysts in this reaction, in addition to $HgCl_2$ and the mentioned halides, were also the $Al(OR)_3$ themselves; according to the patent data, $Al(OPr^i)_3$ can be obtained even in the absence of catalysts (method 1) [1301].

Tishchenko has even proposed a different method of synthesis — the reaction of $Al(OPr^i)_3$ with alcohols, which was later widely used by Mehrotra *et al.* for the preparation of amylates, glycolates, siloxides, derivatives of unsaturated alcohols, and so on. Application of ${}^{t}ROH$ leads only to the formation of $[Al(OR)(OR^t)_2]_2$, R = Et, Pr^i [1107, 655]. It is worth noting the contribution of Baker [94], who was the first to propose the transesterification of $Al(OR)_3$ by esters (for the preparation of butoxides, allyloxides, method 6). Alcohol interchange reactions (method 4) play a much less important role in the preparation of $Al(OR)_3$ compared with the alkoxides of transition metals. Also described in the synthesis of $Al(OR)_3$ have been the applications of such starting reagents as AlR_3, R = Me, Bu^i (for $[Al(OSiPh_3)3THF]$, $Al(OC_6H_3R_2\text{-}2,6)_3$, $Al[OCH(CF_3)_2]_3$), and also $Al(NMe_2)_3$ (for $Al(OBu^t)_3$), $LiAlH_4$ (in the synthesis of $Al(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_3$) (method 4). The metathesis of $AlCl_3$ with alcohol solutions of NH_3 or amines proposed by Bayer AG and described in [1567] has not received any broad application in the synthesis of $Al(OR)_3$ (method 5). Ziegler *et al.* [1811] have described the formation of primary $Al(OR)_3$ on oxidation by oxygen of AlR_3 (obtained by addition of Al and H_2 to double bonds in alkenes). The method has been used for the preparation of otherwise hardly accessible alcohols produced on the hydrolysis of alkoxides. The mechanisms of oxidation reactions have been reported in detail in the works of Razuvaev *et al.* [1341].

12.5.2. Properties

The derivatives of lower alcohols and also $Al(OR^t)_3$, $Al(OC_5H_{11}{}^{neo})_3$ are solids; derivatives of other amyloxides and hexyloxides are liquids; substituted phenoxides are crystalline matters. The oxocomplexes display a much clearer trend to crystallization than the homoleptic alkoxides. Nearly all the derivatives of aluminium can be sublimed or distilled without decomposition.

Numerous investigations have noted the instability of the physicochemical characteristics of $Al(OR)_3$ — the first members of the homologous series, which can display varied physical states, m.p., density, vapor pressure (hysteresis on measurement), viscosity, refraction coefficient, solubility in alcohols, and so on — which has led several authors to to conclude that there can exist different forms of $Al(OEt)_3$ [344, 1103, 1050] and $Al(OPr^i)_3$ [563]. Wilhoit [1745] has, in contrast, attributed this phenomenon to the presence in the samples of the products of uncontrolled hydrolysis or thermolysis. The molecular composition (the presence of aggregates with different size and structure) was considered to be the major factor influencing the characteristics of the samples (see Chapter 6). The stability of the aggregates of $Al(OR)_3$ is rather high. $[Al(OPr^i)_3]_n$, for example, does not react with such strong donors as Diox, THF, Et_3N, and Bu^t_3N. According to ^1H NMR data, such solvents as Py, Me_3N, and Et_2NH form adducts in solution only with the molecules of trimers, while only En and N_2H_4 are capable of destroying the molecule of tetramer [1231, 1472]. The existence of the aggregates in liquid and gaseous phases even at the boiling point of $Al(OR)_3$ is indicated also by high values of evaporation enthalpies and enthropies; the Truton constants are twice higher than the usual value [197, 1107,1745,330,1301]. For more details on the particular features of the physicochemical behavior of $Al(OR)_3$ in connection with the inhomogeneity of its molecular composition, see Chapter 6.

The properties of different samples of $Al(OEt)_3$ differ so greatly that they were considered in the literature as different forms — polymeric β ("alcohol solvate") and oligomeric α ("unsolvated"). The first is formed on the prolonged refluxing of metal with the excess of alcohol; the second on the synthesis of $Al(OEt)_3$ in xylene media or on thermal treatment of the first, especially in hydrocarbon media. The latter form has, in contrast to the former, much higher solubility in hydrocarbons and higher reactivity. The properties of this form vary in a rather broad interval — from a viscous liquid to amorphous solids with m.p. 105 to 146°C (depending on the synthesis conditions and heating rate). The action of alcohol on liquid samples leads to the precipitation of the solid polymer one. The solubility of α-form in xylene is 45 to 55, β- 0.4 to 1.5g/100ml[1103,1640, 344]. In addition to the 2 above-mentioned forms, there has even been described the "crystalline $Al(OEt)_3$," formed from the solution of the α-form in CS_2 [1661]. According to the single crystal X-ray study, it turned out to be an oxocomplex — $Al_{10}O_4(OEt)_{22}$. Its molecule (Fig. 6.4) consists of 2 pentanuclear aggregated connected with each other by planar μ_3-O-groups. The Al atoms possess tetrahedral, octahedral, and trigonal bipyramidal surroundings. It is interesting to note that such large molecules are present even in the gas phase [1785].

An analysis of the extensive literature data and the data of the authors of this book [1640, 1642, 1655] permits a conclusion that the variations in the physicochemical characteristics of $Al(OR)_3$ are caused by the existence of different types of aggregates and the possibility of their mutual transformations. The molecular composition depends on the conditions in the course of sample preparation — temperature, nature of the solvent applied, and the "age" of the sample. An important role is also played by the presence in the samples of microamounts of oxocomplexes, which are always formed on sublimation, distillation, and any other thermal treatments.

The tetrameric molecules present in amorphous $Al(OR)_3$ ($R = Pr^n, Bu^n, Bu^i$),crystalline (CH_2Ph), and liquid samples (C_5H_{11}-primary) should supposedly possess the structure analogous to that of $[Al(OPr^i)_3]_4$ (Fig. 4.8 *b),* while the dimeric s-Bu, s-C_5H_{11}, t-amyl-, hexa-, and heptoxides, and benzyloxide — in analogy with the crystalline $[Al(OBu^t)_3]_2$ [391] — should be built up of 2 tetrahedra sharing a common edge. The same structure was observed also for the phenoxides— $[Al(OC_6H_3Me_2\text{-}2,6)_3]_2$ [141], $[Al(OC_6H_2Bu^t_3\text{-}2,4,6)_2(OEt)]_2$ [1440]. Monomeric molecules were observed only for the sterically crowded phenoxides — triangular $[Al(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_3]$ [723] and tetrahedral solvates $[Al(OC_6H_3Ph_2\text{-}2,6)_3(HCONH_2)]$ [1066] and $[Al(OSiPh_3)_3THF]$ [56]. They are characterized by rather short Al–O distances (1.65 and 1.71 Å) and rather large Al–O–C angles (177.2 and 144°), indicating a noticeable input of π-bonding.

Among the oxoalkoxides there are rather widespread the molecules with a tetrahedral central oxygen atom, as in $[Al_4O(RO)_{10}(ROH)]$, $R = Bu^i, CH_2CF_3$ [1492, 1396], $Al_4O(OPr^i)_5[H(OPr^i)_2]Cl_4$ [1657], where the trigonal bipyramidal $[AlO(OR)_4]$ groups are sharing common edges (Fig. 12.1*b*). In contrast to $[Al(OPr^i)_3]_3$, the presence in these molecules (and also in that of $Al_3Cl_5(OPr^i)_4$) of the 5-coordinated Al atoms does not lead to a decrease in their stability (Fig. 4.4 *b)* (see Table 12.6).

The numerous studies of the thermolysis reactions of $Al(OR)_3$ have been summarized in the review by Piekos [1301]. They permit a conclusion that the the starting temperatures of decomposition are not constant but depend on the rate of heating and the time of preliminary treatment. The general scheme of decomposition proposed by Tishchenko includes for the first step the formation of ethers and $AlO_n(OR)_{3-n}$. Next comes the dehydration of ethers:

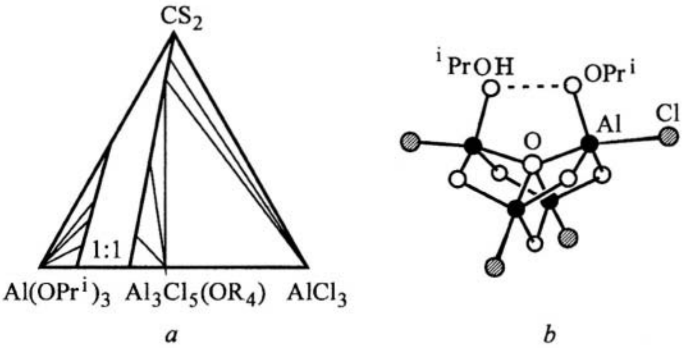

Fig. 12.1. Solubility isotherms in $Al(OPr^i)_3$–$AlCl_3$–L systems at 20°C (wt %) (*a*); The metal-oxygen core in structures of $Al_4O(OPr^i)_5[H(OPr^i)_2]Cl_4$ [1657] (*b*).

$$(C_nH_{2n+1})_2O \rightarrow C_nH_{2n} + H_2O$$

The presence of ether among the decomposition products depends on its stability (maximal for Me_2O and minimal for Bu^t_2O). All $Al(OR)_3$ except the methoxide form alcohols, alkenes, traces of water, and hydrogen.

The hydrolysis of $Al(OR)_3$ and their application in sol-gel processes are considered in Chapter 9.

A special place in the chemistry of the alkoxide complexes of Al is occupied by alkoxide halides — $AlHal_n(OR)_{3-n}$, which have found a very broad application in organic chemistry. A great number of compositions ($R= Pr^i$ mainly) have been reported with Al:Cl ratio varying from 1:2.66 to 1:1. The X-ray single-crystal studies indicate, however, that in $Al(OPr^i)_3$–$AlCl_3$–L ($L = {}^iPrOH, CS_2$) there is present only one complex — $Al_3Cl_5(OPr^i)_4$ (Fig. 12.1 *a)* (already mentioned above as a structure analog of the trimer of $Al(OPr^i)_3$). The well-known crystalline product of $AlCl(OPr^i)_2$ composition (**β-form**) turned out to be an oxoalkoxochloride, $Al_4O(OPr^i)_5[H(OPr^i)_2]Cl_4$ (Fig. 12.1 *b),* resulting supposedly from the decomposition of the former (it is formed from the alcohol solutions with Al:Cl = 1:2).

The liquid **α-form** is not represented by a singular point in the solubility isotherm. The IR and ^1H of these samples contain the sums of the signals for $Al(OR)_3$ and $Al_3Cl_5(OR)_4$, and their mass-spectra are also the fragments of $Al_4O(OPr^i)_5[H(OPr^i)_2]Cl_4$ [1657].

Taking into account the absence in literature of the proofs for individuality of other complexes, the existence of the latter remains in question. In particular, all ethoxide halides can be suspected to be oxocomplexes as they all were prepared starting from the "soluble form of $Al(OEt)_3$, and the reactions were carried on reflux [1661, 1130].

12.5.3. Bimetallic alkoxides

Bimetallic alkoxides of aluminum and alkaline and alkaline earth metals — $M^IAl(OR)_4$ and $M^{II}Al_2(OR)_8$ — are formed on the complex formation between two alkoxides (or M^IOR and $M^{II}(OR)_2$ *in situ)* and also on the alcoholysis of the corresponding $M(AlH_4)_n$. Meerwein [1101] considered them as the salts of unsolvo-acids $HAl(OR)_4$, formed on dissolution of $Al(OR)_3$ in alcohols. However, the solubility of the majority of $M[Al(OR)_4]_n$ in nonpolar solvents, low values of electric conductivity, volatility and trend to aggregation in solution and in the gas phase indicates their molecular or polymeric character. This conclusion has been confirmed by the data of X-ray single-crystal studies. Only a few examples of compounds, whose structures contain isolated alkoxoaluminate ions are known. These are tetrahedra in the structures of $[C_6H_{11}{}^cNH_3]^+[Al(OPr^i)_4]^-$[126], $M[Al(OSiMe_3)_4]$ [1738, 1418], and trigonal bipyramids in the structures of glycolates — $Na_2[Al(OC_2H_4O)_2(OC_2H_4OH)]\bullet nR(OH)_2$ [609] and $Ba[Al_2(C_2H_4O_2)_4]$ [429]. In the structures of the majority of alkoxoaluminates, the hetero- metal atoms share $(\mu\text{-}OR)_2$ edges with the $[Al(OR)_4]$ tetrahedra. This results in dimeric $[LiTHF_2(\mu\text{-}OCEt_3)_2Al(OCEt_3)Cl]$ molecules [546], infinite $[KAl(OPr^i)_4(Pr^iOH)_2]$ chains [1105], trinuclear linear $[M^{II}Al_2(OBu^t)_8]$ molecules (with a tetrahedrally coordinated central Mg atom) [1691], angular (with *cis*-octahedrally coordinated Mg) $[MgL_2Al_2(OR)_8]$-*cis,* $R = Pr^i$, Ph [1402, 1104], tetranuclear zigzag-shaped $[ErAl(OPr^i)_6({}^iPrOH)]_2$ [962] or in $ErAl_3(OPr^i)_{12}$ structure analog of $[Al(OPr^i)_3]_4$ [1774] (Fig. 4.8 *b*). In the molecule of $[PrAl_2(OPr^i)_8Cl(Pr^iOH)]_2$ 2 such groups (with a 7-coordinated Pr atom) are connected via 2 Cl bridges [1598] (Fig. 4.11 *a)*. The determination of the composition of the bimetallic complexes formed were applied through the methods of physicochemical analysis. In the M^IOR–$Al(OR)_3$–L (solvent) systems were found the complexes of only one composition — $M^IAl(OR)_4$ [887, 949] (Fig. 8.1). These are not melting solids; the compounds of Li and Na can be sublimed *in vacuo.* Their thermal stability is higher than that of the components, the thermolysis leading to $M^IAlO_n(OR)_{4-2n}$ and R_2O. The anomalous character in the conductivity variation in solutions indicate the associative character of the current-bearer complexes; the mass-spectra were also found to contain aggregates. Their molecular complexity depends on the synthesis and isolation conditions and their thermal prehistory and increases in time (up to formation of polymers).

In the $M^{II}(OR)_2$–$Al(OR)_3$–ROH (M^{II} = Mg, Ba) there was discovered the formation of the complexes of two compositions — $M^{II}Al_2(OR)_8$ and $M^{II}_3Al_2(OR)_{12}$, — the stability of the latter increasing from Mg to Ba, the stability and the size of the crystallization field for $Ba_3Al_2(OEt)_{12}$ in the diagram being more pronounced than for $BaAl_2(OEt)_8$ [1629] (Fig. 8.1 *e*). According to the mass-spectrometry data, only the derivatives of Mg among the $M^{II}Al_2(OR)_8$ are stable in the gas phase [887], in contrast with the Mehrotras data on volatility of these derivatives for alkaline earth metals [1112]. On the metathesis of MCl_2 with $NaAl(OR)_4$, Meerwein [1101] has obtained the compounds that he described as $M^{II}[Al(OEt)_4]_2$ (M = Cu, Co, Ni). In continuation, a large amount of soluble and often volatile isopropoxides of transition metals and the products of their alcohol interchange have been reported by Mehrotra. The data on the existence of bimetallic aluminum alkoxides containing *3d*-transition metals — $M[Al(OPr^i)_4]_2$ (M = Mn-Cu) and $M[Al(OPr^i)_4]_3$ (M = Cr, Fe), and also trimetallic isopropoxides containing Al-M^{II}-$M^{IV}(M^V)$, [M^{II} = Mn-Cu, M^{IV} = Ti, Zr, Hf, M^V = Nb, Ta] [1493, 1138, 1139] — have not been proved (see also Sections 12.12 and 12.16). In particular, on an attempt to reproduce the syntheses of $Cr[Al(OPr^i)_4]_3$, $Fe[Al(OPr^i)_4]_3$ and $Ni[Al(OPr^i)_4]_2$ on metathesis of MCl_n with $M^IAl(OR)_4$ in conditions of [1493, 501, 1139] the isolated products were found to be $CrCl_n(OR)_{3-n}$, $Fe(OR)_3$, and $Ni(OR)_2$ (i.e., the complex formation did not take place). It was found that the transition of the polymeric alkoxides into solution could occur only on microhydrolysis or pyrolysis with formation of bimetallic oxoalkoxocomplexes of variable composition [1365, 1622, 1561]. In fact, Teyssie *et al.* [1244] and then Kapoor *et al.* [1331, 1465, 1330] have obtained in this way (and also on the reaction of $Al(OR)_3$ with $M(OAc)_2$) the complexes of $M^{II}Al_2O_2(OR)_4$ composition (M = Mg, Zn,Cr, Mo, Fe, Co), which turned out to be soluble in alcohols and hydrocarbons and were applied as highly active and selective catalysts for ethylene oxide polymerization and also for oxidation reactions with molecular oxygen. The conclusion concerning the presence of oxogroups in the molecules of alkoxoaluminates of transition metals does not appear to be valid forbutoxides, as a homoleptic deriavtive of this series, $MAl_2(OBu^t)_8$, M = Co, Ni, Cu [1148a, 1691], has recently been isolated and characterized.

12.5.4. Alkoxoaluminohydrydes

A special class among the bimetallic alkoxides of aluminium are alkoxoaluminohydrydes — $MAlH_n(OR)_{4-n}$, the products of partial alcoholysis of $MAlH_4$ used as reducive agents in organic and organometallic synthesis. $LiAlH(OBu^t)_3$ — a unique, mild, reducive agent with selective action — is used in the synthesis of alcohols from aldehydes (especially for natural products like steroids), aldehydes from chloroanhydrides, amides, and nitriles, of metallic Ge from its tetrachloride. It was described in 1956 by Brown [249] and has long been produced industrially [715]. The other possibility for obtaining these complexes lies in the hydrogenation of $MAl(OR)_4$ (or the MOR +Al + ROH mixtures) under high pressure [299]; the third, in complex formation of $M[Al(OR)_4]_n$ with AlH_3 [627] or $Al(OR)_3$ with MH [1430, 744].

The study of the gaseous and solid products of the reaction

$$MAlH_4 + nROH \longrightarrow MAlH_n(OR)_{4-n} + n/2H_2$$
$$(M = Li, Na, K, Cs; \quad R=H, Me, Et, Pr^i, Bu^t)$$

at different ratios of the reactants has shown that for the primary and secondary alcohols it is finished at the 1:4 ratio with formation of $MAl(OR)_4$. In the case of ^tBuOH at room temperature, the substitution occurs for only 3 H-atoms, while the fourth can be replaced only under reflux (THF, Dig) [1636, 249, 1805]. The X-ray powder and IR study studies of the $MAlH_n(OR)_{4-n}$ alcoholysis products indicate that they consist of the phases of components — $MAlH_4$ and $MAl(OR)_4$. The only exclusions are $MAlH(OBu^t)_3$, being individual compounds [1636, 747, 139].

At the same time, in solutions, according to conductometry [1636], ^1H, ^2D, ^7Li, ^{13}C, ^{27}Al NMR [730, 768, 627] and ebullioscopy [69], the complexes of intermediate compositions are formed — $MAlH_n(OR)_{4-n}$ — that are soluble in other, in contrast to $MAl(OR)_4$ (M = Li, Na, R = Et, Pr^n, Bu^n, C_2H_4OMe) and $MAlH(OBu^t)_3$ [249, 1430, 744, 299, 139]. They are stable supposedly due to the solvation of the cations and disproportionate on removal of the solvents. The disproportionation takes place even in solutions, its speed being determined by the donor activity of the solvent [730, 139, 1060, 718]. It can be

Table 12.6. Aluminium alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
$[Al(OMe)_3]_\infty$↓ **young form**	6	amor.sld., $200/10^{-5}$ (subl.), 160 (dec.), low s. in b. $C_6H_4Me_2$, α=10, **5**, **4**(m-s)	IR, m-s, X-r powd.	10, 212, 1366, 1640, 1655
aged forms, struct. type of $Al(OH)_3$ – bayerite, layers of oct. $[MO_{6/2}]$	1, 5	powd., $480/10^{-5}$ (subl.), 180 (dec.), d_0^{20} 1.3500; α=5	IR, DTG, m-s, X-r powd.	1297, 1567, 1585
$[AlO(OH)_{0.5}(OMe)_{0.5}]_\infty$, struct. type of [AlO(OH)] – boehmite, oct. $[MO_{6/3}]$	3	wh. sld., 280°→Al_2O_3	IR, X-r powd.,electronogr.	965
$[Al(OEt)_3]_\infty$, **young form** struct. type of $Al(OH)_3$ - bayerite	6	sld.	IR, ^{27}Al, m-s, X-r powd., tensim.	10, 1366, 1640, 1655
aged («β-forms ») layered struc. type of $Al(OH)_3$ - gibbsite, oct.$[MO_{6/2}]$	1	140-2 (m.),175/3 (b); d_0^{20} 1.1423; 240-275°C→α-form; 290 (dec.); s. in eth., $C_6H_4Me_2$ 0.5%; α=4-6 (m-s); p-T (polytherm)	parachor	344, 963, 1050, 1107, 1233, 1359, 1585, 1745
$\cdot n\,NH_3$, n=1, 2		-		1239

↓ s. in bz. (t), $+CS_2$ **$Al_{10}O_4(OEt)_{22}$** $=[Al_5(\mu_4\text{-}O)(\mu_3\text{-}O)(\mu\text{-}OEt)_7(OEt)_4]_2$, ($\mu_4$-O is coordinated to 3 trig. bipyr. Al and an oct. Al)		cr., 130 (dec.), α=10 (m-s), 4.4 (s.), μ=1.35, ε=2.286 (20°)	m-s, cryosc., X-r	1640, 1655, 1661, 1785
$AlO_x(OEt)_{3-2x}$ **(«α-form of $Al(OEt)_3$ »)**	1 (t,+ ArH)	visc. liq. or sld., s.in $C_6H_4Me_2$ ~35%		344, 728, 744, 1050, 1103, 1430
$Al(OPr^n)_3$	1, 5, 6	sld., 106 (m.), 224/3 (b.); d_0^{20}1.0578; p-T (polytherm); α=4; μ=1.84-1.92	ebul.,cryosc., tensim., parachor	10, 1081, 1107, 1359, 1567, 1585, 1745
$[Al(OPr^i)_3]_4$= $Al[(\mu\text{-}OR)_2Al(OR)_2]_3$ central Al oct. and 3 Al tetrahs. sharing a 3 $(\mu\text{-}OR)_2$ edge ↑ time	1,5, 6	cr., 140 (m., 118 -from ROH), 115-130/1 (b., subl.) , d_4^{25}0.970; n_D^{25} 1.4321; v.s. in hc., CCl_4, low in Diox, ROH (polytherm), p-T (polytherm); α=4, μ=1.09-2.13; ε=2.28 (20°); ΔH_{form}= -275.6	IR, Raman, ^1H, ^{13}C, ^{27}Al, m-s, cryosc., thermochem. , DSC, X-r, X-r powd., parachor	18, 630, 956, 1081, 1359, 1567, 1642, 1655, 1745, 1661
$[Al(OPr^i)_3]_3$= $ROAl[(\mu\text{-}OR)_2Al(OR)_2]_2$ (?)		visc. liq., 84/0.7, 94,7/1 (subl.); d_0^{20}0.9771-1.0346; n_D^{20}=1.4261; α=3; μ=1.4-2.1; s.in bz.; ΔH_{form}= -275.6	IR, Raman, ^1H, ^{13}C, ^{27}Al, m-s, DSC, cryosc., tensim., termochem.	10, 563, 630, 891, 927, 1043, 1107, 1231, 1359, 1472, 1585, 1661
· **En**		wh. cr. powd.	^1H, ^{13}C, ^{27}Al	18, 997

Al(OBu^n)$_3$	1, 5, 6	sld., 102 (m.), 270/5 (b.), d_0^{20} 1.0251; s. in ROH, p-T (polytherm); μ=1.85-1.94; α= 3.9, ΔH_{form}= 228.0	tensim., ebul., cryosc., parachor	10, 94, 630, 1081, 1107, 1297, 1359, 1567, 1585
Al(OBu^i)$_3$ s. in ROH (10^{-4} %H_2O) $\downarrow$ -R_2O (?)	1, 5	sld., 215 (m.),146/0.5, (b.), sld.-d_0^{20} 0.9555, liq.-d_0^{20} 0.9671, n_D^{23} 1.4443; α=4, μ=0.69-1.05; s. in ROH, bz.	^{27}Al, cryosc., parachor	10, 963, 1081, 1359, 1567, 1585
[Al$_4$O(OBu^i)$_{10}$(^{i}BuOH)] in tetrah. [μ_4-OAl$_4$] – trig. bipyrs. [AlO$_5$], .the Al coord. polyhedra are pairwise sharing common edges [(μ-O)(μ-OR)]		cr., s. in ROH, CHCl$_3$	^{13}C,^{27}Al, m-s, X-r	1492
Al(OBu^s)$_3$	1, 5, 6	visc. liq., 137/1(b.); d_0^{20} 0.9671, n_D^{20} 1.4443; *p-T* (polytherm); α=2 (4 ?), μ=1.85	^{27}Al, ebul., cryosc.,DSCt ensim., parachor	94, 811, 963, 1081, 1107, 1359, 1567, 1585
Al(OBu^t)$_3$ 2 tetrahs. sharing a (μ-OR)$_2$ edge	1, 4, 6	cr., 206 (m.), 246/10 (b.), 115/6 (subl.), s. in THF 26 % (20°), eth. (b.); d_0^{20} 0.9985; >190° (H_2O, O_2-traces)$\rightarrow$ γ-Al_2O_3; p-T (polytherm); μ=0.47-0.73; α=2	^{1}H, ^{27}Al, TGA-MS, calculat. *ab inito*, ebul., cryosc., tensim., X-r	10, 124, 391, 949, 963, 1081, 1107, 1472, 1585
[Al(OBu^t)$_3$(NHMe$_2$)]$_2$, 2 tetrahs. sharing 2 common NH...OR bonds	4	cr., 40/0.1 (subl.), s. in tol.	X-r	351
Al(OBu^t)$_2$(OPr^i)	6	sld., 165(m.), 154/0.5(b.), α=2	^{1}H	91, 94, 1107

$Al(OC_5H_{11}{}^n)_3$	5, 6	colrl. liq., 255/1.0 (b.), α=4	^{27}Al, ebul.	963, 1107, 1567
$Al(OC_2H_4Pr^i)_3$	5, 6	sld., 225 (m.), 195/0.1(b.), d_0^{20}1.002, α=4	^{27}Al, ebul.	963, 1107, 1567, 1585
$Al(OCH_2CHMeEt)_3$	6	liq., ~200/0.6 (b.),α=4	ebul.	1107
$Al(OCHMePr^n)_3$, $Al(OCHMePr^i)_3$	6	liq., 162/0.5 (b.), α=2	ebul.	1107
$Al(OCHEt_2)_3$	6	liq., 165/1.0 (b.), α=2	ebul.	963, 1107
$Al(OC_5H_{11}{}^{neo})_3$	6	sld., 160(m.),180/8.0 (b.), α=2	ebul.	1107
$Al(OC_5H_{11}{}^t)_3$	6	cr., 199 (m.), 130/0.02 (subl), α=2	ebul.	91
$Al(OC_5H_{11}{}^t)_2(OPr^i)$	6	sld., 154/0.5, α=2	ebul.	91, 1107
$Al(OC_6H_{13}{}^n)_3$	6		^{27}Al, ebul.	963
$Al(OCMeEt_2)_3$	6	cr., 155/0.02 (subl.), α=1.84	^{27}Al, ebul.	91, 963
$Al(OCHMeBu^i)_3$	1	visc. liq., 203/0.7	-	811
$Al(OCHMeBu^t)_3$	1	cr., 280/0.5 (subl., dec.)	-	811
$Al(OC_6H_{11}{}^c)_3$	5	-	-	1567
$Al(OCEt_3)_3$	6	cr., α=1.80	ebul.	91
$Al(OC_8H_{15})_3$, $Al(OC_{12}H_{25})_3$	5		-	811, 1567
$Al[OCHMe(CH_2)_5Me]$	1	liq., 249/10^{-2} (b.)		
$Al(OCH_2Ph)_3$	1	cr., 80(m.), s. in bz., petrol. eth., α=3-4, μ=1.8; ε=2.305	^1H, ^{27}Al, cryosc.	963, 1101, 1231, 1661
$Al(OCHPh_2)_3$	6	cr., 95(m.), 150/10^{-2} (b.)	-	1545
$Al(OCPh_3)_3$	5	sld., 300 (m.), s. in bz., ArOH, α=2	IR, TGA	1054

$Al(OPh)_3$	1, 4, 6	gl., 265 (m.,dec.); d^{20}_0 1.23; $\rightarrow PhOH+Ph_2O$; $\alpha=2\text{-}3$, s. in CS_2, PhOH, $\mu=1.75$	IR, ^1H, ^{27}Al, DTA, cryosc.	410, 451, 599, 963, 1054, 1081
$Al(OPh)_n(OBu^n)_{3-n}$, n=1, 2	6			1297
$Al(OC_6H_4R\text{-}2)_2(OPr^i)$, R=Me, Bu^t	6	$\alpha=3$, 3(Me), 2 (Bu^t)	^{27}Al, cryosc.	451
$[Al(OC_6H_3Me_2\text{-}2,6)_3]_2$ 2 tetrahs. sharing a $(\mu\text{-OR})_2$ edge	4	cr., s. in b. tol., ins. in AlkH	^1H, ^{13}C, ^{27}Al, X-r	141
$[Al(OC_6H_3Pr^i_2\text{-}2,6)_3 \cdot Py]$, tetrah.	4	colrl. cr., 199 (m.), s. in C_5H_{12}, bz.	IR, ^1H, ^{13}C, ^{27}Al, X-r	723
$Al(OC_6H_3R_2\text{-}2,6)_n(OPr^i)_{3-n}$, R= Me, Pr^i, Bu^t, n=1,2	6	$\alpha=2$	^{27}Al,cryosc., thermolys.	451, 1170
$[Al(OC_6H_3Ph_2\text{-}2,6)_3(HCONH_2)]$, tetrah. $[AlO_4]$			X-r	1066
$[Al(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_3]$, **$\cdot CH_2Cl_2$**, trian. **$\cdot$L**, L=MeCN, Py, Ph_3PO, **$O{=}C_6H_9Bu^t$**, tetrah.	4	cr., 116 (m.), s. in CH_2Cl_2, C_5H_{12}	X-r	723, 722
$[Al(OC_6H_2Bu^t_3\text{-}2,4,6)_2(OEt)]_2$ 2 tetrahs. sharing a $(\mu\text{-OR})_2$ edge	6	cr., 196 (m.)	IR, ^1H, m-s	1440
$Al(OCH_2CH{=}CH_2)_3$	6	sld., 145 (m.,dec.)	-	94, 1585
$Al(OCHMeCH_2CH{=}CH_2)_3$	6	liq.,132/0.4(b.), n_D^{20} 1.459, $\alpha=2.2$	IR, ^1H	655
$Al(OCMe_2CH{=}CH_2)_3$ **$Al[O(CH_2)_3CH{=}CH_2]_3$**		sld., 141/0.3 (b.), s.in bz.,CH_3Cl, $\alpha=2$		

$Al[OCH(CF_3)_2]_3$, **·L**, L=Et_2O, Et_3N, En, Et_3P, $(Ph_2P)_n(CH_2)_n$ **$[Al(OH)[OCH(CF_3)_2]_2(\eta\text{-}En)]_2$** 2 oct. sharing a $(\mu\text{-}OH)_2$ edge	4, 5	cr.,185 (m.), 75/0.06 (subl.), s.in ROH, α=1 s. in bz.	^1H, ^{13}C, ^{19}F, ^{27}Al, ^{31}P ^1H, ^{13}C, X-r	1085, 997
$Al_4O(OR)_{10}(ROH)$, R=CH_2CF_3, struct. analog of $Al_4O(OBu^i)_{10}$ (^iBuOH)	4	cr., s. in hex.	X-r	1396
$Al(OSiMe_3)_3$	5	cr., 208(m.), 100/ 10^{-2} (subl.), α=2 (in s.), 1(m-s)	^{27}Al, cryosc.	574, 1418
$[Al(OSiPh_3)_3THF]$, **$[Al(OSiPh_3)_3(H_2O)]$ THF],** tetrahs.	4	cr., 353 (m., dec.) 182 (dec.)	IR, ^1H, ^{13}C, ^{17}O, ^{27}Al, ^{29}Si	56
$Al(OC_2H_4OR)_3$, R=Me, Et	1	visc. liq., α=3	^1H, ^{13}C	299, 1424
$Al_2(RO_2)_3\downarrow$, R= $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_2CH$, $(MeCH)_2$, $(Me_2C)_2$ **(1)**	6	amor. sld.(**1**-cr.), >200 (dec.)	IR, DTA	94, 1052, 1107
$[AlO(OH)_x[O(CH_2)_nOH]_{1-x}]_\infty$, n=2-6, struct. type of AlOOH-boehmite,layers of$[O(CH_2)_nOH]_\infty$	6	wh. powd., stab. to moisture	IR, ^{13}C, ^{27}Al, DTA, TGA, X-r powd.	803
$Al_2(O_2C_4H_8)_3$ - 1,3, -1,4, -2,3 **$Al_2[(OCMe_2)_2]_3$**	6	ins. in bz., α=6 s. in bz., α=3	ebul.	1107
$AlF_2(OPr^i)\cdot 0.5THF$ **$AlF(OPr^i)_2$**		cr., 340(dec.), α=14 57 (m.), α=3.3, v.s. in bz.,	IR, ^1H, ^{19}F	569
$Al_3Hal_8(OR)\cdot nROH$, R, Hal, n: =Me, Cl, 1 Et, Cl, 10; Et,Br, 15; Pr^n, Cl, 5.		cr., s. in ROH, dec.		606

«$Al_3Cl_7(OEt)_2 \cdot 7\,EtOH$»	cr., 50(dec.), s. in ROH, bz.		1130
«$AlCl_2(OR)$», R=Me, Et, Pr^n, Pr^i (2THF), Bu^i, Bu^t, Ph, $PhCH_2$, Ph_2CH, C_6H_4Me-4, $C_6H_3Me_2$-2,6, $SiMe_3$, $C_6H_{10}{}^cOSiMe_3$-2	cr. or oil, 50-150/1 (b. or subl.), α=2, s. in bz, Me_2CO, RCl	IR, DTA (R=Ph)	89, 133, 169, 569, 573, 975, 1054, 1130, 1140, 1145, 1265, 1418, 1526
$[AlCl_2(OC_6H_9{}^cMe\text{-}3\text{-}OH\text{-}2)]_2THF_2$, 2 trig. bipyr. sharing a $(\mu\text{-}OR)_2$ edge	cr., 94 (m.), s. in THF	^1H, ^{13}C, ^{27}Al, X-r	133
$[AlCl_2(OC_6H_2Bu^t_3\text{-}2,4,6)(Et_2O)]$, tetrah.	cr., 181 (m.)	IR, ^1H, m-s	1440
$(AlCl_2)_2(C_6H_{10}{}^cO_2\text{-}1,2)$	sld., s. in THF	IR, ^1H, ^{27}Al	133
$AlBr_2(OR)$, R=Me-Bu^t, C_6H_4Cl, $C_6H_3Hal_2$		-	469, 1130, 1526
$Al_3Cl_5(OPr^i)_4$ = $AlCl[(\mu\text{-}OR)_2AlCl_2]_2$ angular mol., the central trig. bipyr. $[AlCl_4O]$ sharing a common $[(\mu\text{-}OR)_2]$ edge with to each of the two Al tetrah.	colrl. cr., 116 (m.), α=1, μ=3.4	IR, m-s, X-r	955, 1661, 1781
«$Al_2Cl_3(OEt)_3$» **$Al_2Hal_3(OPh)_3 \cdot 0.5CS_2$**, Hal=Cl,Br	cr., 117 (m.), α=2.3 wh. powd., s. in CS_2 s in bz, CCl_4, α=4, μ=1.92	-	599, 1661
$Al_4O(OPr^i)_5[H(OPr^i)_2]Cl_4$ (=«$AlCl(OPr^i)_2$») tetrah. $[(\mu_4\text{-}O)Al_4]$, 2 trig. bipyr. $[AlO_4Cl]$ sharing 3 common edges $[O(OR)]$ with the polyhedra of each of the remaining 2 Al	cr., 161 (m., dec.) insol. in org. solv.	X-r, m-s.	611, 1657

"AlCl(OR)$_2$" R=Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, C$_5$H$_{11}$^{i}, C$_7$H$_{15}$^{n}, C$_8$H$_{17}$^{n}, C$_9$H$_{19}$^{n}, C$_6$H$_{10}$^{c}Me-4, Ph, PhCH$_2$,C$_6$H$_3$Me$_2$, Bz **"AlBr(OR)$_2$,"** R= Me, Et, Bu^n, Bu^s, Bu ^{t}, C$_5$H$_{11}$^{i}, Ph, C$_6$H$_4$Me-4, C$_6$H$_3$Me$_2$ **AlCl(OPh)$_2$**	sld.,s. in ROH, bz., CHCl$_3$ α=2	- -	573, 611, 975, 1054, 1130, 1140, 1145, 1490 599
AlH(OPr^i)$_2$ **AlH$_2$(OPr^i)**	cr.,48 (m.), v. s. in bz., THF, α=3, subl. dec., v.s. in THF, α=2	IR, ^{1}H	569
[AlH$_n$(OC$_6$H$_2$Bu^t$_2$-2,6-Me-4)$_{3-n}$L], L= Me$_3$N, Bu^{t}NH$_2$, Et$_2$O искаж. tetrah. or 2 tetrahs. sharing a (μ-OR)$_2$ edge	cr., 123-140 (m.), s. ih hc.	IR, ^{1}H, ^{13}C, ^{27}Al, m-s, X-r	722
Al$_2$H$_3$(OC$_2$H$_4$OMe)$_3$	v.s. in org. solv.	IR,^{1}H, cryosc.	300
[C$_6$H$_{11}$^{c}NH$_3$]$^+$[Al(OPr^i)$_4$]$^-$, anion – tetrah., chain NH…O	cr., s. in ROH	IR, X-r	126
LiAl(OR)$_4$, R=Me, Et, Pr^n, Pr^i, Bu^t, C$_5$H$_{11}$^{i}, C$_5$H$_{11}$^{t}, C$_8$H$_7$	cr., subl. /10^{-2}, dec.: 325, 445 (Et); 380, 435 (Pr^i), 320, 375 (Bu^t); dec. 280 (Me), s. in ROH, ins. in eth., hc., s.in system –THF, α=3-4	IR, conduct., m-s, X-r powd.	249, 764, 887, 949, 1101, 1433, 1518, 1636
NaAl(OR)$_4$, R=Me, Et, Pr^i, Bu^t, PhCH$_2$	sld., m.: 210 (Me), 226 (PhCH$_2$); subl. /10^{-2}, dec.: - , 390 (Me, Et); 380, 430 (Pr^i, Bu^t), s. in system – ROH (Me, Et), -THF (Bu^t), α=2-4	IR, conduct., m-s, X-r powd.	887, 949, 1101, 1105, 1297, 1433, 1636, 1805

$KAl(OR)_4$, R=Me, Et, Pr^n, Bu^n, $C_6H_{11}{}^c$, $PhCH_2$	sld., m.: 157 (Pr^n), 164 (Bu^n), 128 ($PhCH_2$)	X-r powd.	1101, 1433
$[KAl(OPr^i)_4(Pr^iOH)_2]_\infty$, zigzag chain of $[K(\mu\text{-}OR)_4(ROH)_2]$-*cis*, oct., $[Al(\mu\text{-}OR)_4]$ tetrah.	cr., 380 (m.), s. in ROH, ins. in hc., $\alpha=3$ (m-s)	^1H, m-s, X-r	1105
$NaAl(OC_2H_4OMe)_4$	cr., 110(m.)	-	299
$LiAlH(OBu^t)_3$	sld., $220/10^{-2}$(subl.), s. in THF – 1.2 M, Dig- 1.3 M, ins. in eth., MeCN, ROH, $\alpha=2$ (m-s)	^1H, ^2H, ^7Li, ^{13}C, ^{27}Al, m-s	249, 768, 886, 1636
$LiAlH(OC_5H_{11}{}^t)_3$	sld., s. in eth.	-	249
$LiAlH(OCEt_3)_3$	-	-	546
$MAlH(OBu^t)_3$, M=Na, K, Cs	cr., $280/10^{-2}$ (subl.) – Na; 300 (dec.) –K; 170 (m., dec.) – Cs, s. in Dig, THF, $\alpha=4$ (Na)	IR, ^{27}Al, conduct., m-s	886, 1805
$BeAl_2(OR)_8$, R=Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, $C_5H_{11}{}^i$ **$BeAl_2(OPr^i)_2(OR)_6$**, R=Bu^t, $C_5H_{11}{}^t$ **$BeAl(OPr^i)_5$(?)**	vol., s. in bz., CCl_4, $CHCl_3$, $\alpha=1$(with exp.of Me, Et) liq., 156/0.3 (b.), $\alpha=1\rightarrow2$	IR,^1H ^1H, ebul	15, 1117
$MgAl_2(OEt)_8$	cr.,181(m.), 195/0.1 (b.), 315 (dec.), s.in ROH (67%), hc., THF, s. in system $Mg(OR)_2$-$Al(OR)_3$ - ROH, ins. in petr. eth., $\alpha=2$	IR, ^1H, ^{27}Al, m-s	887, 971, 1101, 1112, 1640, 1745
$Mg_3Al_2(OEt)_{12}$	gl., invol., 210 (dec.)		

$[MgAl_2(OPr^i)_8(Pr^iOH)_2$-*cis*$]$ $=[Mg(ROH)_2][Al(\mu\text{-}OR)_2(OR)_2]_2$, angular m central oct. $[MgO_6]$, linked to two $[AlO_4]$ tetrahedra ; ROH...OR (term.)	cr.,114/vac.(-ROH), s. in tol., ROH	^1H, ^{13}C, X-r	1104, 1402
$MgAl_2(OPr^i)_8$ ↑ 105/0.1	sld., 20 (m.), 130/2 (b.)	^1H, ^{13}C, m-s	1101, 1112
$[Mg_2Al_3(OPr^i)_{13}]$, each of the two Mg coord., polyhedra in central - trian. $[Mg_2Al\ (\mu\text{-}OR)_4(OR)]$ shares a common edge $(\mu\text{-}OR)_2$ with tetrahedr Al, CN Mg 4, 5	cr., 105/0.1 (dec.), s. in tol.	^1H, ^{13}C, X-r	1104
$MgAl_2(OR)_8$, R= Pr^n, Bu^n	liq., 225/6, 290/2 (b.)	-	971, 1112
$Mg[Al_2(OPr^i)_4H_3]_2$, $Mg[Al_3(OPr^i)_4H_6]_2$, $MgAl_4(OPr^i)_4H_9$	amor. slds., s in eth., hc.	-	627
$MgAl_2(OBu^s)_8$	liq., 140-165/0.03 (b.), α=1	^1H, ^{13}C, m-s	1104
$MgAl_2H_4(OBu^t)_4$	sld., vol.	-	1680
$[MgAl_2(OBu^t)_8]$, linear chain, central tetrah. $[M^{II}O_4]$ shares common edges $(\mu\text{-}OR)_2$ with 2 $[AlO_4]$ tetrahs.	cr.	X-r	1691
$[MgAl_2(OPh)_8THF_2]$-*cis*, angular mol., central $[Mg(\mu\text{-}OR)_4THF_2$-*cis*$]$ oct. , 2 Al tetrahs. sharing a $(\mu\text{-}OR)_2$ edge	cr., 127 (m.), α=1	^1H, ^{13}C, m-s	1104
$SrAl_2(OMe)_8 \cdot 2MeOH$	cr., s. in MeOH 0.06%	X-r powd.	1433

$M^{II}Al_2(OR)_8$, M^{II}=Ca,Sr, Ba, R=Et, Pr^i	slds., s. in ROH, bz. (?), invol., α=2-3 (Et), vol. (Pr^i) - ?	-	1101, 1112, 1335
$Ca[AlH_{4-n}(OR)_n]_2$, R=Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^t, Am^i,$C_6H_{11}{}^c$, C_2H_4OMe, n=1, 2, 3	cr., s. in THF, tol., v.s. in MeOH	IR, X-r powd.	431
$BaAl_2(OEt)_8$ **$Ba_3Al_2(OEt)_{12}$**	amor., cr., dec. 60, 100, invol., s. in system , in ROH-61.8, 21.2%, in bz.- 31.5, 1.5%	IR, m-s, X-r powd.	1629
$M^{II}Al_2O_2(OR)_4$, M=Mg, Ca, Zn,Cr, Mo, Fe, Co; R=Pr^i, Bu^n, Bu^s, Bu^t,	cr., colrl, pale yel., bl., red-grn., grn., vlt.-bl., α=2-4	IR, ^1H, ^{13}C, m-s, cryosc., UV-sp.	1244, 1330, 1331, 1465
$MAl_3(OPr^i)_{12}$, M=Ga, In; **$Ga_3Al(OPr^i)_{12}$**	slds., s. in ROH, vol.	IR, ^1H	1106
$Ln[Al(OPr^i)_4]_3$, Ln=Y, Sc, La-Lu	sld., Sc, 145/0.5(b.); Y, 180-200/0.1, s. in bz.,α=1	IR,^1H, m-s, ebul.	1118, 1106, 1607
$ErAl_3(OPr^i)_{12}$, struct. analog of $[Al(OPr^i)_3]_4$	pinc cr., 120(m.), 140(dec.), s. in ROH, in tol. 0.62M	IR, electr. sp., X-r	1744
$[ErAl(OPr^i)_6(^iPrOH)]_2$ zigzag chains of 2 central. oct. Er (sharing a $(\mu\text{-}OR)_2$ edge) and 2 tetrahs. Al sharing a $(\mu\text{-}OR)_2$ edge, Er-ROH...OR-Al	pink cr., s. in ROH-tol.	X-r	962
$[PrAl_2(OPr^i)_8Cl(Pr^iOH)]_2$, (**Pr**- praseodymium), 2 trians., gr. $[Pr(\mu\text{-}Cl)_2(\mu\text{-}OR)_4(ROH)]$ (CN Pr 7, base centered trig prism) linked to 2 tetrahs. $[Al(\mu\text{-}OR)_2(OR)_2]$, in the centre - $[Pr_2(\mu\text{-}Cl)_2]$, ·**L**, L=THF, Py	pale-yel. cr., s. in CH_2Cl_2-C_6H_{14}, 200/0.01→L+ **$[PrAl_2(OR)_8Cl]$**	X-r	1598

$\mathbf{Ln^{II}Al_3(OPr^i)_{11}}$, Ln^{II}=Sm, Yb	-	IR, ^1H, ^{171}Yb	514
$\mathbf{Sn^{II}Al_2(OR)_8}$, R= Me, Et, Pr^i, CH_2CF_3, $CH(CH_2Cl)_2$ $\mathbf{Sn^{II}Al_2(OPr^i)_2(OBu^t)_6}$	sld., s. in bz., α=1	IR, ^1H, ebul., conductom	1124
$\mathbf{Sn^{IV}I_2[Al(OPr^i)_4]_2}$, angular mol., in the centre – oct. *cis*-$[I_2Sn(\mu\text{-}OR)_4]$	yel. cr., s. in hex.	IR, ^1H, ^{13}C, ^{27}Al, X-r	1690
$\mathbf{Al_2Zr(OPr^i)_{10}}$, isostr. with its Hf- analog	colrl. cr., 100-128(m), s. in ROH 38%, THF, s. in system $Al(OR)_3$-$Zr(OR)_4$-ROH (20°)	m-s	1116, 1608
$\mathbf{Al_2Hf(OPr^i)_{10}}$= $[Al_2Hf(\mu\text{-}OR)_4(OR)_6]$ angular mol., oct. $[Hf(\mu\text{-}OR)_4(OR)_2]$, 2 tetrahs. $[Al(\mu\text{-}OR)_2(OR)_2]$	cr., 57 (m), s. in ROH 31%, THF, s. in system $Al(OR)_3$-$Hf(OR)_4$-ROH (20°)	m-s, X-r	1608
$\mathbf{AlTa(OAr)_8}$, Ar= Ph, $C_6H_4Bu^t$-4, $C_6H_3Me_2$-3,5,	-	IR, ^1H, ^{27}Al	343
$\mathbf{U^{IV}[Al(OPr^i)_4]_4}$, $\mathbf{U[Al(OPr^i)_4]_2Cl_2}$ (?)	grn. oil, 95/10^{-3} (b.),267(dec.)	-	19
$\mathbf{AlU^V{}_3(OEt)_{18}}$	grn.liq., 111/10^{-3}(b.)	-	855
$\mathbf{NiAl_2(OBu^t)_8}$,isomorph. with its Mg-analog	cr.	X-r	1690
$\mathbf{M_3Al[[O(CF_3)_2]_2]_3}$, M=K, Cs	cr.	-	26
$\mathbf{M[Al(OSiMe_3)_4]}$↓, M=Li,Na,K, $\mathbf{[Me_4Sb][Al(OSiMe_3)_4]}$, anion -tetrah.	250 (dec.), 180 (m., subl. /1), s.in org. solv., stab.in air	IR, ^1H, X-r	1418, 1738
$\mathbf{Na_2[Al(\eta^2\text{-}OC_2H_4O)_2(OC_2H_4OH)]\cdot nR(OH)_2}$, n=4, 5, anion - tetragon. pyr.	cr.	^{27}Al, X-r	609

$Na_2[NaAl_3(\eta^2,\mu\text{-}OC_2H_4O)_5(\eta^2,\mu OC_2H_4OH)_2]\cdot 6R(OH)_2$, anion $Ti_4(OMe)_{16}$ struct. type, 1 $[AlO_6]$ -oct., 2 gr. $[AlO_5]$	cr.		
$M[Al(C_6H_3O_2)_2]\cdot nH_2O$; **$M_3[Al(C_6H_3O_2)_3]\cdot nH_2O$,** M=Na, K, NH_4	-	-	1726
$Ba[Al_2(\eta^2,\mu\text{-}C_2H_4O_2)_2(\eta^2\text{-}C_2H_4O_2)_2]$ anion -2 trig. bipyr. sharing a $(\mu\text{-}O)_2$ edge, CN Ba 8	cr.	^{27}Al, X-r	429
$[LiTHF_2Al(OCEt_3)_3Cl]$, 2 tetrahs. sharing a $(\mu\text{-}OR)_2$ edge	colrl. cr., s. in hex.	^1H, X-r	546

supposed that the mild action of the $MAlH_n(OR)_{4-n}$ is connected with their lower reactivity compared with $MAlH_4$. The selectivity is in fact observed only for $LiAlH(OBu^t)_3$. It is very thermally stable (subl. at 280°C/1), soluble in THF, Dig, and insoluble in ether, MeCN, ^tBuOH; is aggregated in solution; and forms tetrameric molecules in the gas phase, supposedly possessing a cubane-like structure [886].

In addition to the $Al(OR)_3$ application fields already mentioned above, it is necessary to name the production of synthetic and isolator materials, pigments, paints, and resins. Their production is based mainly on alkoxides modified by the introduction of carboxylate, polyster groups, or acetoacetic ester. The alkoxide then plays a role of a binding agent. The synthetic materials formed were called "alucons" by analogy with silicons [1301]. The polymers containing Si–O–Al and P–O–Al fragments are thoroughly described in the monograph by Andrianov [48].

12.6. Gallium, indium, and thallium alkoxides

Studies of the alkoxides of this group started in the middle of 1960s when Funk [602], Mehrotra [1129], and Reinmann [1349] nearly simultaneously reported the synthesis of $Ga(OR)_3$. Indium isopropoxide was first described by Mehrotra in 1972 [1106] (the preparation of $In(OMe)_3$ on reaction of InC13 with 50 equivalents of NaOMe reported by Runge *et al.* [1374] should apparently be questioned). Of the modern studies of primary interest are the preparation of indium (I) phenoxides stabilized by bulky ligands, reported by Roesky *et al.* [1362,1434], and that of the bimetallic butoxide, $In^ISn(OBu^t)_3$, described by Veith *et al.* [1685].

12.6.1. Synthesis

The low values of the standard electrode potentials for gallium and indium (-0.56 and -0.34 V, respectively) prevent them from direct interaction with alcohols. Even the reaction with PhOH (method 1) on reflux occurs very slowly [602]. The anodic oxidation of indium in the solutions containing diols in presence of MeCN (method 2) gave the In(I) diolates in solution; the latter have not been isolated in the pure form and when oxidized by iodine gave solid In(III) derivatives [1041]. Preparation of different members of the $M(OR)_3$ homologous series for both metals has been achieved by the alcohol interchange reaction or by transesterification with esters using $M(OPr^i)_3$ as starting reagent. The latter were prepared by interaction of chlorides with $NaOPr^i$ (method 5). $Ga(OMe)_3$ and $Ga(OEt)_3$ were also obtained by alcohol interchange from the phenoxide (method 6). Indium (I) phenoxides are usually prepared by alcoholysis of $InCp_3$ (method 4).

The composition of gallium isopropoxide corresponds to the formula given above (it appears to be an anlog of $Al(OPr^i)_3$ [1233, 1234]). The indium isopropoxide, according to the X-ray single crystal data an oxoalkoxide, $In_5O(OPr^i)_{13}$, has a molecular structure analogous to those of rare earth metal isoprpoxides [208] (see also Fig. 4.9 *a*). This calls into question the composition of the alcohol interchange products that is also questioned in the case of $Ln(OR)_3$ (Section 12.7). Indium methoxide and ethoxide are polymers that precipitate from solution on action of the alcohols on $In(OPr^i)_3$, while the amorphous butoxides and n-amyloxide described by Chatterjee [332] were isolated on evacuation of solutions and had to contain the oxoligands (which might be the reason for their solubility in organic solvents).* Their formulas are therefore put into Table 12.7 in quotation signs.

12.6.2. Properties

Gallium alkoxides are crystalline substances displaying good solubility in hydrocarbons and lower in alcohols. All except the phenoxide can be distilled in vacuo. Their molecular complexity in solutions and in the gas phase is usually very close to that of the corresponding $Al(OR)_3$. The characteristic features of the physicochemical behavior of $Ga(OPr^i)_3$ are same as those of $Al(OPr^i)_3$: its distillate is a vicous liquid that crystallizes in a few days, whereas the molecular complexity increases from 2 to 4. On dissolution of the solid $Ga(OPr^i)_3$ in benzene, the tetramer dissociates slowly into dimers according to cryscopy and ^1H NMR spectra. These data in combination with the data on fragmentation of different aggregates in mass-spectra permits the analogy in the molecular structures of aluminium [1642, 391] and gallium compounds to be traced (no single crystal X-ray data being reported for the latter so far). The molecular structures of the tetramer, trimer, and dimer can be deduced to be $M[(\mu\text{-}OR)_2M(OR)_2]_3$, $(RO)M[(\mu\text{-}OR)_2M(OR)_2]_2$, and $(RO)_2M(\mu\text{-}OR)_2M(OR)_2$. These molecules contain 6-, 5-, and 4-coordinated metal atoms. The aggregates of the first type are most probably present in the structures of the bimetallic complexes like $Ln[Ga(OPr^i)_4]_3$ and $Ga[Al(OPr^i)_4]_3$ [1119, 1106], where

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* Taking into account the observed analogy in the molecular structures of rare earth and indium alkoxides, the butoxide of the latter should exist only as solvates $[In_3(OBu^t)_9L_2]$.

the gallium atoms occupy the tetrahedrally and octahedrally coordinated sites, respectively.

The information on indium alkoxides is much more restricted. These are amorphous solids that do not melt or evaporate *in vacua*; the "isopropoxide", in particular, is not transferred into the gas phase even under the conditions of the mass-spectrometric experiment (10^{-6} mm) [1618]. The size of their aggregates is unknown, the only exclusion being the isopropoxide — $In_5O(OPr^i)_{13}$, whose molecular structure is a tetragonal pyramid of metal atoms (octahedrally coordinated) centered by an oxygen atom. The mechanical molding of the crystals leads to their partial amorphization, while the action of the alcohol leads to their decomposition into two fractions — a soluble one and a polymeric one. The latter can be partially dissolved in benzene after a prolonged reflux. The product of the evacuation of the solution obtained is a viscous liquid, which is unlimitedly soluble in hydrocarbons — in contrast to the crystals — and rapidly crystallizes on the action of alcohol [1618]. The nature of the molecules existing in the crystal structure suggests a scheme of transformations of the "isopropoxide" in solutions, on mechanical or thermal treatment, and so on. In this case (as well as for many other oxoalkoxides), the action of alcohol leads to solvolytic decomposition of molecules leading to two types of fragments — those that contain and those that do not contain oxoligands. The former ones are oligomeric and able to exist in solution. They contain apparently more than 1/5 of an oxoligand per In atom. The latter form an irregular polymeric structure that can be again oligomerized via reflux with aromatic hydrocarbons. The oligomerization occurs presumably via partial termolysis (and, probably, even microhydrolysis) providing new oxogroups and also via formation of π-complexes. The insertion of alcohol leads to the solvation of these fragments, the aggregation of the latter via hydrogen bonding and subsequent formation of the pentanuclear molecules again. All these processes can never occur quantitatively, and thus no equilibrium values can be achieved on determination of the solubility of "isopropoxide" in alcohol.

In the molecules of $[InOAr]_2$ and $InSn(OBu^t)_3$ the indium atoms display a ψ-triangular coordination $[:In^IO_2]$.

Concerning the application of gallium alkoxides, one can mention the selective catalytic activity of $Ga(OPh)_3$ in the condensation reactions of isobutene with phenols. $In(OR)_3$ is used for the preparation of solutions for production of In_2O_3 and In_2O_3-related conduction films [1618] and also in the synthesis of volatile precursors for MOCVD deposition of In_2O_3 [830].

12.6.3. Thallium alkoxides

In contrast to its analogs, thallium forms the homoleptic alkoxides only in a +1 oxidation state (the trivalent derivatives are known only as $TlR_n(OR')_{3-n}$). The TlOR homologous series is represented by a considerable number of derivatives that has been studied for 140 years. A number of them were first synthesized along with the other main derivatives of thallium in 1860s by Lamy [988], who discovered this element (simultaneously with Crookes). TlOEt was isolated as a viscous oil that separates from solution on dissolution of TlOH in hot EtOH. TlOMe crystallizes on action of MeOH on the ethoxide. The easily accessible ethoxide has become the most useful reactant in the synthesis of other inorganic and organic derivatives of Tl(I).

12.6.3.1. Synthesis

The preparation of TlOEt has been achieved on action of alcohol on Tl_2O, TlOH,* and thallium metal [1482] (method 3). The latter reaction is to be carried out in the flow of dry oxygen as the low value of the standard electrode potential for Tl (–0.34 V) prevents its direct reaction with water or alcohols (even the amalgamated thallium remains inert [1096]). The side products of all these reactions are water or TlOH. The composition and the possibility of purifying the oil-like product remained therefore questioned for more than 100 years. The study of the solubility polytherm in the TlOEt — EtOH system has shown that the layering in it occurs at over 7.5°C; at 20°C the lower layer contains 95%, and the upper 7.0 % of TlOEt; the critical temperature is 123°C. It turned out that TlOH (formed in the synthesis of TlOEt) is concentrated only in the upper layer of the two-phase liquid system and does not effect the purity of the product of purpose. The equilibrium of the reaction

$$TlOH + EtOH \leftrightarrow TlOEt + H_2O$$

is shifted to the right on evaporation of the solvent, which leads again to separation of the oil-like ethoxide that then can be separated nearly quantitatively [1625]. The second most common route to TlOR is the alcohol interchange reaction of the ethoxide used for the preparation of the majority of the homologs (method 6). The application of the exchange reaction of $TlNO_3$ with sodium alkoxides in the liquid ammonia [313], is useful presumably in the preparation of the derivatives of polyols. The same reaction in EtOH as solvent (on reflux) has been patented [1274] (method 5).

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* The heats of these reactions are given in the works of Forcrand [182,1191].

12.6.3.2. Properties

The derivatives of n-alcohols (except TlOMe and $TlOPr^n$) and even isomeric amyloxides are colorless oil-like liquids, unlimitedly soluble in all organic solvents. All T1OR are rather light-sensitive: they quickly decompose when irradiated producing a black colloid sediment. It cannot be filtered out but is easily separated by dissolution of T1OR in boiling alcohols [1482]. The thermal stability of alifatic derivatives is also rather low: they all decompose below 100°C (no melting is observed for solids) and are not present in the gas phase. The molecular weight detrminations have shown that practically all derivatives of alcohols and phenols form tetramers in solutions. Sidgwick [1482] proposed in 1930 that for $[TlOR]_4$ the cubane-like structure is to be preferred over the square planar. This supposition was later confirmed by the single-crystal X-ray studies of TlOMe [439] and $[Tl(\mu_3\text{-}OSiPh_3)]_4{\cdot}C_6H_6$ [714] (see also Section 4.4.3). The Tl atoms, situated in the apexes of distorted cubes, have ψ-tetrahedral coordination (the fourth vertex of the tetrahedron that lie on the volume diagonal of the cube is occupied by an electron pair). Only the derivatives of very bulky sterically hindered phenols like $Tl[OC_6H_2(CF_3)_3\text{-}2,4,6]$ [1362] or biphenyldiol like $Tl(OC_6H_4C_6H_4OH\text{-}2,2')$ [526] form dimeric molecules containing $[Tl_2(\mu\text{-}OR)_2]$ cycles with pseudo tricoordinated Tl atoms. The same kind of coordination is observed also in the bimetallic $TlSn(OBu^t)_3$ complex [1693, 1685].

The ethoxide is applied as the reactant for preparation of different organic and inorganic derivatives of T1(I). Among the numerous reactions of T1OR (R = Me, Et) studied so far, we would like to underline the interaction with CO and CO_2, leading to the insertion of these molecules into the Tl-OR bond with the formation of ROC(O)Tl [1375] and ROCOOT1 [620]. A broad application area is also connected with the use of TlOEt as oxidant for organic compounds such as, for example, acyloins (into β-diketones) [1096]. Kahlbaum [863] has proposed that this substance be used as a heavy liquid in the molecular weight determination for solids (d^{20}_4 3.493). It also was applied later in analytical chemistry as a thermometric titrand for the determination of organic acids and phenols [136, 750]. The two latter possibilities are rather doubtful, however, in the modern laboratory practice as thallium compounds are very poisonous.

Table 12.7. Gallium, indium and thallium (I) alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
Ga				
$Ga(OMe)_3$	6	wh. powd., 275/0.4 (subl.).s. in org.s.	-	151, 602
$Ga(OEt)_3$ **$\cdot NH_3$**	5, 6	wh. cr.,s. in bz., ROH (t), Diox, THF, d=1.23, 144,5 (m.), 180/0.5 (b.), α=**6-2** (m-s),4 (bz.)	ebul. m-s	151, 602, 1233, 1233, 1349
$Ga(OPr^n)_3$	6	colrl. cr., 60 (m.), 198/0.05 (b.), α=4	cryosc.	1349, 151
$Ga(OPr^i)_3$	5, 6	liq.→ cr.(few days), 74 (m.), 120/1 (b.), α=4 **-2** (m-s), 4→ 2 (ebul.)	^1H, m-s, ebul.(bz)	151, 1129, 1106, 1233,
$\cdot Py$, $\cdot MeCN$		sld., 15 (m., dec.), polytherms., α=2	^1H, cryosc.	1234
$Ga(OBu^n)_3$	6	colrl. cr., 184/0.05 (b.), α=4	ebul. (bz)	151
$Ga(OBu^s)_3$	6	colrl. liq., 115/0.4 (b.), α=2	ebul. (bz)	151
$Ga(OBu^t)_3$	6	colrl. cr. 140-50/0.5 (subl.), α=2(bz); t→CH_2CMe_2 +ROH +Ga_2O_3	^1H, m-s, ebul.	151, 1129, 1233, 1684
$Ga(OPh)_3$, $\cdot L$, L= Py, Me_3N	1 (t)	colrl. cr., ins. in eth.	-	602
$Ga(OSiMe_3)_3$	5	colrl. cr., 208(m.), 155/1 (subl.), readily s. in org. solv., α=2, nonreactiv	IR, ^1H, cryosc.	1418
$GaHal(OR)_2\downarrow$, R=Me, Et, Bu^t, Ph; Hal=Cl, Br	wh. sld. amor., 300 (dec.), α=3; 75(m.), 110/0.4 (b.); **Pr^i,Br:** 95(m.), 118/1 (b.),		-	151, 602, 1166, 1551

$GaCl_2(OR)$, R=Me, Et, OPr^n, OPr^i,OBu^n		cr. ,α=1.4-2.5; m.,b : 92,100/10^{-4} (Me) 36,101/10^{-4} (Et); 23, 105/10^{-4} (Pr^n); 42, 122/10^{-4} (Bu^n); Pr^i : liq, .95/1 , α=2	^1H, cryosc. (bz), m-s	151, 602, 1233, 1166, 1418
$GaBr_2(OR)$, R=Me, Et, Pr^n, Bu^n		cr., α=1, 2.2- 2.3 and 4.0 (**Et**); m.,b: 85, 130/10^{-4} (**Me**); 65, 110/10^{-4} (**Et**); 41, 116/10^{-4} (**Pr^n**); 47, 130/10^{-4} (**Bu^n**); **Pr^i**:liq., 95/1, α=2	^1H, cryosc. (bz), m-s	151, 1166, 1233
$[Ga(OC_6H_2Me_3)_2Cl^{\cdot}Bu^tNH_2$ **$[Ga(OC_6H_2Bu^t_2$-2,6-Me-4$)Cl_2(Et_2O)]$** tetrah.		- -	X-r X-r	1551
$MGa(OR)_4$, M=Li, Na,K, R=Me,Et		wh. sld., s. in bz., PhCl, t→ $MGaO_2$; $+H_2O \rightarrow M[Ga(OH)_4]$	IR, TGA, DTA	1355
$MGa(OPh)_4$, M=Li, Na,K		visc. prod.	-	1355
$Ln[Ga(OPr^i)_4]_3$, Ln= La-Yb		cr., 139-165/0.6(b.), s. in bz., ROH, α=0.8-1	ebul.	1119
$M[Ga(OPr^i)_4]_3$, M=Al, In		cr., 105-120/0.1 (b.), α=1	IR, ^1H, ebul.	1106
$M[Ga(OSiMe_3)_4]$, M=Li, Na, K; $[Me_4Sb]$, anion- tetrah.		cr., ins. in org. solv., >250 (dec.); 190 (m., subl. /1), v. s. in org. solv.	IR, ^1H, X-r	1418, 1738
$[Bu^t_4N]^+[Ga_2Cl_6(OC_6H_2Me_3$-2,4,6$)]$ 2 tetrah. with a common (μ-OR) vertex		-	X-r	1551
$Ga[Al(OPr^i)_4]_3$ [1106]				
In(I)				
$[In(OC_6H_2Me_3$-2,4,6$)]_2$, $[In_2(\mu$-$OR)_2]$-cycle	4	-	X-r	1362

$[In[OC_6H_2(CF_3)_3\text{-}2,4,6]]_2$, $[In_2(\mu\text{-}OR)_2]$-cycle	4	colrl. cr., s. in hex.	IR, ^1H, ^{19}F, X-r	1434
$[InM(OBu^t)_3]$, M=Ge, Sn, Pb [1685, 1691]				
In(III)				
$In(OMe)_3\downarrow$, $In(OEt)_3\downarrow$	6	wh. sld.	-	332
$[In_5O(OPr^i)_{13}]$ **("$In(OPr^i)_3$")**, $[M_5]$ tetragon. pyramid, 4 μ_3-OR-over non-basal faces, 4 μ-along edges of basal plane	5	colrl.cr., 150 (dec.), s.in ROH 8-14%, in bz. - 60%, α=4, invol., in system - Py -glass form.	IR, ^1H, m-s,ebul. (ROH), X-r	208, 332, 1106, 1234, 1618
"$In(OBu^n)_3$", "$In(OBu^s)_3$", "$In(OBu^t)_3$""$In(OC_5H_{11}{}^n)_3$"	6	light yel. sld., s. in org.s.	-	332
$[In(OCMe_2CF_3)_3]$, 2 tetrah. sharing a $(\mu\text{-}OR)_2$ edge **$\cdot Py_3$**, oct. –cis,cis; **.Tmp**, tetrah.; **$\cdot H_2NBu^t$**	4	colrl.cr., s. in hex.-CH_2Cl_2	IR, ^1H, $^{13}C\{^1H\}$, X-r	1151
$[H_2Tmp][In(OCMe_2CF_3)_4]$, **$[H_2NEt_2][In(OCMe_2CF_3)_4(HNEt_2)]$** **$[H_3NBu^t][In(OCMe_2CF_3)_4(H_2NBu^t)]$** anions – tetrah., trig. bipyr. and tetragon. pyr.		colrl.cr., 95/0.06 (subl.), s. in hex., tol., eth.- CH_2Cl_2	IR, ^1H, $^{13}C\{^1H\}$, X-r	1151
$NaIn_3(OMe)_{10}\cdot 4MeOH$		-	IR, TGA	149
$NaIn(OPr^i)_4$, $Sn[In(OPr^i)_4]_4$		light yel. amor.sld., s. in ROH, bz, invol., 80, 200(dec.)	IR, TGA	1618
$In[Al(OPr^i)_4]_3$, $ClIn[Al(OPr^i)_4]_2$, [Mehrotra 11,217]				

Tl				
[Tl(μ_3-OMe)]$_4$ ψ-tetrah [:TlO$_3$] in the vertexes of the cube	5, 6	colrl. cr., blackens on storage, s. in ROH, bz., α=3.26-3.86 (bz.), 0,79-1,20 (ROH), 120(dec.)	IR, electr. sp. cryosc., ebul., X-r	254, 313, 439, 580, 976, 981, 1482
TlOEt	3, 5	colrl. oil; turn yel. in the light; 9.5(m.), layering in the system TlOEt-ROH >7.5°, polytherm -, upper layer -7, lower- 95% TlOR (20°), d^{20}_4 3.493, n_D^{20} 1.6783; α=3-4.45; ΔH_{form}= -57	IR, ^{1}H, Raman, parachor, cryosc. (bz.),ebul. (ROH)	313, 580, 981, 1063, 1146, 1274, 1326, 1482, 1542, 1625
TlOPr^n	6	colrl. cr., α=4.	IR,Raman, ^{205}Tl	275, 1063, 1482
TlOBu^n , TlOBu^i	6	oil, sld., α=4	^{205}Tl	275, 863, 1482
TlOBu^t	5	colrl.cr., 110 (dec.), s. in eth., α=4	^{205}Tl, X-r - powd.	1417
TlOC$_5$H$_{11}$^{n} , TlOCHMePr^n	5, 6	oil, α=4	^{1}H, ^{205}Tl	275, 313
TlOC$_5$H$_{11}$^{t}	6	colrl. cr., 50 vac.(dec.), α=4	^{205}Tl, ebul.	200, 275
TlOC$_2$H$_4$CHMe$_2$	5	oil, -80 (m.), ins. in liq. NH$_3$	-	313
TlOC$_6$H$_{11}$^{n}, TlOCHMeBu^n	6	oil, α=4	^{205}Tl	275
TlOC$_6$H$_{11}$^{c}	6	sld., 110 (dec.), α=2.45-3.16	cryosc.	1482
TlOCH$_2$C$_6$H$_5$	6	colrl. cr., 74-8 (m.), s. in ligroin, α=2.95-3.94	^{205}Tl, cryosc.	275, 1482

TlOPh	3, 4, 6	colrl. cr., s. in EtOH, ins. in eth., bz., 233 (m.), α=2.54-3.83 (bz.)	cryosc., ebul.	376, 580, 1096, 1369, 1482
$TlOC_6H_4Me$-2	3	colrl. cr., s. in EtOH, H_2O, ins. in eth.,bz 164 (m., dec.), α=4-5	cryosc.	376, 1096, 1482
$TlOC_6H_4Me$- 3	3	colrl. cr., s. in EtOH, H_2O, ins. in eth.,bz., 199 (m.), α=3.29-4.09	cryosc.	376, 1096, 1482
$TlOC_6H_4Me$-4	3	colrl. cr., s. in EtOH, H_2O, ins. in eth.,bz.., 203 (m.)	cryosc.	376, 1096, 1482
$TlOC_6H_2Bu^t_3$-2,4,6	6	-	-	459
$TlOCH_2CF_3$	3	clrl. cr., 134 (m.), 50 (subl.)	-	1279, 1370
$TlOCH(CF_3)_2$	6	sld., 80/10^{-2} (subl.)	^1H, ^{19}F	1387
$\{Tl[OC_6H_2(CF_3)_3$-2,4,6]$\}_2$ [$Tl_2(\mu$-$OR)_2$]-cycle, CN Tl =2	6	colrl. cr., 164 (m.), s. in hex, α=1	IR, ^{19}F {H}, ^{1}m-s, X-r	1362
$TlOC_{10}H_7$-α	3	colrl. cr., 180-90 (m..)	-	376
$TlOC_{10}H_7$-β, 0.5 Diox	3	light yel. cr., s. in bz., Diox	-	1806
$TlOSiMe_3$	5	colrl. cr., 92/10^{-4} (subl.), 130(dec.), s. in eth., α=4	IR, ^1H, ^{203}Tl, ^{205}Tl, cryosc.	1417
$[\{Tl_2(OSiMe_2)_2O\}_2]_\infty$ bands of alternating [Tl_4O_4]-cubes and [Si_4O_4]-cycles	6	low yel. cr., s. in eth.	X-r	714
$[Tl(\mu_3$-$OSiPh_3)]_4 \cdot C_6H_6$, ψ-tetrah. [:TlO_3] in the vertexes of a cubane mol.	6	colrl. cr.,s. in bz., C_5H_{12}	X-r	714

$TlOC_6H_5OMe$-2	3	colrl. cr., s. in EtOH, 163 (m.), α=3.74-4.34 (bz.)	cryosc.	1096, 1482
$TlOC_6H_4OMe$-3	3	colrl. cr., 148 (m.), v. s. in H_2O, EtOH, α=3.29-4.09 (bz.)	cryosc.	376, 1096, 1482
$TlOC_6H_5OMe$-4	3	colrl. cr.,s. 196 (m.)	cryosc.	1096, 1482
$TlOC_2H_4OH$ **$TlOC_2H_4OTl$↓**	1, 6 5, 6	yel. sld., + H_2O → colrl. yel. powd., 200°→Tl_2O+$R(OH)_2$	-	313, 580, 621
$TlOC_3H_6OTl$	3	sld. yel., s. in H_2O, ins. in bz.	-	1146
$TlOCH_2CH(OH)CH_2OH$ **$TlOCH_2CH(OTl)CH_2OTl$** ↓	6 5	sld. yel. sld. yel.	-	580, 1146
$(TlO)_6C_6H_8$ (derivatives of sorbite, mannite)	3, 5	sld. yel., v. light sensitive	-	313, 1146, 1193
$Tl_2(RO_2$-1,2), $TlOROH$, $R=C_6H_4$, $C_6H_2Bu^t_2$	4	sld., stab. to hydrolysis	^1H, ^{13}C	526
$Tl_2(C_6H_4O_2$-1,3)↓	3	sld., stab. to hydrolysis	-	1369
$[Tl(OC_6H_4C_6H_4OH$-2,2')$]_2$ $[Tl_2(\mu$-$RO_2H)_2]$-cycle,CN Tl 2	4	pale brn., s. in H_2O, 227 (m.)	^1H, ^{13}C , X-r	526
$TlSn(OBu^t)_3$ [1693, 1685]				

12.7. Rare earth elements alkoxides

In the studies of the alkoxides of rare earths that started in 1950s (the first publications were devoted to the derivatives of Ce(IV) in connection with the problem of separation of Ce from Th), one can distinguish two major steps. The first was covering the preparation of **$Ln(OAlk)_3$** derivatives for nearly all the members of the lanthanide series, the compounds themselves being characterized only by microanalysis and IR spectral data. The detailed reviews summarizing these works are published in [1127, 1138]. The second step, which started in the 1980s and included the studies of the alkoxides of Sc, Y, and Ln by NMR and X-ray single-crystal methods established the exact compositions and determined the structures of the most important derivatives of the alifatic series and also characterized the numerous recently prepared derivatives of alkylsubstituted phenols and other derivatives with sterically crowded ligands. The interest in the latter as well as in the bimetallic complexes was connected with the search for soluble and volatile precursors for laser materials, HTSC, sensors, catalists, and so on (a review is provided in the article Hubert-Pfalzgraf [779] and corresponding chapter of Bochkarev *et al.* [164]).

The most important result of the structure studies was undoubtedly the establishment of the fact that the crystalline isopropoxides of all rare earths are not the homoleptic **“$Ln(OPr^i)_3$”** complexes but oxoalkoxides of **$Ln_5O(OPr^i)_{13}$** composition, where Ln = Sc, Y, Er, Yb (see also Fig. 4.9 *a*). They appear to be desolvation products of the very unstable **$[Ln(OPr^i)_3(^iPrOH)]_2$** solvates (perfectly soluble and rather reactive); the complex of such composition has been isolated and characterized only for neodymium, but the IR spectroscopic evidence for the existence of such solvates was obtained also for Pr and Er. Desolvation of **$Ln(OBu^t)_3 \cdot 2L$ (Ln = Y, La; L = ^tBuOH, THF, Py)** leads also to the formation of oxocomplexes: the ions corresponding to the fragmentation of the homoleptic species are absent in their mass-spectra (except for **$[Y_3(OBu^t)_9(^tBuOH)_2]$**, where the **$Y_3(OR)_8^+$** ion was found along with **$Y_3O(OR)_6^+$**).* The same kind transformations have been observed also for

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* At the same time the reaction products of La interaction with **^iPrOH** do always contain the amorphous component, being presumably the polymeric form of **$La(OPr^i)_3$** [953] (it was described by Mazdiyasni as the product of thermolysis or dehydrogenation of soluble yttrium alkoxides).

Ce(IV) alkoxides — $Ce(OPr^i)_4 \cdot {}^iPrOH$ and $Ce(OBu^t)_4 \cdot 2THF$, — which on mild heating (the former) or even on prolonged stirring lose alcohol (and apparently also ethers) and transform into $Ce_4O(OPr^i)_{14}$ or $Ce_3O(OBu^t)_{10}$, respectively. In recognition of this fact the homoleptic compositions are displayed in quotation signs for all the lanthanide elements in table 12.8.

12.7.1. Synthesis

See also Chapter 2. As has been already mentioned, the lanthanide metals react with ${}^iPrOH$ only on prolonged reflux and in the presence of the mercury catalysts [1084] (method 1). The normal chain alcohols do not react at all because of the insolubility of $La(OR^n)_3$.

The soluble derivatives of s- and t- alcohols, "$Ln(OR)_3$", prepared by alcohol interchange from "$Ln(OPr^i)_3$" (method 6, which was the most popular one at the first step of the studies [1084, 1159, 1397, 1122]), are not the homoleptic derivatives either, presumably. In some cases the substitution reactions are even incomplete. Thus it has been established that the refluxing of $Sc_5(\mu_5\text{-}\mu O)(\mu_3\text{-}OPr^i)_4(\mu\text{-}OPr^i)_4(OPr^i)_5]$ with even a huge excess of ${}^tBuOH$ leads only to substitution of the 5 terminal OPr^i-groups by OBu^t [1607]. The same note can be made on the alcohol interchange products of "$Ce(OPr^i)_4$".

The exchange reaction of chlorides with the alkali metals alkoxides in 1:3 ratio (method 5) in spite of its broad application in the preparation of the alkoxides of lanthanides is complicated by the formation of rather stable alkoxide chlorides with a low number of chlorine atoms per molecule, which have been in some cases characterized crystallographically (as, for example, $Nd_6Cl(OPr^i)_{17}$ [41], $Y_3Cl(OBu^t)_8 \cdot 2THF$) [553]. It is important to mention that the introduction of the excess of MOR does not guarantee the complete elimination of Cl either and leads in some cases to the formation of bimetallic alkoxide chlorides, such as, for example, $[LiNdCl(OCBu^t_3)_3(THF)_3]$ [516]. The metathesis is not complicated by the formation of the chloride-containing complexes only in case of phenoxides due presumably to much higher ionic input into the Ln-Cl bond nature in those compounds compared with the alkoxide chlorides [552]. In some cases it was proposed to carry out the interaction of the chloride with sodium phenoxide at rather high temperature (~300°C) in the melt of $C_6H_3Bu^t_3$-1,3,5 [380].

The application of ammoniac in this reaction is limited by the derivatives of Sc and Y as the other $LnCl_3$ form rather stable amine complexes soluble in organic solvents. At the same time the reaction of $LaCl_3$ with ArOH and the solution of sodium in liquid ammonia led to the $[La(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_3)_x]$ complex, which lost NH_3 completely on prolonged reflux in toluene.

It is necessary to mention in particular the application of carboxylates of lanthanides instead of halides in the reactions with Li, Na, and K, alkoxides for the preparation of $M(OR)_3$ -derivatives of almost all the lanthanides patented by Ozaki. The methoxides and n-buthoxides were thus obtained by interaction of formates with NaOR, the ethoxides by that of propionates with LiOEt, n- and isopropoxides by reaction of acetates or bensoates with LiOPr, t-buthoxides by that of oxalates with $KOBu^t$ [1246]. In addition to carboxylates for the interaction with NaOR using the easily accessible anhydrous $Ln(OCOCCl_3)_3$ [1494, 1159] was proposed. The adducts of $Ln(NO_3)_3$ with glycols or polyethers were used for the preparation of phenoxides [73].

The most reliable methods for the preparation of the lanthanide isopropoxides appear to be at present the anodic dissolution of metals (method 2) and especially the alcoholysis of $Ln[N(SiR_3)_2]_3$ (method 4). The reaction of the alcohol interchange starting from "isopropoxides" can be efficiently used only in the cases when the product formed ($M(OR)_3$ or $Ce(OR)_4$) can be purified by recrystallization or is separated like amorphous $M(OR^n)_n$ due to its much lower solubility (the side products containing the residual oxogroups remain in this case in solution). The successful applications of the method 6 are exemplified by preparation of $[Y(OC_2H_4OMe)_3]_{10}$ or $[Ce(OSiPh_3)_4(\eta^2\text{-}Dme)]$ PhMe. The phenoxides of Yb(II) were obtained on oxidation of metal by TlOAr or on reduction of $Yb(OAr)_3$ (see Chapter 2).

The preparation of Ce(IV) alkoxides requires the application of nitrato- or chlorocerrates (IV) as precursors (i.e., $(NH_4)_2Ce(NO_3)_6$ **[670] or** $(PyH)_2CeCl_6$ [206], as $CeCl_4$ does not exist). The alkoxylation is carried out by a solution of ammonia in alcohol or by that of NaOR. In the former case it turned out to be possible to isolate the intermediate crystalline products of incomplete substitution for the nitrate-ligands, such as $Ce(NO_3)_2(OBu^t)_2(^tBuOH)_2]$ [547] (for the application of $(NH_4)_3Ce(NO_3)_6$ in the preparation of $Ce(OR)_3$ see [671]).

12.7.2. Properties

The alkoxides of almost all the lanthanides (except for $Ce(OR^t)_4$ with bulky radicals) are solids. The derivatives of the radicals with the normal chain structure are usually not volatile and insoluble polymers, while the derivatives of branched alcohols are crystalline and consist of oligomeric molecules with the molecular complexity from 1 to 10 (their polymerics are only the solvates with bidentate ligands as Dmfa, Dme, *etc.*). The low temperatures of their transition into the gas phase and their solubility in nonpolar organic solvents are provided by the low size of their molecules. The color of the derivatives of an element does usually correspond to that of the correspondent ion in water solution.

The peculiarity of the lanthanide alkoxides structures in comparison with those of the common inorganic derivatives lies in rather low CN for the Ln atoms. It is presumably this fact that leads to the structures of the lanthanide alkoxide being dependent only on the nature of radical and not the radius of the central atom and thus the isostructurality of the analogous derivatives along the whole lanthanide series. The most thoroughly investigated are the structures with the sterically overcrowded ligands like CBu^t_3, $C_6H_2R_3$-2,4,6, $C_6H_3Bu^t_2$-2,6, $C_6H_3Ph_2$-2,6. They contain the tricoordinated metal atoms in monomers (trigonal pyramids) or dimeric $[Ln(OR)_2]_2$ (2 triangles sharing a common edge). Tetrahedral coordination is observed in $[Ln(OR)_4]$ (R = $C_6H_3Ph_2$-2.6, $SiPh_3$), monomeric molecules of $[Ln(OR)_3THF]$,with sterically overcrowded radicals, or dimeric $[Ln(OR)_3]_2$ (R = CPh_3, $SiPh_3$, $CHBu^t_2$), being pares of edge-sharing tetrahedra. The latter are able to attach the solvating molecules of THF, MeCN forming monomers — $[Ln(OR)_3L_2]$ or $[Ln(OR)_2L_3]$ (trigonal bipyramids) and increasing CN to 5.

Octaherdal coordination has been observed for the derivatives of least ramified radicals such as isopropoxides and t-buthoxides (or their analogs containing F or Si atoms). It is necessary to mention that the coordination sphere of the Ln atoms contains in addition to OR-groups the smaller ligands such as oxoatoms, molecules of THF, NH_3, and so on. Among the few dimers being edge-sharing pairs of octahedra one can mention $[Ce(OPr^i)_4(^iPrOH)]_2$ or $\{Sc[OCH(CF_3)_2]_3(NH_3)_2\}_2$. The examples of trimers — the $[M_3]$ triangles, centered with 2 μ_3-OR-groups — are provided by $[Ln_3(OR^t)_9L_2]$ (Ln = Y, La, Pr; R^t = Bu, C_5H_{11}), bimetallic alkoxides of yttrium and cerium and yttrium alkoxide halides. The only example of a tetramer with octahedral coordination of the atoms remains the unstable solvate $[Nd(OPr^i)_3(^iPrOH)]_4$ with the structure belonging to the $[Ti(OMe)_4]_4$ type. The heptacoordinated atoms are found in several structures such as the monomeric $[La(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_3)_4]$ (monocapped octahedron), dimeric $[Lu(OCR_2CH_2OMe)_3]_2$, tetranuclear $[Ce_4O(OPr^i)_{14}]$ and the product of its photoreduction $[Ce^{3.75+}{}_4O(OPr^i)_{13}(^iPrOH)]$, decanuclear $[Y(OC_2H_4OMe)_3]_{10}$ (pentagonal bipyramids). In the first case the high CN is achieved due to the smaller size of the other ligand, and in all other cases the lengths of two bonds with the oxygen atoms turn out to be ~0.4 Å longer than the other ones.

It is necessary to mention the presence of the Ln-η^n-Ar, where n = 1–6 interactions increasing the CN for the Ln atoms in addition to the OAr-bridges in the molecules of mono- and bimetallic phenoxides of La, Nd, Sm, and Yb(II) and Yb(III) with branched Ar-groups. The Ln-C interaction has even been observed in the structures of $[Ln(OC_5H_{11}{}^{neo})_3]_4$, Ln = La, Nd, in the absence of a phenyl ring. About the structures $MLn(OAr)_4$ see. Section 4.2.

The special emphasis should be made on oligonuclear oxoalkoxides. Their stability, low solubility in parent alcohol, and low reactivity (in particular in the complex formation with $Al(OR)_3$ [1309,1607]) is connected probably with the highly symmetric structure of the molecules containing 3 to 8 metal atoms bound by a polydentate oxogroup. The examples are provided by $[Ce_3(\mu_3\text{-}O)(OBu^t)_{10}]$ — triangle [547], $Ce_4(\mu_4\text{-}O)(OPr^i)_{14}$—tetrahedron [1497], $[M_5(\mu_5\text{-}O)(OPr^i)_{13}]$ — tetragonal pyramid [783,1607], $[Na_2Gd_4(\mu_6\text{-}O)(OBu^t)_{12}]$ — octahedron [1441], and a spherical $[Pr_8(\mu_4\text{-}O)_4(OC_2H_4OMe)_{16}(OPMe_3)_2]$ 8-vertex polyhedron [783]. The first 3 molecules are present even in the gas phase. The special stability of the pentanuclear isopropoxides is demonstrated by the possibility of exchange for single atoms in it with formation of heterometallic $M_4M'O(OPr^i)_{13}$ complexes, containing $[Y_4Pr]$, $[Nd_4Ti]$ [782], $[Sm_4Ti]$ [444], and $[(Tb_{0.9}Eu_{0.1})_4Ti]$ [1179] cores.

The investigated chemical properties of the alkoxides of this group cover a tremendous number of reactions of partial or complete substitution for the OR-groups with different O, N, S-containing ligands such as carboxylates, **β-diketonates,** ketoesters, amides, imides, Schiff bases, alkanolamines, semicarbazides, thiophenols, Cp, BH_4, and so on. The compounds obtained were characterized usually by the data of chemical and spectral analysis. Taking into account that these were usually "$Ln(OPr^i)_3$" that were used as precursors and also the non-crystalline nature of the majority of complexes described, it is possible to conclude that their composition and individuality require a further proof. An incomplete review of this class of compounds is given in [1138]. It is necessary to mention two crystalline **β-diketonate** complexes obtained from metal alkoxides — i.e., $[Ce_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(acac)_{12}]$ [1590] and $[Y_4Ba_2(\mu_6\text{-}O)_4(\mu_3\text{-}OEt)_8(dpm)_6]$ [1150]. The octahedral core of the first of these molecules is

Table 12.8. Scandium, yttrium and lanthanoids alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
Sc				
$Sc(OMe)_3$↓	2, 5, 6	sld. wt., invol.	IR	597, 1246, 1607
$Sc(OEt)_3$	2, 5	sld. wt., s. in ROH, hex.	IR	597, 1607
$Sc_5O(OPr^i)_{13}$ (=«$Sc(OPr^i)_3$») struct. analog of $Y_5O(OPr^i)_{13}$	1,2,4,5	cr., s. ROH (polytherm),hc., 220-80/0,1(subl.);290(dec.)	IR, ^1H, m-s, X-r	208, 953, 1246, 1607
$Sc_5O(OPr^i)_8(OR)_5$, R=Me, Bu^n	6	visc. liq., vol.	IR, m-s	1607
$Sc_5O(OPr^i)_8(OBu^t)_5$	6	colrl. cr., vol.	IR, m-s	“
«$Sc(OBu^n)_3$»	5, 6	oil, slowly crist.	IR	597, 1607
$Sc_5O(OBu^s)_{13}$	6	sld. wt., s. in ROH, hc.	IR, m-s	1607
$Sc(OBu^t)_3$	5	-	-	1246
[$Sc(OC_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)_3$], trian., **·THF**	4	150 (m.), 250/10^{-3} (subl.), α=1	IR,^1H,^{13}C, m-s, cryosc., X-r	758
[$Sc[OCH(CF_3)_2]_3]_2$ **[$Sc[OCH(CF_3)_2]_3(NH_3)_2]_2$**- ***trans,SS*** 2 oct. with a common (μ-OR)$_2$ edge	4	colrl. cr.	IR, ^1H,^{19}F ,X-r	208

Y				
$Y(OMe)_3$↓, $Y(OPr^n)_3$	5	-	-	1246
$Y_5O(OPr^i)_{13}$ (=«$Y(OPr^i)_3$») $[M_5(\mu_5\text{-}O)(\mu_3\text{-}OR)_4(\mu\text{-}OR)_4(OR)_5]$, in the $[M_5]$ tetragon. pyr. -4 μ_3-OR -over the side faces, 4 (μ-OR) in the basal plane, $[MO_6]$ -oct.	1, 2, 5	colrl.cr., 200/0,1(subl.); 280 (dec.), s.in ROH (polytherm), hc., α=5, diamagn.	IR, ^1H, ^{13}C, ^{89}Y, ^{29}Si, TGA, electr. sp., m-s, X-r	208, 251, 395, 626, 671, 953, 1084, 1246, 1309
$[Y_4Pr(\mu_5\text{-}O)(OPr^i)_{13}$, isostr. with $Y_5O(OPr^i)_{13}$	-	light grn. cr., s. in tol., ins. in petrol. eth.	IR, ^1H, ^{13}C	442, 783
$Y(OBu^n)_3$	5	-	-	626
«$Y(OBu^t)_3$"	5 , 6	wh.sld.,s. in bz., 242/2 (subl.)		209, 1084, 1246, 1761
$[Y_3(OBu^t)_9(^tBuOH)_2]$ **$[Y_3(OBu^t)_9L_2]$, L=THF, Py**	4	wh.sld., 171(m.), 235/10^{-2} (b.), in m-s: $Y_3(OR)_8^+$	IR, ^1H, ^{13}C, ^{89}Y, m-s	
$Y(OCHMePr^n)_3$, $Y(OCHMePr^i)_3$	6	wh. sld., 225 (m.,dec.), s. in bz., α=1.5-1.7	-	1084
$[Y_3(OC_5H_{11}{}^t)_9 \cdot 2{}^tC_5H_{11}OH]$	4	sld., 84(m.), 150/10^{-3} (b.)	IR, ^1H, ^{13}C, ^{89}Y	209
$Y(OC_6H_{13}{}^n)_3$	5	wh. sld.	-	1246
$Y(OCHMeBu^n)_3$	6	wh.sld., 260(m.,dec.),s.in bz.	-	1084
$Y(OCHEtPr^n)_3$	6	wh.sld., s.in bz., 275 (m.,dec.)	-	1084
$[Y(OCMe_2Pr^i)_3]_2$	4	wh. sld., 161(m.), 70/10^{-3} (b.), α=2 (m-s)	IR, ^1H, ^{13}C, m-s	209

$Y(OCHEtBu)_3$	5	-	-	1246
$[Y(OCMeEtPr^i)_3]_2$	4	wh. sld., 196 (m.), 170/ 10^{-3} (b.), α=2 (m-s)	IR, ^1H, ^{13}C, ^{89}Y , m-s	209
$Y(OCEt_3)_3$	4	wh. sld., 198 (m.), 225/10^{-2} (b.), α=2 (m-s)	IR, ^1H, ^{13}C , ^{89}Y , m-s	209
$Y(OC_8H_{17})_3$	5	wh. sld.	-	1246
$Y(OCH_2CHEtBu^n)_3$	6	wh. sld., 275 (dec.)	IR	1084
$Y(OCHBu^t_2)_3$, $Y(OCPr^iBu^t_2)_3$	4	wh.sld., 160/10^{-3} (b.), α=1	IR, m-s	737
$Y(OCBu^t_3)_3$	4	wh. sld.	-	736
$Y(OPh)_3 \cdot 4C_6H_{12}$	1	wh.sld., 310 (m.,dec.)	-	1084
$[Y(OC_6H_3Me_2\text{-}2,6)_3THF]_2$, 2 tetragon. pyr. with a common (μ-OR)$_2$ edge THF-ax. **$[Y(OC_6H_3Me_2\text{-}2,6)_3THF_3]$** -*fac*, oct.	5	colrl. cr., s. in tol. colrl. cr.	IR, ^1H, ^{13}C, X-r	544, 552
$[Y(OC_6H_3Bu^t_2\text{-}2,6)_3]$, trian., **$\cdot$nTHF**	5	colrl. cr., 250/10^{-3} (subl.)	^1H, X-r	758
$Y(OC_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)_3$, struct. analog of Sc-complex, **$\cdot$THF**	4, 5	colrl. cr., 178(m.), 250/10^{-3} (subl.), α=1	IR,^1H, ^{13}C, m-s, X-r, cryosc.	758
$Y[OCMe_2(CF_3)]_3$, $\cdot$2.5 THF	4	wh. sld., 118(m.), 115(m.)	IR, ^1H, ^{19}F, m-s	210
$[Y[OCH(CF_3)_2]_3]_x$ **$\cdot$n L,** L=NH_3 (n=0.5; 2), THF(3), ^{i}PrOH	4, 5, 6	cr., s. in hc., 60-80 (m), 164 (m), 120/10^{-1} (b.,-L)	IR, ^1H, ^{19}F, TGA, m-s	210, 982, 1084
$\{Y[OCMe(CF_3)_2]_3\}_n$	4	wh. slds., 175(m.), 110/10^{-3} (subl.), α=2	IR, ^1H, ^{89}Y, ^{19}F, m-s, X-r	208, 210, 734

$[Y[OCMe(CF_3)_2]_3THF_3]$, oct. **$[Y[OCMe(CF_3)_2]_3 \cdot Dig]$**, oct. **$\cdot 5NH_3$, $\cdot$ $0.33Et_2O$, $\cdot 3Bu^tOH$**		164-182 (m.) 201(m.),$140/10^{-2}$ (subl.), in m-s: $[Y(OR)_2Dig]^+$		
$[Y_2(OSiMe_2Bu^t)_6(SiMe_2Bu^tOH)]$, trig. bipyr. and tetrah. with a common $(\mu\text{-}OR)_2$ edge. **$[Y(OSiMe_2Bu^t)_3THF_3]$**	4	colrl. cr. -	IR, ^1H, ^{13}C, X-r	1091
$[Y(OSiPh_3)_3]_2$, 2 tetrah. with a common $(\mu\text{-}OR)_2$ edge **$Y(OSiPh_3)_3 \cdot 3\ Py$** **$[Y(OSiPh_3)_3THF_3] \cdot THF$** -***fac***, oct. **$[Y(OSiPh_3)_3(POBu^n{}_3)_2]$**, trig.bipyr.	4 5, 6 5	colrl. cr. - colrl. cr., 135 (m.) -	IR, ^1H, ^{13}C, ^{89}Y, ^{29}Si, X-r	397, 395, 671, 1092, 1091
$[Y(\eta^2,\mu\text{-}OR)_2(\eta^1\text{-}OR)]_{10}$, $R{=}C_2H_4OMe$,cycle of 10 pentag. bipyr. $[Y(\mu\text{-}O)_4(O\text{-eth.})_2O]$	1, 6	colrl. cr., v. s. in hc., invol.	IR, ^1H, ^{13}C, ^{89}Y, ^{29}Si, X-r	395, 1308
$Y(OCR_2CH_2OMe)_3$, R=Me, Et, Pr^i	4	wh. sld., $95/10^{-3}$ (subl.), $\alpha=2$	IR, ^1H, ^{13}C,m-s	734, 54
$[Y(OCBu^t{}_2CH_2OEt)_3]$	4	wh. sld., 95 /10^{-3} (subl.), s. in.hex., $\alpha=1$	IR, ^1H, ^{89}Y, m-s	734
$Y(OCH_2CHOCH_2O) \cdot H_2O$	3	wh. sld., 160 (dec.)	IR, TGA	1248
$[YCl(OBu^t)THF_5]^+[BPh_4]^- \cdot 2THF$ cation - pentag. bipyr., Cl and OR-ax.		colrl. cr.	X-r	552
$[Y_2Cl(OBu^t)_4THF_4]^+[BPh_4]^-$ cation- 2 oct. sharing a $[(\mu\text{-}Cl)(\mu\text{-}OR)_2]$ face		colrl. cr.,, s. in THF, ins. in tol.	IR, ^1H, X-r	552

$Y_3Hal_2(OBu^t)_7\cdot 2THF$, Hal=Cl, Br, trian. $[Y_3]$, 1 oct. $[YHal_2(OR)_4]$ and 2 oct. $[YHal(OR)_4THF]$	colrl. cr.,	IR, ^1H, ^{13}C, X-r	553, 1761
$Y_3Cl(OBu^t)_8.2THF$, trian. $[Y_3]$, 1 oct. $[YCl_2(OR)_4]$ and 2 oct. $[YCl(OR)_4THF]$ (2 modifications)	colrl. cr., s. tol., hex.	IR, ^1H, ^{13}C, ^{89}Y, X-r	553
$[Y_3Cl(OBu^t)_7THF_3]^+[BPh_4]^-\cdot MePh$= $[Y_3(\mu_3\text{-}Cl)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_3THF_3]^+[BPh_4]^-$, in cation- trian. $[M_3]$, 3 oct. $[YClO_5]$	colrl. cr., s. tol.	IR, ^1H, X-r	552
$Y_4OCl_3(OBu^t)_7THF_3$, in $[(\mu_4\text{-}O)M_4]$ tetrah. - 1 at. Y CN= 7, 3 at.- oct. $[YO_6]$ and μ_3-OR	colrl. cr.	X-r	546
$[Y_7Cl_5(\mu_4\text{-}O)(OBu^t)_{14}THF_2]_2$, 4 $[M_3(\mu_3\text{-}OR)(\mu_3\text{-}Cl)(\mu\text{-}OR)_3(OR)_nTHF_m]$ trian., μ-Cl, 2 $[Y(\mu\text{-}OR)_2(\mu\text{-}Cl)_2]$	colrl. cr., s. in tol., hex.	IR, ^1H, ^{13}C,	553
$[YCl(OC_6H_2Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6)_2]_2$= $[YCl(\mu\text{-}OR)_2(OR)_2]$	colrl. cr., s. in THF-eth.	IR, ^1H, ^{13}C	758
$[Li(MeOCH_2\text{-})_2]_2Y(\mu\text{-}OAr)_4(OAr)]$, linear chain and sharing a $(\mu\text{-}OR)_2$ edge central $[YO_5]$ tetragon. pyr. **$[KY(OAr)_4THF_5]$**, oct. $[YL_2(\mu\text{-}OAr)_2(OAr)_2]$, $[KL_3(\mu\text{-}OAr)_2C_2]$, Ar= $C_6H_3Me_2$-2,6	colrl. cr., s. in hex.-THF	IR, ^1H, ^{13}C, X-r	544
$Na_2Y[OCMe(CF_3)_2]_5\cdot 3THF$ angular mol.,central $[Y(\mu\text{-}OR)_4(OR)THF]$ oct. sharing $(\mu\text{-}OR)_2$ with 2 $[Na(\mu\text{-}OR)_2(THF)F_5]$	s. eth., hc.,C_6F_6, subl. (-THF)	IR, ^1H, ^{13}C, m-s, TGA, X-r	996

$Na_2Y[OCMe_2(CF_3)]_5(THF)]$	colrl. cr., s. eth., hc.,C_6F_6, subl. (-THF)	IR,^1H, ^{13}C , m-s, TGA	996
$Na_3Y[\mu\text{-}OCH(CF_3)_2]_6 \cdot 3THF$, central $[Y(\mu\text{-}OR)_6]$ oct. sharing $(\mu\text{-}OR)_2$ with 3 $[Na(\mu\text{-}OR)_2(THF)\ F_5]$	colrl. cr., s. eth., hc.,C_6F_6, $110/10^{-3}$ (subl.,-THF)	IR, ^1H, ^{13}C, ^{19}F, m-s, TGA, X-r	982, 996
$Na_3Y[\mu\text{-}OCH(CF_3)_2]_6$	colrl. cr., 132(m.)		
$[Ba_2Y(OBu^t)_7(^tBuOH)]$ trian. $[M_3]$, 3 $[MO_5]$ 5-vertex polyhedra, **$\cdot 2THF$**	colrl. cr. s. eth., 90°→2THF	^1H, X-r	175
$[K(Dme)]^+[Y(OSiPh_3)_4Dme]^-$, anion - oct.. **$[K(18\text{-}crown\text{-}6)]^+[Y(OSiPh_3)_4]^-$**		X-r	1091
$[Na_8YX(OBu^t)_{10}]$, X=Cl,OH, $=[Na_8Y(\mu_9\text{-}X)(\mu_4\text{-}OR)(\mu_3\text{-}OR)_8(OR)]$, $[Na_8]$ - monocapped square antiprism [Y(OR)] cap	colrl. cr., s. tol., ins. in hex., $125/10^{-3}$ (subl.)	^1H, X-r	553
$Li_8Y_8Cl_4O_2(OBu^t)_{24}$, linear chain, 2 central $[Li_2(\mu\text{-}OR)_2]$, sharing 2 μ-Cl with 2 butterflies $[Y_4(\mu_4\text{-}O)]$, Li- tetrah., Y-oct.	colrl. cr., s. in hex., tol., ins. in THF	IR, ^1H, ^{13}C, X-r	553
$LiYCl_n(OC_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)_{4-n}THF_2$, n=2,3	-	IR, ^1H, ^{13}C	992
$Li_3Y[(C_{10}H_6O)_2]_3 \cdot 6\ THF$, $Ar(OH)_2$= 1,1'-binaphtol, sphere, in the centre - oct. Y	colrl. cr., s. inTHF-eth.	X-r	73
$[CuY(OSiPh_3)_4(Me_2PhP)]$ [396]			

La				
La(OMe)$_3$↓	5	wh. sld.	-	211, 1001, 1158
La(OEt)$_3$↓	5	wh. sld.	-	626, 1001, 1246
La$_5$O(OPr^i)$_{13}$·n^{i}PrOH (=«La(OPr^i)$_3$») ↓ ROH (t) **[La(OPr^i)$_3$]$_\infty$↓**	1, 2, 5	needles , s. in ROH (polytherma), hc; 120(m.), 250/0,1; 170/10^{-2} (subl.); 260 (dec.), α=1, diamagn.	IR, electr. sp., TGA, ebul., m-s, X-r IR, m-s	251, 626, 953, 1001, 1158, 1246, 1495 953
La$_4$TiO(OPr^i)$_{14}$		colrl. cr., s. in tol., THF	IR, ^{1}H, ^{13}C	442
La(OBu^s)$_3$	5, 6	-	-	1158
«La(OBu^t)$_3$»	4	wh. sld., 280/10^{-4} (subl.)	-	211, 1158
[La$_3$(OBu^t)$_9$L$_2$], L= THF (**1**), Bu^{t}OH (**2**), [La$_3$(μ_3-OR)$_2$(μ-OR)$_3$(OR)$_4$L$_2$], trian.[M$_3$], La -oct. ↓t		colrl. cr., s. tol.; **2**- 192 (m), 240/10^{-3} (b.), α=3	IR, ^{1}H, ^{13}C, X-r, m-s	209, 553
[La$_4$O(OBu^t)$_{10}$]$_2$ ↓ Zn(NR$_2$)$_2$ [t, - Zn(OR)$_2$]↓		colrl. cr., s. in tol.	IR, ^{1}H	445
[La$_5$O(OBu^t)$_{13}$] struct. analog of Y$_5$O(OPr^i)$_{13}$		colrl. cr., s. in tol.	IR, ^{1}H	
[La$_4$(μ-OC$_5$H$_{11}$^{neo})$_8$(OC$_5$H$_{11}$^{neo})$_4$]·4PhMe, square palnar [La$_4$] – of trig. bipyr. [LaO$_5$]	4	bl. (?)cr., s. in hc.	IR, ^{1}H, ^{13}C, X-r	105

$[La(OCMe_2Pr^i)_3]_2$	4	colrl. cr.,119 (m.), 135/10^{-3} (b.), in m-s $La_2(OR)_5^+$	IR, ^1H, ^{13}C, m-s	209
$[La(OCMeEtPr^i)_3]_2$	4	colrl. cr., 112(m), 150/10^{-3} (b.), in m-s $La_2(OR)_5^+$	IR, ^1H, ^{13}C, m-s	209
$[La(OCPh_3)_3]_2 \cdot 3C_7H_8$ 2 tetrah. with a common (μ-OR)$_2$ edge, **$\cdot$x THF**	4	colrl. cr., s. in THF (t)	IR, ^1H, ^{13}C, X-r	548
$[La(OC_6H_3Me_2\text{-}2,6)_3]$ **$[MeO(C_2H_4O)_4Me]$,** CN La=5+3 (ether O-at. coplanar)	5	colrl. cr., s. in THF (t), paramagn.	IR, ^1H, ^{13}C, X-r	73
$[La(OC_6H_3Pr^i_2\text{-}2,6)_3]_2$ 2 trig. pyr, bound by (η^6,μ-Ar)$_2$, **3Py** **$[La(OC_6H_3Pr^i_2\text{-}2,6)_3THF_2]$-*trans*,** trig. bipyr **$[La(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_3)_4]$**, moncapped oct **$[La(OC_6H_3Pr^i_2\text{-}2,6)_3(NH_3)]_2$** 2 trig. pyr., bound by (η^6-Ar)$_2$	5	colrl. cr., s. in bz., poorly in hex.	IR, ^1H, ^{13}C, X-r	283, 381, 383 105
$[La(OC_6H_3Ph_2\text{-}2,6)_3THF_2] \cdot 2THF$- ***trans***,dist. trig. bipyr., THF and OR- ax.	7		X-r	464
$La(OC_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)_3$, struct. analog of Sc-complex, **THF**		195 (m.), 250/10^{-3} (subl.), α=1	^1H, ^{13}C, ms, cryos., X-r	758
$[La[OCMe_2(CF_3)]_3THF_{1.5}]$	4	78-86 (m.)	IR, ^1H, ^{19}F	209

$[La[OCMe(CF_3)_2]_3]_n$, $\cdot 0.33Et_2O$	4	$130/10^{-2}$ (subl.,dec.) 178(m.), $90/10^{-2}$ (subl.,eth.)	IR, ^1H, m-s	209
$[La[OCMe(CF_3)_2]_3\,THF_3]$, oct.	4	180 (dec.), in m-s $Ln_2F_n(OR)_{5-n}^+$	X-r	
$[La[OCMe(CF_3)_2]_3\,Dig_{1.5}]$ ↓ subl.		colrl. cr.		
$[La[OCMe(CF_3)_2]_3\,Dig]$		m-s- $Ln_2(OR)_2Dig^+$		
$[La[OCMe(CF_3)_2]_3\,(NH_3)_n]$, n=1, 4		**n=1**: 148(m.), **n=4**: 158 (m.), $85/10^{-2}$ (subl., $-NH_3$)	IR, ^1H, ^{19}F, m-s	
$La(OC_6F_5)_3$	5	stab. to air, 250(dec.), α=2	IR, ^{19}F, m-s	536
$[La(OSiPh_3)_3]_n$	4	-	IR, ^1H, ^{13}C, X-r	1091, 1092
$[La(OSiPh_3)_3]_2\cdot 2C_7H_8$, 2 tetrah. sharing $(\mu\text{-}OR)_2$		colrl. cr., s. in THF		548, 671
$[La(OSiPh_3)_3L_3]\cdot L$ -*fac*, L=THF(oct.), Py, $POBu^n_3$		-		
$La(OC_2H_4OMe)_3$	1	visc. sld.	IR	1652
$La(OCH_2CHOCH_2O)\cdot H_2O$	3	wh. sld., 160 (dec.)	IR, TGA	1248
$K_2La_6O(OBu^t)_{18}THF_4$, $[BaLa_3O(OBu^t)_9THF]_2$ $[PbLa_3(OBu^t)_{11}]_2$, $CuLa_6O(OBu^t)_{18}THF_3$		colrl. cr., s. in tol., THF	IR, ^1H, ^{13}C, ^{207}Pb	442
$[LiLa(OC_6H_3Pr^i_2\text{-}2,6)_4\,THF_2]$, trig. bipyr. for La and trian. for Li sharing $(\mu\text{-}OR)_2$		colrl. cr., s. in tol., hex.	IR, ^1H, X-r	383
$[Me_4N]^+[Na_2La_2(OAr)_9THF_5]$, in anion $[(\mu_4\text{-}OR)M_4]$ tetrah., term. OR- only at La, CN La 7, Na- 5 and 6		colrl. cr., s. in tol., hex.	IR, ^1H, X-r	548

$Na_3La_2(OAr)_9$ Dme_6THF_2, asymm. anion struct. type of $Ti_4(OMe)_{16}$, 2 of (μ_3-OAr) belong to coord. of 1 at. Na, III -of another at. Na		“	“	
$[Na_3La_2(OAr)_9Diox_6]_\infty$ trig. bipyr. [M_5], 2 [La(μ-Diox)]-ax., [μ_4-ONa_2La_2], μ-OR –along 6 edges, 2 Na - 1 (μ-Diox)], 1- term. (CN 6), at 1 Na –1 Diox (CN 5), CN La 7		colrl. cr., s. in bz., Diox, THF	“	
$[NaTHF_3La(\mu\text{-}OAr)_2(OAr)_2]\cdot 2PhMe$, trig. bipyr. for La and tetrah for Na sharing (μ-OR)$_2$, Na…C(1)		colrl. cr., s. in tol., hex.	IR, ^1H, X-r	383
$[KLa(\mu\text{-}OAr)(OAr)_3]_\infty$, in a layer alternating $[La(OR)_4]$ tetrah. and 12-vertex polyhedron [K(η^6-Ar)(η^3-Ar)(η^2-Ar)(η^1-Ar)]		-	IR, ^1H, X-r	381
$[CsLa(OC_6H_3Pr^i_2\text{-}2,6)_4]_\infty$, in a layer alternating $[La(OR)_4]$ tetrah. and 12-vertex polyhedron [Cs(η^3-Ar)$_4$]		pink powd., s. in tol., hex.	IR, ^1H, X-r	383
$Cs_2[La(OC_6H_3Pr^i_2\text{-}2,6)_5]$, anion - trig. bipyr.				380
$[NaLa(\mu\text{-}OAr)_2(OAr)_2THF_2]_2$, Ar= C_6H_2Me-4-Bu^t_2-2,6		-	-	758,
$[LiLaCl_3(OAr)THF_2]$		-	IR, ^1H,^{13}C	992
$Li_3La[(C_{10}H_6O)_2]_3\cdot 6$ THF, $Ar(OH)_2$= 1,1’-binaphtol, isostr. to its Y-analog		colrl. cr., s. inTHF-eth.	X-r	73
$[La_2Zr_3O(OPr^i)_{16}]$ [898]				
Ce(III)				
$Ce(OMe)_3$↓, $Ce(OEt)_3$↓,«$Ce(OPr^i)_3$»	5	yel. powd.	-	1001, 1246
$[Ce(OCHBu^t_2)_3]_2$ 2 tetrah. with a common (μ-OR)$_2$ edge	4	yel. powd.	^1H, X-r	1528

$[Ce(OCBu^t_3)_3]$, trig. pyr. **nL,** L=THF, Ph_2CO, Am, MeCN, n=1, 2 **$[Ce(OCBu^t_3)_2(OBu^t)]_2$** 2 tetrah. sharing ($\mu$-OR)$_2$	4 7	yel. cr.,$160/10^{-3}$ s. in bz., $C_5H_{12} \rightarrow Ce(OCHBu^t_2)_3$ yel. cr.	^1H, ^{13}C, X-r	737,1458, 1528
$[Ce(OCPh_3)_3]_2$ 2 tetrah.sharing (μ-OR)$_2$, **3THF**	4	yel. cr., s. in THF	IR, ^1H, ^{13}C, X-r	548
$[Ce(OC_6H_3Bu^t_2\text{-}2,6)_3]$, trig. pyr. **·nL,** L=THF, Ph_2CO, Am, MeCN, n=1,2 **$[Ce(OC_6H_3Bu^t_2\text{-}2,6]_3(Bu^tN{=}C)_2]$** trig. bipyr., 2 at. C -ax.	4	yel-grn. cr.	IR, ^1H, X-r	1528
$Ce(OC_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)_3$	4	yel.-grn. cr.,180 /10^{-5} (subl.), s. in org. solv.	IR, ^1H	1528
$Ce(OC_6H_2Bu^t_3\text{-}2,4,6)_3$	4	yel.cr., 180/10^{-5} (subl.)	IR, ^1H	1528
$[Ce(OSiPh_3)_3]_2 \cdot 2C_7H_8$, 2 tetragon. pyr. sharing (μ-OR)$_2$, Ce-C 2.98 **$[Ce(OSiPh_3)_3THF_3] \cdot THF$ -*trans*,** oct.	4, 5	yel. cr., s. in THF yel. cr., 145 (m.)	IR, ^1H, ^{13}C, X-r	548 671, 1092, 1091
Ce(IV)				
$Ce(OMe)_4\downarrow$, $\cdot MeOH$	5, 6	yel. cr., sld., dec. 280	^1H	206, 670
$Ce(OEt)_4\downarrow$, $Ce(OPr^n)_4$	5, 6	yel. cr., 200(dec.), α=4	ebul.	206
«$Ce(OPr^i)_4$» **$\cdot Py$**	5	yel. gl., s.org. solv., 160/0.05 (subl.),α=3,13	ebul.	670, 2040

$[Ce(OPr^i)_4 \cdot {}^iPrOH]_2$ 2 oct. sharing $(\mu\text{-}OR)_2$, 2 ROH...OR (ax) $\downarrow 70^\circ/10^{-3}$	4, 5	yel. cr., no react. with $Ba(OPr^i)_2$	IR, ^1H, ^2H, ^{13}C, X-r	206,789, 793 ,1589, 1665
$Ce_4O(OPr^i)_{14}$ $=[M_4(\mu_4\text{-}O)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_8]$, the $[OCe_4]$ tetrah, 2 oct. $[CeO_6]$ and two 7-vertex polyhedra sharing $[O(\mu\text{-}OR)_2]$	-	or. cr., s. in org. solv., 145 (m.), 170 (dec.)	IR, ^1H, ^{13}C, X-r	1497
$Ce^{3.75+}{}_4O(OPr^i)_{13}({}^iPrOH)$ = $[Ce_4(\mu_4\text{-}O)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_7(ROH)]$, butterfly type	7	or.-brn. cr., $\mu_{eff}=2.7$	IR, ^1H, ESR, magn. prop., electr. sp., X-r	1803
$Ce(OBu^n)_4$, $Ce(OBu^i)_4$, $Ce(OBu^s)_4$ *	4, 6	yel.sld., 200 (dec.), $\alpha=4$	ebul.	2040
«$Ce(OBu^t)_4$»	6	sld.,140/0.1 (subl.), $\alpha=2.5$	IR, ^1H, ^{13}C,ebul	547, 2040
$[Ce(OBu^t)_4THF_2]$, 20° (72 h.) $\rightarrow$**$Ce_3O(O$**	5	yel. powd.		
$Ce(OBu^t)_2(OCBu^t{}_3)_2$	7	yel.-or.-brn. sld., v. instab.		1458
$Ce(OC_5H_{11}{}^i)_4$, $Ce(OCHEt_2)_4$, $Ce(OCHMePr^n)_4$, $Ce(OCHMePr^i)_4$	5, 6	yel. sld., 200 (dec.), $\alpha=3$	ebul.	2040
$Ce(OC_5H_9{}^{neo})_4$	5, 6	yel.sld.260/0.05(subl.), $\alpha=2$	ebul.	206
$Ce(OCMe_2Et)_4$	6	yel. sld., 240/0.1 (subl.), $d^o=1.064$, $\alpha=2.4$	ebul., surface tension	230, 2040
$Ce(OCMeEt_2)_4$	6	yel. liq., d^o 1.1064, 140/0.06 (b.), $\alpha=1.4$ (bz.)	ebul., surface tension	230, 2040
$Ce(OCMe_2Pr^n)_4$	6	yel.liq.,146/0.05(b.),$\alpha=1.4$	ebul.	2040
$Ce(OCMe_2Pr^i)_4$, $Ce(OCMeEtPr^n)_4$	6	yel. liq., 132/0.5 (b.), $\alpha=1$	ebul.	2040
$Ce(OCEt_3)_4$	6	yel. liq., 154/0.05 (b.), $d^o=1.0879$, $\alpha=1.1$	ebul., surface tension	230, 2040

$Ce(OC_8H_{17}{}^n)_4$	5	or.-red oil, 240 (dec.)	^1H, m-s	670
$Ce_2O[O(CMe_2)_2O]_2[O(CMe_2)_2OH]_2]_2$	6	yel. powd., polymer	IR	782
$[Ce_2(\mu\text{-}C_6H_4O_2\text{-}1,4)(OCBu^t{}_3)_6]$, 2 tetrah. sharing $(ArO_2)_2$	7	purple-blk. cryst., s. in hc.	IR, ^1H, ^{13}C, X-r	1458
$Ce[OCH(CF_3)]_4{\cdot}nL$, L= THF (n=2); Tmeda (1)- oct.; Dipy (2), Dig (1)- CN Ce=7	5,6	yel.cryst.,s.in hex., $70/10^{-4}$ (subl.), 155-234(m), 200 (dec.)	IR,^1H,^{19}F, X-r	781, 782
$[Ce[OCH(CF_3)]_4(\eta^2\text{-}Tmeda)]$, oct.		-	-	«
$Ce(OCMe_2CCl_3\}_4{\cdot}Py$	5	-	-	233
$Ce(OSiMe_3)_4{\cdot}{}^iPrOH$	6	yel. cryst.,143 (m.), s. in org. solv.	^1H, ^{13}C, ^{29}Si, X-r powd.	671
$Ce(OSiEt_3)_4$	6	« 134(m.)	^1H, ^{13}C, ^{29}Si	671,
$[Ce(OSiPh_3)_4(\eta^2\text{-}Dme)]{\cdot}PhMe$, oct. **$Ce(OSiPh_3)_4{\cdot}5Dme$**	6	wh. powd., s. in tol., eth., stab. to hydrol.	IR, ^1H, ^{13}C, ^{29}Si, X-r	547, 671
$Ce(O_2SiPh_2)_2$	6	yel. sld., s. in org. solv., 155 (m., dec.)	^1H, ^{13}C, ^{29}Si	671
$Ce[(OSiMe_2)_2O]$	6	« 200 (m., dec.)	^1H, ^{13}C, ^{29}Si	671
$CeCl_3(OPh)$		brn. cr., s. in petr. eth.	IR, electr. sp.	686
$[NaCe_2(OBu^t)_9]$, trian. $[M_3]$, 1 gr. $[NaO_4]$, 2 gr.$[CeO_6]$; **$Na_2Ce(OBu^t)_6THF_4$** **$[Na_2(\eta^2\text{-}Dme_2Ce(OBu^t)_6]$,** trian. $[M_3]$, 2 $[NaO_5]$ 5-vertex polyhedra and $[CeO_6]$ oct.		yel. cryst., s. in hex.,THF, 20°, 2 weeks→**$Ce_3O(OR)_{10}$** yel. cryst. yel. cryst.	IR, ^1H, X-r	547
$BaCe_2(OPr^i)_{10}$; + ROH → **$BaCe_4(OPr^i)_{18}$,** struct.analog of $BaTi_4(OR)_{18}$		yel. cryst., s. in hex.	IR, ^1H,^{13}C,	789

$[HL]^+_2 [Ce[OCH(CF_3)]_6]^{2-}$, L=$MeN(C_2H_4NMe_2)_2$ anion- nearly a crown (CN 6, Ce...F)		yel.cryst.,s.in ROH, THF, 113 (m.), 182 (dec.), $70/10^{-4}$ (subl.)	IR, ^1H, ^{19}F , X-r	781
$[Ce_2Ti_2O_2[O(CMe_2)O]_4(OPr^i)_6(^iPrOH)_2]$, $[Ce_2Nb_2O_2[O(CMe_2)O]_4(OPr^i)_6]$ [782]				
Pr				
$Pr(OMe)_3\downarrow$, $Pr(OEt)_3\downarrow$	5	brigt grn. sld.	electr. sp.	626, 842 1158, 1246
$Pr(OPr^i)_3 \cdot {}^iPrOH$ (?) $\rightarrow R_2O+Pr_5O(OPr^i)_{13}$ («$Pr(OPr^i)_3$»), struct. analog of $Y_5O(OPr^i)_{13}$ $[Pr_4TiO(OPr^i)_{14}]$	1, 5	v. unstab. yel.-grn.cr., s. in tol., 175/ 0.04 (subl.), 200(dec.), paramagn., s. decreas estime grn.cr., s. in tol.,THF, ROH, ins. in hex.	IR IR, ^1H, ^{13}C, electr. sp., TGA, X-r	251, 783, 1158, 1246, 1494 442, 783
$Pr(OBu^n)_3$, $Pr(OBu^s)_3$, "$Pr(OBu^t)_3$"	5	-	-	1158, 162
$Pr_3(OBu^t)_9(^tBuOH)_2$	4	yel.-grn. cr., s. in tol.,THF, ins. in hex.	IR	783
$Pr_5O(OC_5H_{11}{}^i)_{13}$=«$Pr(OC_5H_{11}{}^i)_3$»	1	grn.cr., s. in org. solv.	IR	783
$[Pr_4O_2(OC_5H_{11}{}^{neo})_8]_m$, $[Pr_4O(OC_5H_{11}{}^{neo})_{10}]_m$	1	grn.cr., s. in tol., THF	IR	783
$Pr_3(OC_5H_{11}{}^t)_9(^tC_5H_{11}OH)_2$	4	«	IR.	783
$[Pr(OC_6H_3Me_2\text{-}2,6)_3]$ $[MeO(C_2H_4O)_4Me]$ isostr. to its La-analog	5	pale grn. cr., s. in THF (t), paramagn.	IR, ^1H, ^{13}C, X-r	73

$\mathbf{[Pr(OC_6H_3Pr^i{}_2\text{-}2,6)_3]_2THF_2]}$-***trans*** trig. bipyr., THF-ax.	5	brn. cr., s. in tol., THF	IR, ^{1}H, X-r	105, 283
$\mathbf{Pr(OC_6H_2Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6)_3}$, struct. analog of Sc-compl., ·**THF**	4, 5	yel. cr., 200 (m.), 250/10^{-3} (subl.), α=1	^{1}H, ^{13}C, m-s, cryos., X-r	758
$\mathbf{[Pr[OCMe_2(CF_3)]_3]_3}$, trian. $[M_3]$, 1 $[PrO_6]$, 2 $[PrO_5]$, Pr...F complete CN to 6 and 7	4	grn. cr., 180 (dec.)	^{1}H, ^{19}F, X-r	208, 209
$\mathbf{[Pr[OCMe(CF_3)_2]_3]_3}$ trian. $[M_3]$, 1 gr. $[PrO_6]$, 2 gr. $[PrO_5]$ $\mathbf{[Pr[OCMe(CF_3)_2]_3(NH_3)_2]_2}$, 2 oct. sharing a $(\mu\text{-}OR)_2$ edge, 2 N-ax., 2 equ. $\mathbf{[Pr[OCMe(CF_3)_2]_3THF_3]}$ $\mathbf{[Pr[OCMe(CF_3)_2]_3\,Dig_{1.5}]}$, subl. → $\mathbf{[Pr[OCMe(CF_3)_2]_3\,Dig]}$	4	wh. (?) cr., 135 (m., dec.), 140/10^{-2} (subl.) pale grn. cr., 126 (m.) grn. cr., 180 (m.,dec.), in m-s $M_2F_n(OR)_{5-n}{}^+$ grn. cr., in m-s $M_2(OR)_2Dig^+$	IR, ^{1}H, m-s, X-r	208, 209
$\mathbf{[Pr(OSiPh_3)_3THF_3]\cdot THF}$ -***fac***, oct.	5	grn. cr., 130 (m.)	IR, ^{1}H, ^{13}C, X-r	671
$\mathbf{[Pr_4O_2(OC_2H_4OMe)_8]_m}$	1, 6	grn. cr., s. in tol., THF	IR, ^{1}H, ^{13}C, TGA	783
$\mathbf{[Pr_4O_2(OC_2H_4OMe)_8(OPMe_3)]_2}$, in the spherical centrosym. mol. built up of 8 Pr oct., 4 μ_4-O lie in 2 perpendic. $[M_4]$ planes	1	grn. cr.	IR, X-r	783
$\mathbf{Pr(OCH_2CHOCH_2O)\cdot H_2O}$	3	grn. cr., 160 (dec.)	IR, TGA	1248
$\mathbf{PrCl_2(OBu^t)\cdot THF}$; $\mathbf{PrCl_2OPh\cdot nTHF}$ $\mathbf{[Pr{*}Al_2Cl(OPr^i)_8(^iPrOH)]_2}$ (*-praseodym) [1598]		-	-	162, 338

Nd				
$Nd(OMe)_3\downarrow$, $Nd(OEt)_3\downarrow$	5	pink-viol. powd.	electr. sp.	1158, 842, 1246
$[Nd(OPr^i)_3(^iPrOH)]_4$= $[Nd_4(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_6(ROH)_4]$ $Ti_4(OMe)_{16}$ struct. type (details not published)	1	bl.-pinc cr., instab., 20°/vac.→ **$Nd_6O_5(OR)_8$**, paramagn.	IR, X-r	726, 1308, 1494
$[Nd_5O(OPr^i)_{13}\cdot 2^iPrOH$ (=«$Nd(OPr^i)_3$») in trig. bipyr. $[M_5]$ -2 μ_3-OR -capping faces one over, one below the eq. plane, 6 μ- mer., all M- ax., 2 M-eq. connect to 1 term. OR, 1 M-eq. - 3 term. gr. (1 OR and 2ROH), all M -oct.	1, 5	pale-bl. cr., 250/0,1 (subl., dec.), paramagn.	IR, ^1H, magn. prop., electr. sp., TGA, X-r	251, 626, 726, 1158, 1246
$Nd_4TiO(OPr^i)_{14}$		colrl. cr., s. in tol.,THF	IR, ^1H, ^{13}C	442
$Nd(OBu^n)_3$	6	-	-	626, 1158
$Nd(OBu^s)_3$, «$Nd(OBu^t)_3$»	6	-	-	1158
$[Nd_4(\mu\text{-}OC_5H_{11}{}^{neo})_8(OC_5H_{11}{}^{neo})_4]\cdot 4PhMe$, struct. analog of La-complex	4	bl. cr., s. in hc.	IR, ^1H, ^{13}C, X-r	105
$[Nd_2O(OC_5H_{11}{}^{neo})_4]$, 2 tetrah. sharing $[(\mu\text{-}O)(\mu\text{-}OR)_2]$-face	4			1791
$[Nd(OCHPr^i{}_2)_3L]_2$, L=THF, Py, 2 trig. bipyr. sharing $(\mu\text{-}OR)_2$-equ. and ax., L- *trans* to μ-OR	4	pale bl. cr., s. in hex., Dme	IR, ^1H, X-r	105
$[Nd(OCHPr^i{}_2)_3]_2\cdot Dme$, zigzag chains of dimers bipyr sharing $(\mu\text{-}OR)_2$, bound by Dme				

$[Nd(OCHBu^t_2)_3]_2$, struct. analog of Ce-complex **$[Nd_2(OCHBu^t_2)_6(MeCN)]$**, trig. bipyr. and tetrah. with a common $(\mu\text{-}OR)_2$ edge	4	bl. cr., 175 (m.), $170/10^{-3}$ (subl)., 317(dec.), v. s. in hc.	IR, ^1H, ^{13}C, m-s, TGA, X-r	735, 737
$[Nd(OCPr^i_3)_3]_2$, $[Nd(OCBu^tPr^i_2)_3]_2$ **$[Nd(OCBu^t_2Pr^i)_3]_2$**, 2 tetrah. with a common $(\mu\text{-}OR)_2$ edge	 4	220/, $160/10^{-3}$ (subl.) bl. cr., subl., v. s. in hc.	- m-s, TGA, X-r	732 737
$Nd(OCBu^t_3)_3$ $160/10^{-3} \rightarrow {}^iC_4H_8 +$ **$Nd(OCHBu^t_2)_3$** **$[Nd(OCBu^t_3)_3THF]$**, tetrah. **$[Nd(OCBu^t_3)_3(MeCN)_2] \cdot MeCN$**, trig.bipyr.	4	pale-bl. cr., s. in hex. 145 (m.) bl. cr.	IR, m-s, X-r	516, 735, 736, 737, 1722 735
$[Nd(OC_6H_3Me_2\text{-}2,6)_3THF_2]_2 \cdot 2THF$, 2 oct. sharing $(\mu\text{-}OR)_2$	5	bl. cr.	IR, ^1H, X-r	544
$[Nd(OC_6H_3Pr^i_2\text{-}2,6)_3]_2$, 2 η^6-π-Ar-bridges **$[Nd(OC_6H_3Pr^i_2\text{-}2,6)_3THF_2]$**	4	grn. cr., s. in tol., $\alpha=2$ pale bl. cr.	IR, ^1H, X-r	105
$[Nd(OC_6H_3Ph_2\text{-}2,6)_3]$, $[Nd(OC_6H_3Ph_2\text{-}2,6)_3THF]$ trig.pyr. (intermol. M-Ar bonds) **$[Nd(OC_6H_3Ph_2\text{-}2,6)_3THF_2] \cdot 2THF$- *trans***, tetragon. pyr. (trig. bipyr.), isostr. to its La-analog **$[Nd(OC_6H_3Ph_2\text{-}2,6)_3(\eta^2\text{-}Dme)] \cdot THF$**, tetragon. pyr.	4, 7	bl. cryst., s. in THF, subl., $\alpha=1$	IR, ^{13}C, m-s, electr.sp, X-r	459, 461, 462, 464, 466

$[Li(THF)_3ClNd(OCBu^t_3)_3]$ 2 tetrah. sharing common vertex (μ-Cl)		pale-bl., 138(m.), α=1	IR, ^1H, ^{13}C, m.-s, X-r	516
$[NaNd(OC_6H_3Ph_2\text{-}2.6)_4]$ $=[NaC(\mu\text{-}OR)_3Nd(OR)]$, 3 bonds Na-C, 2 Nd-C **$[NaDme_3][Nd(OC_6H_3Ph_2\text{-}2,6)_4]$** **$[NaDig_2][Nd(OC_6H_3Ph_2\text{-}2,6)_4]$**, cation - oct., anion - tetrah.		bl. cr., s. in C_5H_{12}, tol., THF, Dme	IR, electr. sp., X-r	380, 460
$[KNd(OC_6H_3Pr^i_2\text{-}2.6)_4]_\infty$, in a layer alternating $[Nd(OR)_4]$ tetrah. and 14-vertex polyhedron $[K(\eta^6\text{–}OR)_2(\eta^1\text{-}OR)O]$		pale bl., s. in tol.	IR, ^1H, X-r	381
Sm(II)				
$Sm(OEt)_2\downarrow$	5	-	-	1194
$[Sm(OC_6H_4Me\text{-}4)_2THF_3]THF$, trig. bipyr.	7	-	-	1325
$[Sm(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2THF_3]$, struct. analog of Eu-complex	4	red cr., 133 (m.)	-	1668
$[KSm(\mu\text{-}OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_3THF]_\infty$ zigzag chains of $[Sm(\mu\text{-}OR)_3THF]$ tetrah. and $[K(\mu\text{-}OR)_2(\eta^6,\mu\text{-}Ar)]$ trian.		blk. cr.	X-r	545
$SmAl_3(OPr^i)_{11}$ [514]				
Sm(III)				

$Sm(OMe)_3\downarrow$, $Sm(OEt)_3\downarrow$	5, 6	yel. powd.	-	1246, 1001, 1397
«$Sm(OPr^n)_3$»	6	yel.powd., s. in bz.	-	1397
«$Sm(OPr^i)_3$»	5	yel. powd.,s. in bz., ROH, eth., 80/0.04, 200/0.1 (subl.), 200 (dec.), α=4, paramagn.	IR, ^1H, electr. sp., ebul.,TGA, magn. prop.	251, 1001, 1246, 1397, 1494
$[Sm_4TiO(OPr^i)_{14}]$, $[M_5]$ - trig. bipyr.-$[TiO_{1/5}O_{2/2}O_2]$, oct. $[LnO_{1/5}O_{1/3}O_{3/2}O]$- eq.	1, 5	colrl. cr., s. in tol., THF, ROH, $\mu_{eff}=2.54$	IR, ^1H, ^{13}C, X-r	444
$[Sm_4ZrO(OPr^i)_{14}]$		s. in tol., THF	IR, ^1H, ^{13}C	442
$Sm(OBu^n)_3$, $Sm(OBu^i)_3$, $Sm(OBu^s)_3$, «$Sm(OBu^t)_3$,» $Sm(OC_5H_{11}{}^n)_3$, $Sm(OC_5H_{11}{}^i)_3$, $Sm(OC_5H_{11}{}^t)_3$	6	yel. sld., s. in bz., ROH, eth.	IR	1397
$Sm(OC_6H_{13}{}^n)_3$, $Sm(OCMe_2Pr^n)_3$ $Sm(OC_8H_{17})_3$, $Sm(OPh)_3$	5, 6	yel. sld., s. in bz., ROH, eth.	-	1246, 1397
$[Sm(OC_6H_3Pr^i{}_2\text{-}2,6)_3]_2$, 2 η^6-π-Ar-bridges $[Sm(OC_6H_3Pr^i{}_2\text{-}2,6)_3THF_2]$-*trans*, trig. bipyr.	4 5	yel. cr., s. in tol., α=2	IR, ^1H, ^{13}C, X-r	105
$Sm(OC_6H_3Ph_2\text{-}2,6)_3$	4, 7	pale-yel. cr., s. in THF	IR, ^{13}C, m-s, electr. sp., X-r	466
$[Sm(OAr)_3THF]\cdot THF$, tetrah. $[Sm(OAr)_2(OCHPh_2)HMPA_2]$, trig. bipyr. $[SmO(OC_6H_3Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6Ar)_2Hmpa_2]$	5 1 	yel. cr., 135(m.) yel. cr, yel. cr.	m-s, X-r X-r -	1325, 1796
$Sm(OCH_2C_5H_4FeCp)_3$	5	s. in tol.	IR, ^1H, m-s,	665

$[Sm(RO_2)(RO_2H)]\cdot R(OH)_2$, R=$C_2H_4$, C_3H_6, C_4H_8, C_5H_{10}	6	yel. sld., ins. in bz., invol.	-	1397
$Sm(OCH_2CHOCH_2O)\cdot H_2O$	3	160 (dec.)	IR, TGA	1248
$SmCl_2(OPh)\cdot nTHF$		yel. cr.	-	338
$[Li_5Sm(OBu^t)_8]$ =$[Li_5Sm(\mu_4\text{-}OR)_2(\mu_3\text{-}OR)_4(OR)_2]$, 2 cubes with common $[Li_2O_2]$ face, CN Li 3, Sm – oct.		yel. cr., 135/0.5 (subl.), stab. to hydrolysis	IR, ^1H, ^{13}C, m-s , X-r	1441
$[Li_3Sm(O_2Ar)_3THF_3]$, $Ar(OH)_2$=$(C_{10}H_6OH)_2$, binaphtol		-	-	1556
Eu(II)				
$[Eu_2(OC_6H_3Me_2\text{-}2,6)_4Dme_3]$, oct. and 7-vertex polyhedron sharing a $(\mu\text{-}OR)_3$ face	1	cr., s. in liq. NH_3 , Dme	X-r	551
***cis*-$[Eu(OC_6H_2Me\text{-}4\text{-}Bu^t\text{-}2,6)_2THF_3]\cdot THF$,** trig. bipyr.	4	yel. cr.	^1H, ^{13}C, X-r	463, 1668
$[Eu(OC_2H_4OMe)_2]_n$	1	or.sld., s.in hex.,α>10, μ_{eff}=7.7	IR, magn. prop.	549
$[H^+Eu(OC_2H_4OMe)_2(OC_6H_3R_2\text{-}2,6)]_4$, R=Me, Pr^i, $[Eu_4]$-tetrah., CN Eu 7	6	yel. cr., μ_{eff}=7.9	X-r	
$[EuM^{II}_2(OBu^t)_6]$, M^{II}=Ge, Sn [1681]				
Eu(III)				
$Eu(OEt)_3$	5	or. sld.	-	1246

«$Eu(OPr^i)_3$»	1	or. sld., 200 (dec.), paramagn.	IR, ^1H, magn. prop., electr.sp	251
$[Eu[OCMe_2(CF_3)]_3]_3$	4	pale-yel. sld., 210 (dec.)	IR, ^1H, ^{19}F	209
$[Eu(OCMe(CF_3)_2)_3]_n$ **$2NH_3$** **$[Eu(OCMe(CF_3)_2]_3(THF)_3]$** **$[Eu\{OCMe(CF_3)_2\}_3Dig]$**	4 4 4	cream cr., 133(m.), 120/10^{-2} (subl.) colrl. cr., 240 (m.) 180 (m., dec.), m-s: $MF_n(OR)_{5-n}^+$ in m-s $MF(OR)_2L^+$	IR, ^1H, m-s	209
$Eu(OCH_2CHOCH_2O)\cdot H_2O$	3	pale-yel. sld., 160 (dec.)	IR, TGA	1248
$[Na_8EuX(OBu^t)_{10}]$, X=Cl,OH, isostr. to its Y-analog	pale-yel. cr., s. in tol., 125/10^{-3} (subl.)		^1H, X-r	553
$Na_3Eu[(C_{10}H_6O)_2]_3(H_2O)$, $\cdot$6THF, $Ar(OH)_2$= 1,1'-binaphtol	colrl. cr., s. inTHF-eth.		-	73
Gd				
$Gd(OMe)_3\downarrow$, $Gd(OEt)_3\downarrow$, $Gd(OPr^n)_3$	5	wh. powd.	IR	121, 1122, 1246
«$Gd(OPr^i)_3$»	1, 5	wh. powd., s. in bz., ROH, 200/10^{-2} (subl.), 200(dec.), α= 4, paramagn.	IR, ^1H, magn. prop., electr. sp., TGA	121, 251, 1122, 1246
$Gd(OBu^n)_3$, $Gd(OBu^s)_3$, «Gd(OBu $Gd(OC_5H_{11}{}^n)_3$, $Gd(OC_5H_{11}{}^i)_3$, «$Gd(OC_5H_{11}{}^t)_3$»	6	wh. sld., α=4.3-3	IR, ebul.	121, 1122
$Gd(OPh)_3$	6	brn. sld., poorly s. in bz.	IR	1122

$[Gd(OC_6H_3Pr^i_2\text{-}2,6)_3THF_2]$- ***trans***, trig. bipyr.	5	yel. sld., s. in tol., THF	IR, ^1H, ^{13}C	105, 283
$Gd_6O(OC_2H_4OMe)_{16}$, 2 $[M_3]$ trian. –orthogonal planes bound by μ_4-O, CN Gd 7 and 8	1, 6	yel.cr.,s. inorg. solv., includ. petrol. eth.	IR, ESP, X-r	446
$Gd(OCH_2CHOCH_2O){\cdot}H_2O$	3	yel.sld., 160 (dec.)	IR, TGA	1248
$GdCl_2OPh{\cdot}nTHF$		-	-	338
$[Na_2Gd_4(\mu_6\text{-}O)(\mu_3\text{-}OBu^t)_8(OBu^t)_4]$ *-trans*, oct. $[M_6]$, 2 ax. $[NaO(\mu_3\text{-}OR)_4]$ -tetrag. pyr., 2 eq. Gd - oct.		-	X-r	1441
Tb				
$Tb(OEt)_3$	5	wh. sld.	-	1246
«$Tb(OPr^i)_3$»	1	wh. sld., 190/0,1(subl.), 200(dec.), paramagn.	IR, ^1H, magn.prop., electr .sp., TGA	251, 1246
$[Tb(OCPr^i_3)_3]_2$,		$200/10^{-3}$ (subl.)	-	732
$[(Tb_{0.9}Eu_{0.1})_4TiO(OPr^i)_{14}]$, $[M_5(\mu_5\text{-}O)]$, trig. bipyr., $[TiO_{1/5}O_{2/2}O_2]$ - eq., oct. $[LnO_{1/5}O_{1/3}O_{3/2}O]$- eq. and ax.		pale pink cr.	IR, X-r	1179
Dy				
$Dy(OMe)_3\downarrow$, $Dy(OEt)_3\downarrow$, $Dy(OPr^n)_3$	5	yel. sld.	-	1246
«$Dy(OPr^i)_3$»	1, 5	brigt-pink. sld., 190/0.17 (subl.), 250 (dec.), paramagn.	IR, ^1H, electr..sp, magn. prop., TGA	251, 1084, 1246

«Dy(OBu^t)$_3$», Dy(OC$_6$H$_{13}$^{n})$_3$	5	-	-	1246
Dy(OCHBu$^t_2$)$_3$ **[Dy(OCHBu$^t_2$)$_3$(MeCN)$_2$]**, trig. bipyr.	4	210(m.), 230/10^{-3} (subl.) cr., subl./vac.	IR, ^{1}H, ^{13}C, m-s, TGA ,X-r	735 737
[Dy(OCPr^{i}Bu$^t_2$)$_3$], trig. pyr.	4	cr., subl., α=1	m-s, X-r	737
Dy(OCBu$^t_3$)$_3$	4	wh. sld.,210(m.), 230/10^{-3} (subl.), s. in hex.	IR, m-s	735
Dy(OC$_6$H$_2$Me-4-Bu$^t_2$-2,6)$_3$, struct. analog of Sc-complex, ·THF	4, 5	cr., 214 (m.), 250/10^{-3}(subl.), α=1	^{1}H,^{13}C, m-s, cryosc., X-r	758
Dy(OCH$_2$CHOCH$_2$O)·H$_2$O	3	160 (dec.)	IR, TGA	1248
Ho				
«Ho(OMe)$_3$»↓, «Ho(OEt)$_3$»↓	5, 6	light-yel. slds.	-	1106, 1246
«Ho(OPr^i)$_3$»	1	pink powd., 195/0,18 (subl.), 250 (dec.), paramagn., α=4	IR, ^{1}H, electr. sp, magn. prop., TGA	251, 1106, 1246
Ho(OCBu$^t_3$)$_3$	4	light yel. oil, 200 (dec.)	IR, ^{1}H, ^{13}C, m-s, TGA	735
Ho(OC$_6$H$_2$Me-4-Bu$^t_2$-2,6)$_3$, struct. analog of Sc-complex, · THF	4, 5	yel. cr.,198 (m.), 250/10^{-3} (subl.), α=1	^{1}H,^{13}C, α, m-s , cryos., X-r	758
Ho(OCH$_2$CHOCH$_2$O), H$_2$O	3	160 (dec.)	IR, TGA	1248
Er				
«Er(OMe)$_3$»↓, «Er(OEt)$_3$»↓	5, 6	-	IR	1122, 1246

«$Er(OPr^n)_3$»	6	-	-	121
$Er(OPr^i)_3 \cdot x\ ^iPrOH$ $\downarrow H_2O$ **$Er_5O(OPr^i)_{13}$ (=«$Er(OPr^i)_3$»)** struct. analog of $Y_5O(OPr^i)_{13}$	1, 5 1, 5	pink powd., instab., s. in ROH - 0.8M, decreasing in time , v. low in tol., hex. pink cr., s in tol., hex. ~0.5 M, low s. in ROH, $180/10^{-2}$ (subl.), 260 (dec.), α=3.8, paramagn.	IR, electr. sp., TGA IR, electr. sp., TGA, ebul., m-s, X-r	1734 121, 251, 1122, 1246, 1734
$Er(OBu^n)_3$, $Er(OBu^s)_3$, «$Er(OBu^t)_3$» , $Er(OC_5H_{11}{}^n)_3$, «$Er(OC_5H_{11}{}^i)_3$», $Er(OC_5H_{11}{}^t)_3$	6	pink sld., α=4-3	IR, ebul.	1122
$Er(OPh)_3$	6	brn. sld., poorly s.in C_6H_{12}	IR	1122
$[Er(OC_6H_3Pr^i{}_2\text{-}2,6)_3]_2$ **$[Er(OC_6H_3Pr^i{}_2\text{-}2,6)_3\ THF_2]$-*trans*,** trig. bipyr.	4	pink cr., s. in tol., THF, α=2	IR, ^1H, X-r	105 283
$[Er(OC_6H_3Ph_2\text{-}2,6)_3]$	4, 7	pink cr., s. THF	IR, ^{13}C, m-s, electr. sp.,X-r	466
$Er(OC_6H_2Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6)_3$, struct. analog of Sc-complex, **$\cdot$THF**	4, 5	cr., 180 (m.), $250/10^{-3}$ (subl.), α=1	^1H, ^{13}C, m-s, cryos., X-r	758
$Er(OCH_2CHOCH_2O) \cdot H_2O$	3	cr., 160 (dec.)	IR, TGA	1248
$[NaEr(OC_6H_3Ph_2\text{-}2.6)_4]$ **$M[Er(OC_6H_3Ph_2\text{-}2,6)_4]$,** M= $[NaDme_3]$, $[NaDig_2]$, struct. analogs of Nd-complex		pink cr., s. in C_5H_{12}, tol., THF	IR, electr. sp., X-r	460

$[KEr(OC_6H_3Pr^i_2\text{-}2.6)_4]_\infty$, in a layer alternating $[Er(OR)_4]$ tetrah. and 12-vertex polyhedron $[K(\eta^6)(\eta^3)(\eta^2)O]$		pink cr., s. in tol.	IR, ^1H	381
$[LiErCl_3(OC_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)THF_2]$		pink cr.	IR, ^1H, ^{13}C	992
$[ErAl_3(OPr^i)_{12}]$; $[Er_2Al_2(OPr^i)_{12}(^iPrOH)_2]$ [1744, 962]; **$[Er_2Ti_4O_2(OEt)_{18}(EtOH)_2]$** [1735]				
Tm				
$Tm(OEt)_3$↓	5	-	-	1246
«$Tm(OPr^i)_3$»	1	grn. sld.,185/0.06 (subl.), 250 (dec.), paramagn.	IR, ^1H, electr. sp, magn. prop., TGA	251, 1246
$[Tm_2(OCBu^t_3)_6[\mu\text{-}CH_2(SiNH_2Me_2)_2]]$ 2 $[TmO_3N]$ tetrah., bound via [N~N]	-	-	X-r	736
Yb(II)				
$Yb(OEt)_2$↓	5	-	-	1194
$Yb(OBu^t)_2$	4	-	-	1328
$[Yb(\mu\text{-}OCBu^t_3)(OCBu^t_3)]_2$ 2 trian. sharing $(\mu\text{-}OR)_2$, **$[Yb(OCBu^t_3)_2THF_2]$**, tetrah. **$[Yb(OCBu^t_3)(OC_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)]$, ·2THF,·nPy**	4	red cr. grn. cr. red cr.	^1H, ^{13}C, ^{171}Yb, electr. sp., X-r	1668
$[Yb(OC_6H_3Bu^t_2\text{-}2,6)_2THF_3]$	4, 5	yel.cr.,112(m.),s.in hex.	IR, electr. sp.	1668, 463

$[Yb(OC_6H_3Ph_2\text{-}2,6)_2THF_3]$, trig. bipyr., 2 OR-ax. ***trans*-$[Yb(OC_6H_3Ph_2\text{-}2,6)_2(\eta^2\text{-}Dme)_2]$**, oct.	7	red cr.	IR,electr.sp., m-s, X-r	461
$[Yb(OC_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)_2]_2$ 2 trian. sharing $(\mu\text{-}OR)_2$, **nL**, L=Py, Dmpe	4, 5	red cr.,	^1H, ^{13}C, ^{171}Yb, X-r	465, 459, 1668
$[Yb(OAr)_2L_2]$, L=Et_2O, THF, tetrah.	4	or.-red cr.		
$[Yb(OAr)_2THF_3]$ tetragon. pyr.(!), THF-ax., Yb...Me 3.42	7	yel. cr.	IR, electr. sp.,	463
$[Yb(OAr)_2Hmpa_2]$, tetrah.	1	-		1796
$[Yb(OC_6H_2Bu^t_3\text{-}2,4,6)_2THF_3]$, dist.trig.bipyr. or tetragon. pyr., **THF** **$[Yb(OC_6H_2Bu^t_3\text{-}2,4,6)_2THF_2]$**	4	yel. cr., 110(m.)	^1H, ^{13}C, X-r	463, 459, 465, 1668
$[Yb(OSiMe_2Bu^t)_2(\eta^2\text{-}Dme)]_2$ two 5-vertex polyhedra sharing $(\mu\text{-}OR)_2$	1	diamagn.	^{13}C, ^{29}Si, ^{171}Yb, magn. prop., X-r	505
$\{[Yb[OC(CH_2OPr^i)_2Bu^t]_2\}_2$	4	cr.,115/10^{-3} (subl.)	-	732
$YbI(OC_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)$ THF_x	4	yel.-or. cr.	^1H, ^{13}C, ^{171}Yb	1668
$YbAl_3(OPr^i)_{11}$ [514]				
Yb(III)				
$Yb(OMe)_3$ ↓	5, 6	wt. sld.	-	121, 1001, 1246
$Yb(OEt)_3$↓	5, 6	-	-	" 1597
$Yb(OPr^n)_3$	5	-	-	121, 1246

$Yb_5O(OPr^i)_{13}$ (=«$Yb(OPr^i)_3$») struct. analog of $Y_5O(OPr^i)_{13}$	1, 5	s. bz., 195/0.2 (subl.), 250 (dec.), paramagn.	IR, ^1H, m-s, magn. prop., TGA, X-r	121, 208, 251, 1001, 1084, 1246, 1597
$Yb(OBu^n)_3$, $Yb(OBu^s)_3$, «$Yb(OBu^t)_3$», $Yb(OC_5H_{11}{}^i)_3$, $Yb(OC_5H_{11}{}^t)_3$	6	-	-	121
$Yb(OC_6H_{13}{}^n)_3$, $Yb(OC_8H_{17})_3$	5	-	-	1246
$[Yb(OC_6H_3Pr^i{}_2\text{-}2,6)_3THF_2]_2$	5	yel.. sld., s. in tol., THF	IR, ^1H	105
$[Yb(OC_6H_3Ph_2\text{-}2,6)_3]$, trig. pyr. **$[Yb(OC_6H_3Ph_2\text{-}2,6)_3THF_2]\cdot 2THF$-*trans*,** trig. bipyr. **$[Yb(OC_6H_3Ph_2\text{-}2,6)_3(\eta^2\text{-}Dme)]\cdot 0,5Dme$** tetragon. pyr. (intramol. M-Ar contact)	7, 4	or. cr., $250/10^4$ (subl.), s. in THF	IR, electr. sp., m-s	461, 462, 464, 466
$Yb(OC_6H_2Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6)_3$, struct. analog of Sc-complex , **$\cdot THF$, $\cdot POPh_3$**	4, 5	215(m.), $250/10^{-3}$ (subl.), α=1	^1H, ^{13}C, ^{171}Yb m-s, cryosc., X-r	758
$[Yb(OC_6H_2Bu^t{}_3\text{-}2,4,6)_3THF]$, tetrah. **$[Yb(OC_6H_2Bu^t{}_3\text{-}2,4,6)_2(OH)THF]_2\cdot 1.74$ TH** two 5-vertex polyhedra sharing $(\mu\text{-}OH)_2$	4, 7	or.-red cr., α=1 α=1	IR, electr. sp., X-r	459
$Yb(OCH_2C_5H_4FeCp)_3$	5	s. in tol.	IR, ^1H, m-s,	665
$Yb(OCH_2CHOCH_2O)$, $\cdot H_2O$	3	160-290 (dec.)	IR, TGA	1248
$[YbCl_2(OC_6H_2Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6)THF_3]$, oct.		yel. cr., s. in THF	IR, X-r	1788
$LiYbCl(OC_6H_2Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6)_3$		maroon	^1H, ^{13}C	758

$[NaYb(C_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)_4THF_2]$ = 2 tetrah. with a common $(\mu\text{-OR})_2$ edge		-	-	758
$Li_3Yb[(C_{10}H_6O)_2]_3 \cdot 6\ THF$, $Ar(OH)_2$= 1,1'-binaphtol, isostr. to its Y-analog		colrl. cr., s. inTHF-eth.	X-r	73
Lu				
$Lu(OMe)_3\downarrow$, $Lu(OEt)_3\downarrow$	5	colrl. sld.	-	626, 1246
«$Lu(OPr^i)_3$»	1	198/0,1; diamagn.	IR, ^1H, electr.sp.	251, 1246
$[Lu(OC_6H_3Pr^i_2\text{-}2,6)_3THF_2]$-*trans*, trig. bipyr.	4	grn. cr., s. in bz.,THF	IR, ^1H, ebul., X-r	105, 283
$Lu(OC_6H_3Ph_2\text{-}2,6)_3$	4, 7	colrl. sld., s. in THF	IR, electr. sp.	466
$[Lu(OCR_2CH_2OMe)_3]_2$, R=Me, Et, Lu - oct. and 7-vertex polyhedron sharing a $(\mu\text{-OR})_3$ face	4	cr., $100/10^{-3}$ (subl.), α=2	IR, ^1H, ^{13}C, m-s, X-r	54
$[Lu_4O(OH)(OCMe_2CH_2OMe)_9]$, $[Lu_4(\mu_4\text{-}O)]$ tetrah. of 2 oct. and 2 7-vertex polyhedra	I+H$_2$O	cr., $220/10^{-3}$ (subl.), α=3	IR, ^1H, ^{13}C, m-s, X-r	54
$Lu(OCH_2CHOCH_2O)$, $\cdot H_2O$	3	powd.,160 (dec.)	IR, TGA	1248
$[KLu(OC_6H_3Pr^i_2\text{-}2.6)_4]$		sld., s. in tol.	IR, ^1H	381

$Ln[Zr_2(OPr^i)_9]Cl_2$, Ln=Y-Lu; **$Ln[Al(OPr^i)_4]_3$**, Ln=Sc- Lu [1118, 1607, 1232]; **$Ln[Ga(OPr^i)_9]_3$**, Ln= La- Yb [1119, 1232]; **$[LnCu^I_2(OBu^t)_5]_2$**, Ln=La,Pr,Nd, Sm,Lu [1213] analogous to those of hydroxides and alkoxides of Sn and Pb (II) but is so far unknown for the derivatives of quadrivalent metals. The core of the second one is an oxo-centered metal octahedron analogous to that in $[Na_2Gd_4(\mu_6\text{-}O)(\mu_3\text{-}OBu^t)_8(OBu^t)_4]$ [1441]. Hydrolysis of $Ln(OR)_3$ is discussed in Chapter 9.

The t-butoxides of Pr, Sm, and Yb have found an interesting application in the preparation of metalorganic compounds containing the chains of different atoms like $Ln\{Cu[Ge(C_6F_5)_3]_2\}_3$ [163]. Very good prospects were observed for the "$Ln(OPr^i)_3$" in catalysis. In particular, their activity in the Meerwein-Ponndorf-Oppenauer-Verlay reaction is much higher than that of $Al(OPr^i)_3$ [1230, 1001, 1194]. The majority of publications are devoted to the stereoregular synthesis of polymers with Ziegler catalysts containing neodymium alkoxides (see, for example, [339, 1772]). The catalytical systems for the gas-phase preparation of methanol based on Na and Sm alkoxides and CuCl have been patented [541]. Concerning the application of yttrium alkoxides in the synthesis of HTSC ceramics, see [755, 958, 1614, 1620, 1633].

12.8. Germanium alkoxides

Tabern [1553] and Schwarz [1443] were the first to describe single $Ge(OR)_4$ in the 1920s and 1930s. The systematic study of the homologous series was carried out from 1953 to 1956 by Bradley [222] and Jonson [857]. Much less stable $Ge(OEt)_2$ was obtained only in 1979 by Silverman and Zeldin [1488]. Fundamental synthetic and structural studies of homo- and heterometallic t-butoxides of germanium and its analogs were carried out from 1980 to 1990 by Veith *et al.* [1681, 1683, 1684].

12.8.1. Synthesis

The alkoxides of both oxidation states were obtained by metathesis of germanium halides (chlorides and iodides) with alkali alkoxides [1488, 1142, 857, 1535]. The yields can be increased by application of $GeCl_4$ solvates with Py or NH_3 or amines [3, 222] (method 5) and also by alcohol interchange of ethoxides (method 6) or alcoholysis of $Ge[Si(NR_3)_2]_2$ [568, 1543] (method 4). The application of alkali alkoxides in the preparation of $Ge(OR)_4$ is possible in contrast to that of analogous derivatives of Sn(IV) and Zr due presumably to the much lower stability of corresponding alkoxogermanates the intermediate products of the corresponding reactions because of stability — of the tetrahedral coordination for Ge. The direct electrochemical preparation of $Ge(OEt)_4$

by anodic oxidation of metal in the alcohol in presence of NH_4Cl as electrolyte has been patented [1599] (method 2).

12.8.2. Properties

$Ge(OR)_2$ described in the literature are yellow crystalline compounds. They are strong reductive agents and require stabilization by highly ramified ligands (R^t, 2,6-substituted phenols). $Ge(OAr)_2$ are soluble in hydrocarbons in contrast to the polymeric ethoxide. It is interesting to note that $Ge(OEt)_2 \cdot 2EtOH$ is not only soluble in ethanol and hydrocarbons but also volatile [1488]. The known $Ge(OR)_2$ molecules are monomeric (the only exclusion is the dimeric $Ge(OBu^t)2)$. The presence of the localized nonshared electron pair at the Ge atom its coordination is usually characterized by incomplete polyhedra — **ψ-triangle** (angular coordination), **ψ-tetrahedron,** or **ψ-trigonal** pyramid.

The properties of $Ge(OR)_4$ allow them to be considered more likely to be the esters of an inorganic acid than metal alkoxides: these are colorless volatile liquids, containing monomeric tetrahedral molecules. The solid crystalline form is known only for $R = Bu^t$, $OC_6H_{11}{}^c$, and also 2,6-substituted phenoxides. All the members of the $Ge(OR)_4$ homologous series are characterized by thoroughly determined physical characteristics — density, refraction index, surface tension, viscosity (and calculated parachor values), dipole moments in different solvents [222, 857, 1537] (Table 12.9). The results of the investigation of vapor pressure, density, viscosity polytherms, and so on. permitted rectification for the preparation of samples of high purity for sol-gel and MOCVD applications [682, 884].

It is necessary to note the application of the ethoxide in the synthesis of GeH_4 (on reaction with $NaAlH_4$) [1804] and that of glycols and derivatives of diatomic phenols for the preparation of cyclic ethers [51, 796, 1123, 1183, 1404, 1486] and germocins [572]. Phenoxides are proposed as catalysts of terephtalate polycondensation [827]. The application of $Ge(OEt)_4$ in the sol-gel discussed in Chapter9.

Table 12.9. Germanium alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
Ge(II)				
$[Ge(OEt)_2]_\infty\downarrow$ $\cdot$n EtOH	5	polymer, s. in PhCl, cr., s. in hc., vol.	IR, ^1H, m-s, TGA	1488
$Ge(OPr^n)_2$	6	-	-	1488
$[Ge(OBu^t)_2]$, 2 trian. sharing a $(\mu\text{-}OR)_2$ edge	4, 5	cr., 52 (m.), s. in ArH, $45/10^{-3}$ (subl.), α=2, t→α-Ge +ROH+..	^1H, m-s, TGA, X-r	679, 1684, 1682
$Ge(OCBu^t_3)_2$, mol. - ψ-trian..	4	-	X-r	568
$Ge(OC_6H_3Pr^i_2\text{-}2,6)_2$	5	yel. cr., 160 (m), s. in hex., α=1	^1H, m-s	1142
$Ge(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2$ angular mol. (ψ-trian..)	4, 5	yel. cr., 189 (m), s. in ArH, THF, diamagn., α=1	^1H, m-s, . X-r magn. prop	311
$Ge(OC_6H_2Bu^t_3\text{-}2,4,6)_2$	5	yel. cr., 167 or 205 (m), $160/10^{-3}$ (subl.), s. in hex., α=1	^1H, m-s	1142
$Ge[OCH(CF_3)_2]_2\cdot L$, L=Py, $PhNH_2$, ψ-trig. pyr.	4	-	IR, ^1H, ^{13}C, X-r	1543
$Ge(OC_6F_5)_2$	5	α=1	^1H, m-s	1142
$Ge[OC_6H_2(CF_3)_3\text{-}2,4,6]_2THF$	4	108 (dec.), s. in hex, α=1	IR, ^1H, ^{19}F, m-s	1361

$Ge_6O_4(OCMe_2CH_2OMe)_4$ 8 faces of $[M_6]$ oct. centered alternatively by μ_3-O and μ_3-OR, $[:GeO_4]$-ψ-trig. bipyr.	-	-	X-r	732
$[GeCl(OBu^t)]_2$ 2 trian. (ψ-tetrah.) sharing a $(\mu\text{-OR})_2$ edge		colrl. cr., 104 (m., dec), 35/ 10^{-4} (subl.), s. in ArH, α=2	cryosc., m-s, X-r	1682
$[R_4N][Ge(OR)_3]\cdot nROH$, R=Me, Et, Pr^i		-	IR, ^1H	616
$[NaGe(OBu^t)_3]_2$		cr., s. in ArH, 305 (m., dec)	^1H	1681,1683
$M^IGe(OBu^t)_3$, M=In, Tl, ψ-tetrah. $[:GeO_3]$ and $[:MO_3]$ sharing a $(\mu\text{-OR})_3$ face		cr., 52 and 87 (m.)	^1H, X-r	1695
$M^{II}Ge_2(OBu^t)_6$= $[Ge(\mu\text{-OR})_3M^{II}(\mu\text{-OR})_3Ge]$, M^{II}=Mg,Ca,Sr,Ba,Zn,Cd,Eu,Pb, Cr, Mn, mol. -linear chain, central oct. $[MO_6]$ and sharing common $(\mu\text{-OR})_3$ face with 2 ψ-tetrah. $[:GeO_3]$		cr., s. in hc., vol., α=1, m: 208 - **Mg**,; 320 (dec.)- **Ca**; 330 –**Sr**; 305 –**Ba;** 234 (dec.)-**Zn**; 214 – **Cd**; 325 –**Eu**; 154 –**Pb;** 233 (dec., grn., μ_{eff}=5.02,-**Cr**; 259 (colrl., μ_{eff} =5.98- **Mn**; t→ α-Ge+ CH_4+ROH+CH_2CMe_2	IR, ^1H, ^{13}C , ^{113}Cd , m-s, cryos., thermolys, X-r	1681, 1683, 1684
$M^{II}{}_2Ge_2(OBu^t)_8$= $[M^{II}{}_2Ge_2(\mu\text{-OBu}^t)_6(OBu^t)_2]$, M^{II}=Co, Ni, mol.- linear chain with 2 Co tetrah. in the central and 2 Ge ψ-tetrah. in the peripheral parts		vlt. cr., s. in ArH, hex.; (m., dec.), μ_{eff},: 285, 8.26- **Co** ;248; 4.51- **Ni**	magn. prop., X-r	1683
$GePb_2(OBu^t)_6$ [1681]				

Ge(IV)				
$Ge(OMe)_4$	5, 6	colrl. liq., -18(m.),75/30(b), d^{20}_4 1.3135, n_D^{20}1.4021, μ=2.00 (hex.)	IR, p, η-polytherms	222, 857, 1443, 1537
$Ge(OEt)_4$	2, 5	colrl. liq., -72(m.), 75/10 (b), d^{20}_4 1.1395, n_D^{20}1.4073, η_{25} 8.56, μ=1.94 (hex.)	IR, ^{73}Ge, p, η-polytherms	3, 222, 682, 857, 884, 1183, 1481, 1455, 1537, 1553, 1599
$Ge(OPr^n)_4$	5	colrl. liq., -170 (m.), 111/10 (b.), d^{20}_4 1.0664, n_D^{20}1.4200, μ=1.74	IR, d, p, η-polytherms	3, 222, 682, 857, 884, 1302, 1500, 1455, 1537
$Ge(OPr^i)_4$ $\downarrow H_2O$ **$[Ge(OPr^i)_3]_2O$**	6 -	colrl. liq., 81/7(b), d^{20}_4 1.0271, n_D^{20}1.4050; μ= 1.43 (hex.) colrl. liq., 80/0.1(b), α=1	d, p, η-polytherms cryosc.	222, 682, 884, 1302, 1443, 1537 1443
$Ge(OBu^n)_4$	5, 6	colrl. liq., 80/0.2(b), d^{20}_4 1.0216, n_D^{20}1.4270, η_{25} 20.47; μ=1.54	IR, d, p, η-polytherms	3, 222, 682, 857, 1302, 1537
$Ge(OBu^i)_4$	6	colrl. liq., 110/0.1 (b), d^{20}_4 1.0039, n_D^{20}1.4210; η_{25} 25.32; μ=1.47	IR, p, η-polytherms	222, 1537
$Ge(OBu^s)_4$	6	colrl. liq., 136/54 (b), d^{25} 1.0164, n_D^{25}1.4291, η_{25} 25.23	p, η-polytherms	222, 1302
$[Ge(OBu^t)_4]$, **$Ge(OEt)(OBu^t)_3$**	5, 6	colrl. cr., 44(m.), 224 /atm (b.), d^{25} 1.0573	" parachor	222, 1535

$Ge(OC_5H_{11}{}^n)_4$	5, 6	colrl. liq., 120/0.03 , 145/0.3(b.), $d^{20}{}_4$ 0.9936; $n_D{}^{20}$1.4340; μ=1.55; α=1	IR	222, 857, 1537
$Ge(OC_5H_{11}{}^t)_4$	6	d^{25} 1.0425	-	222
$Ge(OC_6H_{13}{}^n)_4$	5	colrl. liq., 150/0.04 (b.), d^{25} 0.9672 , $n_D{}^{25}$ 1.4372, μ=1.37	IR	857, 1537
$Ge(OC_6H_{11}{}^c)_4$	5	colrl. cr., 67 (m.); 165/0.01 (b); μ=1.25	IR	857, 1537
$Ge(OC_7H_{15}{}^n)_4$	5	colrl. liq., 208/0.4 (b), $d^{20}{}_4$ 0.9596, $n_D{}^{20}$ 1.4430; μ=1.34 (hex.)	IR	1537
$Ge(OC_8H_{17}{}^n)_4$	5	colrl. liq., 187/0.4 (b), $d^{20}{}_4$ 0.9596, $n_D{}^{20}$ 1.4430; μ=1.13 (hex.)	IR	1537
$Ge(OPh)_4$	5	colrl. visc. oil, 210/0.1 (b); $d^{20}{}_4$ 1.3018,$n_D{}^{20}$1.5900; μ=1.30 (hex.)	IR	1123, 1443, 1537
$Ge(OC_6H_4Bu^t-2)_4$	5	cr., 240(m.),235/10^{-3}(subl.), s in hex.	^1H, m-s	1142
$Ge(OC_6H_3Me_2-2,6)_4$	5	cr.,144(m.), 180/10^{-3}(subl.), s.in hex.	^1H, m-s	1142
$Ge(OR)_4$, R=$CMe_2CH{=}CH_2$, $CH_2CH{=}CHMe$, $CHMeCH_2CH{=}CH_2$,	6	colrl. liq., 105/1-56/0.1(b.), $n_D{}^{30}$ 1.436-1.491, α=1	IR, ^1H, ebul.	655
$Ge(OC_2H_4F)_4$	5	colrl. liq., 157/15 (b.)	-	1183
$Ge[OCH(CF_3)_2]_4$	5	wh. sld., 35(m.), 145/vac. (subl.), s. in tol., ROH, α=1 (m-s)	IR,^1H, ^{19}F, m-s, TGA	880, 1085, 1387
$Ge(OC_2H_4Cl)_4$	4, 5	colrl. liq., 183/0.01 (b.), $d^{20}{}_4$ 1.5115, $n_D{}^{20}$ 1.4815	-	1183, 1815

$Ge(OSiPh_3)_4$	5	wh. sld., 472 (m.,dec.), 400/10^{-4} (subl.), s.in bz., stabl. to MOH, HCl	-	690
$Ge(RO_2)_2$, R=1.3-C_3H_6, 1.3-, 2.3 or 1.4-C_4H_8, 1.3-$C_3H_4Me_2$-2.2, 2.3-$C_4H_6Me_2$-2.3, 1.6-$C_6H_{12}{}^n$	6	**1.3, 2.2, 2.3**- visc. liq., 90-130/0.1 (b), s. in bz., **1.4, 1.6**- polymers	-	1123
$Ge[\eta^2-(C_6H_{10}{}^c)_2O_2]_2$	5	colrl. cr., 279 (m)	-	1183
$[Ge(3.5-Bu^t{}_2C_6H_2O_2-1.2)_2]_\infty$	4	-	^1H	1404
$Ge(\eta^2-C_6H_4O_2-1.2)_2 \cdot 2L$, L=$H_2O\downarrow$, ROH (R=Me, Et, Pr^i), Hmpa	3	colrl. cr.	IR, ^1H, ^{13}C	51, 796, 1404
$Ge[\eta^2-(C_6H_4)_2-2.2-O_2]_2$	5, 6	colrl. cr., 330 (m), 270/vac. (subl.)	IR	1183, 1486
$Ge(C_6F_4O_2-1,2) \cdot 2Dmfa$	4		IR, electr. sp.	1044
$GeHal_n(OMe)_{4-n}$, Hal=F, I; n=1,2,3	colrl. liq.		IR, ^1H ^{19}F	178, 273
$GeCl_n(OMe)_{4-n}$	colrl. liq., b.p.:181(n=**1**),120 (n=**2**), 100 (n=**3**); $n_D{}^{25}$ 1.4104-1.4396		IR	1399
$GeBr_n(OMe)_{4-n}$	colrl. liq., b.p.: 153(n=**1**),160 (n=**2**), 169 (n=**3**); $n_D{}^{25}$ 1.4456-1.5551		IR	1399
$GeCl_n(OEt)_{4-n}$, n=1, 2, 3 **$GeBr_n(OEt)_{4-n}$**	colrl. liq., b.p.: 181(n=**1**),157 (n=**2**), 120 (n=**3**); $n_D{}^{25}$ 1.3991-1.4283 colrl. liq., b.p.: 186 (n=**1**),183 (n=**2**), 181 (n=**3**); $n_D{}^{25}$ 1.4371-1.5524		IR IR	1123,1302 1399
$GeCl_n(OPr^n)_{4-n}$, n=1, 2, 3	colrl. liq., b.p.: 75/6 (n=**1**), 113/92 (n=**2**), 97/atm (n=**3**); $n_D{}^{25}$ 1.4258-1.4480		-	1302

$GeCl_n(OPr^i)_{4-n}$, n=1, 2, 3	colrl. liq., b.p.: 60/1 (n=**1**), 60/82 (n=**2**), 154 (n=**3**)	-	1123, 1302
$GeCl_n(OBu^n)_{4-n}$, n=1, 2, 3	colrl. liq., b.p.:102/6(n=**1**), 85/5 (n=**2**), 70/20 (n=**3**)	-	1123, 1302
$GeCl_n(OBu^t)_{4-n}$, n=1, 2, 3	colrl. liq., b.p.: 73/0.8 (n=**1**), 59/0.5 (n=**2**), 38/4 (n=**3**), n_D^{25} 1.4227-1.4313;	-	1302
$GeCl_2(OC_6H_{13}{}^n)_2$	colrl. liq., 120/0.5 (b), n_D^{25} 1.4414	-	1302
$GeCl_n(OC_6H_3Ph_2\text{-}2.6)_{4-n}$, n=1 (tetrah.), 2	colrl. cr., s. in tol.	^1H, X-r	1505
$GeHal_3(OC_6H_2Bu^t{}_3\text{-}2.4.6)$, Hal=Cl,Br	colrl.cr., 24 (m.), s. in hex., α=1; t/vac.→ArOH	^1H, m-s	1142
$Na[Ge(OH)(RO_2)_2]$, R=1.2-C_3H_6, 1.2-C_4H_8, 1.2-C_6H_{12}	colrl. cr., stab. to hydrolysis	IR, ^1H, ^{13}C	796
$[Et_4N]^+{}_2[Ge(C_6H_4O_2\text{-}1,2)_3]^-$ **$[Et_4N]^+[Ge(\eta^2\text{-}C_6H_4O_2\text{-}1,2)_2\,Hal]^-$**, Hal=F,Cl,Br, anion- tetragon. pyr.,$Cl_{ax.}$ **$2H_2O$**, polymer -chain of dimeric cycles $[Ge_2O_2]$, bound via $[H_2O...H]$ **$[Et_3NH][Ge(3.5\text{-}Bu^t{}_2C_6H_2O_2\text{-}1.2)_2X]$**, X=Cl, OH, anion - tetragon. pyr.	grey-grn. powd., 250(dec.) grey powd., 203-227(m.), s. in MeCN, stab. to hydrolysis F>Cl>Br -	^1H ^1H, X-r ^1H, X-r	1404
$Na[Ge(OMe)[(C_6H_{10}{}^c)_2O_2\text{-}\eta^2]_2]$	-	-	1183

12.9. Tin alkoxides

The obtaining of tin(IV) alkoxides was first reported in a well-known publication by Meerwein and Bersin [1101] devoted to bimetallic alkoxides. At the end of the 1950s Bradley [222] and Make [1049] practically simultaneously devoted the synthetic approaches to and described the properties of nearly all major representatives of the $Sn(OR)_4$ homologous series. During the last 10 to 20 years interest in these compounds was renewed due to the prospect of their application in the synthesis of optically transparent and conducting films based on SnO_2, and also of related ceramic materials. The alkoxides of Sn(IV) were considered in detail in a review by Hampden-Smith *et al.* [702].

The synthesis of the alkoxides of tin(II) was first reported at the beginning of the 1960s when the preparation of the cyclic derivatives of diatomic phenols (Zuckermann *et al.*) [1814] and also that of their precursor methoxide was described. Recently it has also been reported that the synthesis and structural characterization of $Sn(OBu^t)_2$, derivatives of sterically hindered phenols, and also of the bimetallic complexes (mainly with alkaline and alkaline earth metals) (Veith) [1682–1685, 1688, 1692–1695].

12.9.1. Synthesis

At the primary step, the preparation of $Sn(OR)_4$ was seriously hindered by taking into account the formation of rather stable bimetallic $NaSn_2(OEt)_9$ complexes (compare Section 12.12) on the reaction of $SnCl_4$ with NaOR [1101, 202]. Therefore, on continuation the sodium alkoxides were replaced with ammoniac [1049, 1048, 831], Et_2NH [702] (method 5)* and also $ROSnEt_3$ [1143]. The reaction of $SnCl_4$ with LiOAr was applied for the preparation of phenoxides [1506]. Another very widespread approach to $Sn(OR)_4$ is based on the alcohol interchange and transesterification reactions [1125] (method 6). Certain homologs were even prepared by alcoholysis of $SnPh_4$ [44] or $Sn(NMe_2)_4$ [702, 1506].

All the above mentioned approaches have been used in preparation of the derivatives of Sn(II) (the most convenient for the preparation of the methoxide being the reaction of $SnCl_2$ with MeOH and Py or Et_3N [766]) and the universal approach being provided by alcoholysis of $Sn[N(SiMe_3)_2]_2$ [311, 568] or

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* At the same time Reuter [1350] succeeded in preparing of $[Sn(OPr^i)_4 \cdot {}^iPrOH]_2$ on reaction of $NaOPr^i$ with $SnCl_4$.

$SnCp_2$ [710, 766, 554]. The electrochemical synthesis of $Sn(OMe)_2$has been patented in Japan [828].

12.9.2. Properties

The trend of $Sn(OR)_2$ to oxidation by oxygen is much smaller than for the analogous derivatives of germanium, and they are therefore much better studied. Both methoxide and ethoxide are polymeric and insoluble in organic solvents. The further homologs are soluble in alcohols and hydrocarbons and evaporated at comparably low temperatures forming dimeric molecules in the gas phase (2 triangles sharing a common edge as was established by gas electronography for $Sn(OBu^t)_2$ [568]). In the case of sterically hindered radicals like CBu^t_3 [568], $C_6H_3Bu^t_2$-2,6, are formed, $C_6H_2Bu^t_2$-2,6-Me-4 [107, 311], monomeric angular molecules (ψ-triangles) are formed, and for less sterically hindered ones in presence of additional ligands, ψ-trigonal pyramids like $\{Sn[OCH(CF_3)_2]_2(Me_2NH)\}$ or even ψ-trigonal bipyramids like $[Sn(OC_6H_3Pr^i_2\text{-}2,6)_2Tmeda]$ are formed [1543, 1534].

Regarding the molecular complexity for the first members of the $Sn(OAlk)_4$ series (including $Sn(OBu^n)_4$), for solid amorphous substances it is equal to 3 to 4 and decreases to 1.5 to 1.1 for liquid amyloxides — heptyloxides. This picture is quite analogous to that observed for the "$Zr(OAlk)_4$" homologous series (see Section 12.12). Taking into account the presence of the fragmentation patterns of the oxoalkoxides, $M_3O(OR)_{10}$ and $M_4O(OR)_{14}$ in their mass-spectra [1612], it can be supposed that the samples of $Sn(OAlk)_4$ in this series do also have a uniform molecular composition (their formula is given in citation signs in Table 12.10). The triangular oxoalkoxide molecules — $[Sn_3(\mu_3\text{-}O)(OBu^i)_{10}(^iBuOH)_2]$ (three edge-sharing octahedra), — were discovered in the structure of the hydrolysis product of the *i*-butoxide [1350].

The isopropoxide and isobutoxide form crystalline solvates with alcohols having 1:1 composition. These are along with $Sn(OR^t)_4$ ($R = Bu^t\text{-}C_7H_{15}$) really individual compounds as it has been proved by the X-ray single crystal data. The molecules of $[Sn(OR)_4{\bullet}ROH]_2$, as well as the corresponding $[Zr(OR)_4{\bullet}ROH]_2$, are built up of two edge-sharing octahedra supported by two intramolecular hydrogen bonds [324, 702, 1350] (see Fig. 4.1. *b*). An analogous structure has also been observed for the amine adduct $[Sn(OCH_2Ph)_4(Me_2NH)]_2$ [1506]. The molecule of $[Sn(OSiPh_3)_4Py_2]$, containing rather bulky radicals is monomeric [297] (it should be taken into account also that two positions in the octahedron are occupied by a comparably strong but rather efficient donor ligand — Py). The crystalline $Sn(OBu^t)_4$ consists of tetrahedral molecules [702], to be found evidently also in the monomeric liquid $Sn(OR^t)_4$. In solution in alcohol the $Sn(OBu^t)_4$ forms, however, a 1:1 solvate, and the CN of the metal atom increases to 5 [297]. In the molecules of the majority of $Sn(OAr)_4$ there occurs the formation of a rather strong Sn-C bond with a carbon atom in the benzene ring (cyclometallation) [1506], and so on. These metalorganic derivatives are not considered in the present review.

The pyrolysis of $Sn(OR)_2$, $R = Pr^i, Bu^t$, as well as that of their Ge and Pb analogs results in the formation of metal and not of oxides, which is of primary interest for their application in the CVD technique [1563,1684]. The thermolysis of bimetallic tin (II) derivatives results in two phases containing Sn^0 and Sn^{IV}, respectively. For example, that of $[BaSn_2(OBu^t)_6]$ provides small spheres of Sn, which are then covered by a new layer forming a fractal structure (that resembles a blackberry), whose surface is covered by $BaSnO_3$ [1684].

The systematic study of bimetallic t-butoxides of tin and mono- and divalent metals carried out by Veith (see Table 12.10) established that the complexes of $M^ISn^{II}(OBu^t)_3$ composition are formed by all alkaline metals, while those of $M^ISn^{IV}(OBu^t)_5$ are formed only by K, Rb, and Cs. It has been therefore concluded that $Sn(OR)_2$ should be stronger Lewis acids than $Sn(OR)_4$ [1692]. In the molecules of its bimetallic complexes, the atoms of Sn^{II} have a **ψ-tetrahedral** coordination, all the OR-groups being bridging. The compounds of Sn^{IV} display octahedral or distorted octahedral coordination (see also Chapter 4).

Hydrolysis of tin alkoxides and its application in sol-gel technology is considered in Chapter 9. Among the application domains of tin alkoxides one can mention the organic synthesis, where they are used along with other $M(OR)_n$ for the reduction of aldehydes into primary alcohols (Meerwein-Schmidt reaction), as alkoxylating agents in synthesis of orthocarbonates $C(OR)_4$ [1383], and esters of dibasic acids [1225]. In the inorganic synthesis they are used as convenient precursors in the preparation of SnH_4 [1211], $Sn(BH_4)_2$ [35], carboxylates [835], and SnR_4 [1049]. Cyclic esters of the stannic acid (resulting from the reaction of SnO with polyatomic phenols) have been proposed as refractory materials [562]. In polymer technology, the $Sn(OR)_4$ have been used as solidifiers of epoxyresins, additives improving the structure of pores in polyester-based solid foams and improving the thermal stability of polyvinyl resins

Table 12.10. Tin alkoxides

composition. Structure	Synth. route	Properties	Investig. methods	Ref.
Sn(II)				
Sn(OMe)$_2$ ↓ H_2O (bz., t) **[$Sn_6O_4(OR)_4$]** , R=Me, Pr^i =[$Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}OR)_4$], 8 faces of the [$M_6$] oct. - centered alternatively by μ_3-O, μ_3-OR	2, 4, 5 -	amor. powd., 242 (260 ?) (m.), 180/10^{-3} , 80/10^{-4} (subl.), low s. org. solv. clrl. cr., s. in bz.	IR, ^{1}H, m-s, Mössb. IR, ^{119}Sn, X-r	35, 117, 430, 710, 766, 828, 1143 492, 710, 1401
Sn(OEt)$_2$	5, 6	powd., 200 (dec.), 80/10^{-4} (subl.), α=2 (CH_2Cl_2)	IR,^{1}H, m-s, Mössb.	430, 1175
Sn(OPr^i)$_2$	4	sld., 120/10^{-2} (subl.); s. in ROH, t→Sn+Me_2CO+ROH	m-s	1563
Sn(OBu^n)$_2$	6	powd., 171(m.), 80/ 10^{-1} (subl.), s. in org. solv., α=2	IR, ^{1}H, m-s, Mössb.	430
[Sn(OBu^t)$_2$]$_2$ 2 trian.(ψ-tetrah.) with a common (μ-OR)$_2$ edge	4	cr., vol., 73 (m.), 60/10^{-3} (subl.), α=2 (bz.), 1 (m-s); t→ +β-Sn+SnO_2 + …	^{1}H, ^{119}Sn, m-s, cryosc., X-r, gas-electronogr.	568,678, 1682, 1694, 1684

[Sn(OCBu$^t_3$)$_2$], angular mol. (ψ-trian.)	4	clrl. cr., vol./vac.	^{119}Sn, X-r,gas. electronogr	568
Sn(OAr)$_2$, Ar=C_6H_4Me-2(**a**), -3 (**b**) or –4 (**c**), C_6H_3Me$_2$-3,5 (**d**) or –2,6 (**e**)	4, 6	slds., m.: (**a**)60 (dec.), (**b**) 214 , (**c**) 161, (**d**) 231, (**e**) 116 ; α=3 (**a**)	Mössb.	554, 1713
[Sn(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Tmeda], ψ- trig. bipyr.	-	-	^{1}H, ^{119}Sn, X-r	1534
Sn(OC$_6$H$_3$Bu^t-2-Me-4)$_2$	6	sld., 169 (m.,dec.), α=1.4	-	1713
[Sn(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$], angular mol.	5	colrl. cr., s. in tol.	m-s, cryosc., X-r	107
[Sn(OC$_6$H$_2$Bu$^t_2$-2,6-Me-4)$_2$], angular mol.(ψ-tetrah.)	4, 5	yel. cr., 219 (m.), s. in ArH, THF, diamagn., α=1	^{1}H, m-s, ebul., magn. prop. , X-r	311
[Sn(OC$_6$H$_2$Bu$^t_3$-2,4,6)$_2$]	4, 5	yel. cr., 205 (m.), s. in ArH, THF, α=1	H, m-s, ebul.	311
Sn[OCH(CF$_3$)$_2$]$_2$ **·L**, L=Me$_2$NH (ψ-trig. pyr.), Py	4	cr., vol./vac.	IR,^{1}H,^{13}C ,X-r	1543
Sn[OC$_6$H$_2$(CF$_3$)$_3$-2,4,6]$_2$THF	4	cr., 74 (m.), s. in hex, α=1	IR,^{1}H,^{19}F, m-s	1361
Sn(OSiR$_3$)$_2$, R=Me, Ph	4, 5	ivory powder, s. in bz., ins. in AlkH, α=2	IR,^{1}H,^{13}C, ^{119}Sn, Mössb.	710,678, 1090, 1558
Sn(OSiMe$_2$Bu^t)$_2$	4	cr., s. in C_5H_{12}, α=2		1090
[Sn(η^2-OCMe$_2$ CH$_2$OMe)$_2$]$_2$, ψ- trig. bipyr. sharing a (μ-OR)$_2$ edge		cr., quantitatively subl.	X-r	732
Sn(OC$_6$H$_4$OMe-2)$_2$	6	sld., 134 (m.), α=2	-	1713

$(SnOC_6H_4OMe\text{-}2)_2O$	6	cr., 217 (m.)	-	554
$Sn[OCH(CCl_3)OMe]_2$	6	cr., 73 (m.)	IR, Mössb.	710
$Sn(RO_2)$ - cyclic esters, R= C_6H_4-1,2, 3-MeC_6H_3-1,2, C_6H_4-C_6H_4 –2,2', β-$C_{10}H_7$-3,2	1, 3, 4	wh. sol., dec..500°, stab. to hydrol., invol., s. in Py (t)	Mössb.	402, 554, 766, 1814
$[Sn(RO_2\text{-}1,2)]$ ∞, R= Me-3, C_6H_2-1,3 or –1,2	3	colrl. cr., s. in ArH, Py, subl. vac.	IR, ebul.	402
$[SnCl(OMe)]_2$↓		colrl. powd., α=2	m-s	1682
$[SnHal(OBu^t)]_2$, Hal=Cl, Br 2 trian. sharing a $(\mu\text{-}OR)_2$ edge, 2 Cl- anty		cr., **Br**:200 (m., dec.), α=2	^1H, ^{119}Sn, m-s, cryosc., X-r	1682, 1816
$[SnCl(OBu^t)(THF)]_\infty$, dimers of 2 ψ-5-vertex polyhedra sharing a $(\mu\text{-}OR)_2$ edge bound in chains by μ-THF		-	^1H, ^{119}Sn, X-r	
$MSn(OR)_3$, M=Na, K; R=Me,Et, Pr^n, Pr^i,Bu^n, Bu^t,$C_5H_{11}{}^i$		sld., s. in ROH, α=1	IR, ^1H	74
$MSn(OBu^t)_3$ =$[M_2Sn_2(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4]$, M=Li, Na 2 pseudocubes sharing $[M_2(\mu_3\text{-}OR)_2]$ edge, 2 tetrah. $[M(\mu_3\text{-}OR)_2(\mu\text{-}OR)_2]$, 2 ψ- tetrah. $[:Sn(\mu_3\text{-}OR)(\mu\text{-}OR)_2]$		cr., s. in bz., eth., α=2 (bz.), 1(m-s); d=1.34; **Li:** 90 (m.), 70/10^{-3} (b.); **Na:** 94 (m), 80/10^{-3} (b.)	^1H, m-s, cryos., X-r	1692

$[MSn(OBu^t)_3]$ $=[M^ISn(\mu_3\text{-}OR)_2(\mu\text{-}OR)]_\infty$, M=K, Rb, Cs, zigzag chain of trig.bipyr. $[M(\mu_3\text{-}OR)_4(\mu\text{-}OR)]$ and ψ- tetrah. $[:Sn(\mu_3\text{-}OR)_2(\mu\text{-}OR)]$	cr., low s. in bz., readily in eth.; d=1.38, 234 (m.)(**K**); d=1.48, 270 (m.) (**Rb**); d=1.63, 277(m.) (**Cs**)	^1H, X-r	1692
$[MSn(\mu\text{-}OBu^t)_3]$, M=In, Tl, ψ- tetrahs. $[:SnO_3]$ and $[:MO_3]$ sharing a $(\mu\text{-}OR)_3$ face	cr., 41, 43 (m.), $40/10^{-3}$ (subl. **Tl**), s. in hc.	^1H, ^{119}Sn, X-r	1685, 1693, 1695
$KSn[\mu\text{-}OSi(OBu^t)_3]_3$ $[K(OSi)_3(OBu^t)_3]$ –oct., ψ-tetrah. $[:SnO_3]$	cr., 89 (m., dec.) s. in C_5H_{12}	IR, ^1H, X-r	1571
$[M^{II}Sn_2(\mu\text{-}OBu^t)_6]$, M^{II}= Ca, Sr, Ba,Cd, Eu, Pb, linear chains, 2 ψ-tetrah. $[:SnO_3]$ sharing $(\mu\text{-}OR)_3$ face with central oct. $[MO_6]$	cr., s. in ArH; m.: 160 (**Ca**), 22(**Sr**), 270(**Ba**), 158 (**Cd**), 250(**Eu**), 243(**Pb**); t→β-Sn $+CH_4+$ ROH +…	IR, ^1H, ^{13}C, ^{119}Sn, ^{113}Cd, ESR, m-s, X-r	1683, 1681, 1684
$[M^{II}_2Sn_2(OBu^t)_8]$, M^{II}= Mg, Cr, Mn, Co, Ni linear chain, 2 central tetrahs. $[MO_4]$ with a common $(\mu\text{-}OR)_2$ edge, each connected via a common $(\mu\text{-}OR)_2$ edge with ψ- tetrah. $[:SnO_3]$	cr., s. in ArH, THF; (m.,dec.),, colr: 165, colrl. **(Mg)**; 210, bl.**(Cr)**; 220,pink **(Mn)**; 225, vlt., μ_{eff} =8.20 **(Co)**; 200, bl. μ_{eff} =4.4, s. in hex-tol. **(Ni)**	IR,^1H,^{13}C ,^{119}Sn, ESR, m-s, X-r	1683
$NaSn(OPh)_3{\cdot}THF$	cr., 123 (m.)	^1H	422
$[LiSn(OC_6H_3Ph_2\text{-}2,6)_3]$ trig. pyr. Li and ψ- tetrah. Sn with a common $(\mu\text{-}OR)_3$ edge, 3 bonds Li-C	-	IR, X-r	1506

$[KSn(OSiPh_3)_3Dme_2]_2$, oct. K and ψ-tetrah. Sn with a common $(\mu\text{-}OR)_3$ face **$[KSn(OSiMe_2Bu^t)_3]$**		cr., s. in THF, hex.	X-r	1090
$Cd_5CrSn(OSiMe_3)_2$, $Cd_5WSn(OSiPh_3)_2$		-	Mössb.	678
$SnAl_2(OR)_8$, $SnAl_2(OPr^i)_2(OBu^t)_6$ [1124]; **$SnGe^{II}_2(OBu^t)_6$** [1681]; **$SnZr(OR)_6$** [1565]; **$\{SnI[M_2(OPr^i)_9]\}_2$**, M=Ti, Zr [1688]				
$Sn^{II}Sn^{IV}(OEt)_6$ **$Sn^{II}Sn^{IV}(OPr^i)_6$**	4, 5	colrl. oil (cr.), s. in C_5H_{12}, 70/10^{-2} (subl.), 295°→α-Sn+ ROH+ Me_2CO	H, $^{13}C\{^1H\}$, m-s	701, 1102, 1563
Sn(IV)				
$[Sn(OMe)_4]_\infty$	5, 6	powd., 180/0.1 (dec.), α=4	ebul.	202, 835, 1048, 1049, 1125
$[Sn(OEt)_4]_\infty$	5, 6	powd., 175/0.05 (dec.), α=4; t→ ROH +$Sn(OR)_2$ +MeCHO	ebul.	202, 701, 1048, 1049, 1102
"$Sn(OPr^n)_4$"	5, 6	waxy sld., 120/0.03 (dec.), α=3.85	ebul.	202, 1048, 1049
$[Sn(OPr^i)_4(^iPrOH)]_2$ (2 forms ?), 2 oct. with a common $(\mu\text{-}OR)_2$ edge ↓-ROH **"$Sn(OPr^i)_4$"**	4, 5, 6	cr., α=2; 120/0.1→ROH+ +R_2O +$Sn_3O(OR)_{10}$ +...., (visc. liq., α=3.1) visc. liq., 120/0.05 (b.), 350°→ α-Sn+ ROH+ Me_2CO	IR, ^1H, ^{13}C, ^{119}Sn,ebul., m-s, X-r	202, 540, 702, 1048, 1049, 1350, 1612 1563, 1579
"$Sn(OBu^n)_4$"	5	powd., α=3.7	ebul.	1048, 1049

$[Sn(OBu^i)_4(^iBuOH)]_2$ 2 oct. with a common $(\mu\text{-}OR)_2$ edge $\downarrow H_2O$ **$[Sn_3O(OBu^i)_{10}(^iBuOH)_2]$=** $[Sn_3(\mu_3\text{-}O)(\mu\text{-}OR)_3(OR)_7(ROH)_2]$, trian. $[M_3]$, 3 oct.$[SnO_6]$ with a common $[\mu\text{-}(O)OR]$ edge	5, 6	cr., s. in hc., ROH, α=2 -	^1H, ^{13}C, ^{119}Sn, X-r	324, 702, 1350 1350
“$Sn(OBu^s)_4$”	6	powd., 154/0.2 (subl.,dec.)	-	202
$[Sn(OBu^t)_4]$ tetrah.	5, 6	cr., 40 (m.), 50/0.1 (b.), α=1, in s. $[Sn(OR)_4(ROH)]$, CN Sn=5	IR, ^1H, ^{13}C, ^{119}Sn, ebul., X-r	202, 297, 324, 702, 1125, 1579, 831
$Sn(OBu^t)_n(OR)_{4-n}$, R=Me, Et, n=1-3	6	t→ $Sn(OBu^t)_4$+ $Sn(OR)_4$	-	1125
$Sn(OBu^t)_n(OSiMe_3)_{4-n}$, n=2, 3	6	-	-	297
“$Sn(OC_5H_{11}{}^n)_4$”	6	yel. liq., 160/0.1 (b., dec.), α=1.5	ebul.	202, 1049
“$Sn(OR)_4$“, R= $CHEt_2$, $CHMePr^n$, $CHMePr^i$	6	yel. liqs., 204/2 (b.), α= 1.1 (ROH)	ebul.	1049
$Sn(OC_5H_{11}{}^t)_4$	6	yel.-red liq., 140/0.4 (b.), d^0 1.1229, α=1 (ROH)	ebul.	202, 230, 1049
“$Sn(OC_6H_{13}{}^n)_4$“	6	yel. liq., 230/0.1 (b.), α=1.2	ebul.	1049
$Sn(OCHMeBu^n)_4$	6	yel.sld., 120/10^{-3} (b.), α=1	ebul.	1049
$Sn(OCMe_2Pr^n)_4$, $Sn(OCMeEt_2)_4$	6	liq., d^0 1.0724; 140/0.4 (b.)	ebul.	202, 230
“$Sn(OC_6H_{11}{}^c)_4$“, “$Sn(OC_7H_{15}{}^n)_4$”	6	liq., 130/10^{-3} (b.), α=1.4	ebul.	1049

$Sn(OCHEtBu^n)_4$, $Sn(OCEt_3)_4$, **"$Sn(OC_8H_{17}{}^n)_4$"**	6	yel.-red liqs.,b.:135/, 150/10^{-3} , α=1	ebul.	1049
$[Sn(OCH_2Ph)_4(Me_2NH)]_2$, 2 oct. with a common $(\mu\text{-}OR)_2$ edge	4	colrl. cr., s. in tol., ins. in hex.	^1H, ^{13}C, X-r	1506
$[Sn(OCMe_2Ph)_4]$, tetrah.	4	clrl. liq.	X-r	1506
$Sn(OPh)_4$	6	sld., 50 (m.), α=1.4	IR	1049
$Sn(OSiMe_3)_4$ **$Sn(OSiPh_3)_4$** ***trans*-$[Sn(OSiPh_3)_4Py_2]{\cdot}0.5Py$,** oct. **$Sn[OSi(OBu^t)_3]_4$**	5, 6 5 6 6	colrl. liq., 74/0.3 (b.) sld., 322 (m., dec.), s. in bz. - 121 (dec.), s. in hex., α=2,	- - X-r IR, ^1H	1125, 1558 690 297 2, 1571
$Sn(RO_2)_2\downarrow$, $Sn(RO_2)(OPr^i)_2$, R= C_2H_4, C_3H_6-1.2, -1.3, C_4H_8-1.3, -1.4, -2.3, C_5H_{10}-1.5, C_6H_{12}-1.6	6	wh. sld., low s. in bz.	-	1125
$Sn(\eta^2\text{-}ArO_2)_2$, R= C_6H_2-1.2, C_6H_2-C_6H_2-2.2' **$\cdot Ar(OH)_2$, $\cdot 2Py$, $\cdot 2Et_3N$**	4	s. in polar. solv.	IR	44
$[SnHal_3(OMe)(MeOH)]_2$, Hal=Cl, Br, 2 oct. with a common $(\mu\text{-}OR)_2$ edge, **$\cdot$MeOH**		cr., α=2	X-r	202, 632, 1350, 1496, 1531
$[SnCl_n(OEt)_{4-n}]$, n=1, 2, 3		slds., m: 87 (n=1), 118 (195 ?) (2), 151(3)		1300, 1798
$[SnCl_3(OEt)(EtOH)]_2$, 2 oct. with a common $(\mu\text{-}OR)_2$ edge, bond ROH…Cl **$SnCl_3(OEt)L$,** L=Dmfa, $OPMe_3$		cr., 191(m.), α=2	ebul., X-r	202, 632, 1282, 1282, 1496, 1721
$SnHal_3(OR)(ROH)$, Hal=Cl, Br, R=Pr^n, Pr^i **$SnCl_n(OPr^i)_{4-n}$,** n=1, 2, 3		crs., s. in bz. m: 85 (n=1),114 (2),145(3)	-	202, 1125, 1300, 1798

$[SnCl_n(OR)_{4-n}]\cdot mL$, R=Me, Et, Pr^i, L=Et_3N, $N(C_2H_2OH)_3$, n=1-3, m=1, 2	-	-	1300
$[SnCl(OBu^i)_3(Bu^iOH)]_2$ 2 oct. with a common $(\mu\text{-}OR)_2$ edge	-	X-r	1350
$[SnCl_3(OPh)(PhOH)]$	-	conduct.	1055
$[SnCl_3(OC_6H_4R\text{-}4)]$, R=H, Me, Bu^t, OMe **$[Sn_3(\mu\text{-}OC_6H_4R\text{-}4)_4Cl_8]$**, R=H, Bu^t, OMe, **$[Sn_3(\mu\text{-}OC_6H_4Me\text{-}4)_4Cl_8]$**, linear chain, central oct. $[SnO_4Cl_2]$ and 2 trig. bipyr. $[SnCl_3O_2]$ sharing $(\mu\text{-}OR)_2$ edges	colrl. cr., m:180,183,195, 138 (dec.), s. in bz. colrl. cr., m: 219, 225, 210 (dec.) 212 (m.)	IR, ^1H, m-s X-r	849
$SnCl_3(OC_2H_4Cl)$, $\cdot 2L$, L=Py, RNH_2	cr.	IR	1282
$MSn_2(OR)_9$, M=Na, K, R=Et, Pr^i	cr., 260 (dec.), s.in bz., ROH	-	202, 1510, 1691
$[MSn(OBu^t)_5\cdot 0.5C_7H_8]_\infty$, M=K,Rb,Cs (Li, Na do not exist.), spirals of ψ-oct. $[:Sn(\mu\text{-}OR)_4(OR)]$, tetrah. $[K(\mu\text{-}OR)_2]$	colrl. cr., s. in eth., hex., m: 190 (dec.) **(K)**, 94 (**Rb**), 80 **(Cs)**, α=1.3	^1H, X-r	1692
$M^{II}[Sn_2(OR)_9]_2$, M^{II}=Mg, Ba, Zn, Cd **$[BaSn_2(OPr^i)_{10}]_2$**	slds., α=1	^1H, ^{13}C, ^{119}Sn, ebul.	1510
$M^{II}Cl[Sn_2(OPr^i)_9]$, M^{II}=Mg, Zn, Cd	slds., α=2	^1H, ^{13}C, ^{119}Sn	1510
$\{BaI[Sn_2(OPr^i)_9]\}_2$		X-r	1691
$CdI[Sn_2(OPr^i)_9]$, isostr. with its Zr- analog	colrl.cr., s. in tol.-hex.	^1H, ^{13}C, ^{113}Cd, X-r	1688
$[BaCdSn_2(OPr^i)_{12}]_2$ isostr. with its Zr- analog	-	X-r	1686,1687, 1690, 1691

$M^{II}Sn(OBu^t)_6$, M^{II}=Ca, Sr, Ba			1684
$[Tl_2Sn(OEt)_6]_\infty$, linear chain of oct. $[Sn(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4]$ and tetrah. $[Tl(\mu_3\text{-}OR)_2(\mu\text{-}OR)_2]$	colrl.cr., s. in tol., ~90 (m., rapid), α=1	^1H, cryosc., m-s, X-r	701
$Pb_3SnO(OPr^i)_8$	waxy, $128/10^{-2}$ (subl); s. in THF, t→Pb+PbO+Sn+ Me_2CO + ROH	^1H, ^{13}C, ^{17}O, ^{119}Sn, m-s	1563

$SnI_2[Ti(OPr^i)_5]_2$, $SnITi_2(OPr^i)_9$, $SnI[Zr_2(OPr^i)_9]_2$, $SnI_3Zr(OPr^i)_5$, $SnI_2[Al(OPr^i)_4]_2$, $SnI_2[Nb(OPr^i)_6]_2$ [1688, 1690]

[715].

12.10. Lead alkoxides

In contrast to its analogs, lead forms alkoxides only in +2 oxidation state. For tetravalent lead, there have been described quite stable metalorganic derivatives of R_3PbOR type; however, the attempts to obtain $Pb(OR)_4$ starting from $(PyH)_2PbCl_6$ or $Pb(OAc)_4$ led to $Pb_2Hal(OMe)_3$ and $Pb(OAc)_2$, respectively, in combination with the oxidation products — aldehydes, esters, and so on. [34, 1259]. $Pb(OMe)_2$ was first reported by Szilard [1552] in 1906 as a product of anodic oxidation of metal in the NaOMe solution in MeOH. Chablay [313] in 1911 to 1917 succeeded in preparing $Pb(OR)_2$ with the aid of metathesis reactions of lead iodide or nitrate with NaOR in liquid ammonia. Recently there have been described and structurally characterized volatile and hydrocarbon soluble $Pb(OR)_2$— derivatives of ramified radicals [649] and also bimetallic t-butoxides of lead and divalent metals [1681, 1683, 1684].

12.10.1. Synthesis

The most often used are metathesis reactions of lead salts with sodium alkoxides (method 5). The repeated study of the reaction in liquid ammonia has shown that the only derivative that can be obtained in a pure form by this reaction is polymeric $Pb(OMe)_2$, which can be purified from the $NaNO_3$ admixture by extraction with liquid ammonia and from unreacted NaOR by that with MeOH). The samples of alcohol soluble $Pb(OR)_2$ always contain considerable amounts of sodium [1627]. The application of $PbHal_2$ (Hal = F, Cl, Br, I) gives rather stable $3Pb(OMe)_2 \cdot PbHal_2$ (analogs of $3Pb(OH)_2 \cdot PbHal_2$) as the major products. The halide-free $Pb(OMe)_2$ was obtained on the action of five-fold excess of KOMe on PbF_2 [34]. The reaction of $Pb(OAc)_2$ with NaOR in alcohol media patented as the synthetic route to $Pb(OR)_2$ ($R = Bu^n, Pr^i, C_6H_{11}{}^c, PhCH_2, C_2H_4$) [1271] can be applied only for the preparation of the isopropoxide, as for all the other derivatives the intermediate $Na_2Pb(OAc)_2(OR)_2$ complexes appear to be so stable that the reaction solution contains both metals. However, in certain cases, when the sodium admixture does not hinder the further application of the solution (as, for example, in some sol-gel applications), the solution prepared by metathesis reaction in ^nBuOH, containing minimal admixture of sodium can be used directly [1627]. The attempt to repeat the electrochemical preparation of $Pb(OMe)_2$ and other homologs (method 2) has not led to success because of cathodic reduction causing the electrochemical refinement of metal. The oxocomplex of $Pb_6O_4(OPr^i)_4$ composition was obtained, however, with low yields from the ^{i}PrOH-based electrolyte [1786]. In the modern research works the preparation of $Pb(OR)_2$ is achieved usually by alcoholysis of $Pb[N(SiR_3)_2]_2$ [311, 649, 1254, 1543, 1681].

12.10.2. Properties

Lead alkoxides are colorless crystalline matters (with the only exception for red $Pb(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2$ [311]). Methoxide, isopropoxide, 2-methoxyethoxide, phenoxide, glycolate, and glycerate, of lead are insoluble in organic solvents and have polymeric structures. The structure of $Pb(OMe)_2$ (CdI_2-type) is built up of octahedra (see also Section 4.8.2), while those of $Pb(OR)_2$, where $R = Pr^i$, C_2H_4OMe is built of the chains of tetrahedra [1627, 649]. The majority of lead alkoxides are oligomeric; the coordination of the central atoms can vary considerably: these can be octahedra, ψ-trigonal bipyramids, tetrahedra, and ψ-tetrahedra. As has been mentioned, these are only $Pb(OR^t)_2$ and their bimetallic derivatives, which can exist in the gas phase. At the same time all $Pb(OR)_2$ are rather prone to decomposition reactions, followed by ether elimination and the formation of oxoalkoxides. In the case of $[Pb(OMe)_2]_\infty$ these are apparently –O–Pb–O–Pb– polymers [34]. Isopropoxide gives on decomposition oligomeric products — $[Pb_4(\mu_4\text{-}O)(\mu_3\text{-}OPr^i)_6]$, $[Pb_6(\mu_3\text{-}O)_4(\mu_3\text{-}OPr^i)_4]$ (Fig. 4.10 *b*) and $[Pb_7O_2(OPr^i)_6]$ being obtained in particular on reaction of $Pb(OPr^i)_2$ with water in different communications [1786, 1254, 1563]. Tetranuclear alkoxides of the same kind are known even for $R = Bu^t$ and $SiPh_3$ [1254, 608], and heptanuclear for $R = SiMe_3$ [1724] (Table 12.11). The considerable stability of the octahedral core is illustrated also by the structure of the known bimetallic complex $[Pb_6Nb_4O_4(OEt)_{24}]$ [1253], which can be considered as $[Pb_6(\mu_3\text{-}O)_4(\mu_3\text{-}OR)_4]$ coordinating with the aid of its four oxo-ligands 4 $[Nb(OR)_5]$ groups, each of the latter forming 3 more (μ-OR) bridges to Pb atoms (see also Section 4.7.1).

Hydrolysis of $Pb(OR)_2$ is discussed in Chapter 9. The most important application domain for $Pb(OR)_2$ is at present the sol-gel technology of inorganic materials and, first and foremost, ferroelectrics (see Chapters 9, 10).

A traditional area of application for $Pb(OR)_2$ is also the technology of polymers, where they are recommended for the stabilization of vinyl polymers, polyvinylchloride, and so on. [715, 1271]. Cresolate is also used for the purification of oil from sulfur-containing compounds [715]. A number of pub-

Table 12.11. Lead alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
$Pb(OMe)_2$↓, struc. type $Mg(OH)_2$, [ROMOR] layers, $[MO_{6/3}]$-oct., $[OM_3]$-trig.pyr.	2, 5	wh. powd., ins. in NH_3 (liq.); 65°→ $PbO_n(OR)_{2-2n}$ + Me_2O	IR, X-r-powd.	34, 313, 1552, 1627
“$Pb(OEt)_2$”↓	5	wh. powd., ins. in common org. solv., NH_3 (liq.)	-	313, 1135, 1627
$Pb_4O(OEt)_6$	6	colrl. cr., s. in hc.	X-r-parametrs	1254
$[Pb_6O_4(OEt)_4]$	4, 5 (t)	« «		
$[Pb(OPr^i)_2]_\infty$, linear chains of $[Pb(\mu\text{-}OR)_4]$ tetrah. sharing opposite $(OR)_2$ edges, **$\cdot 2^iPrOH$**	4, 5	colrl. cr., $130/10^{-4}$ (subl.), s. in ROH ~1, bz. 3, THF 5%, α=3.5-4.7; t→Pb+ROH +.....	IR, ebul., X-r	649, 832, 1135, 1254, 1271, 1627, 1767
35° → **$[Pb_4O(OPr^i)_6]$** ($-R_2O$)	5	colrl. cr., s. in ROH, tol.-hex., α=1	^1H,^{13}C,^{207}Pb, ^{17}O, m-s	1563
$[Pb_6(\mu_3\text{-}O)_4(\mu_3\text{-}OPr^i)_4]$, 8 faces of $[M_6]$ oct. centered alternatively by μ_3-O and μ_3-OR, $[:PbO_4]$ - ψ-trig. bipyr.	2, hydrol.	colrl. cr., ins. in ROH, s. in THF, $110/10^{-2}$ (dec.)	^1H,^{13}C, ^{17}O, ^{207}Pb, m-s, X-r	40, 1627, 1786
$[Pb_7O_2(OPr^i)_{10}]$			^1H,^{13}C, ^{207}Pb	1563
“$Pb(OBu^n)_2$”	5, 6	wh. powd., s. in ROH	-	1135, 1271, 1627
“$Pb(OBu^i)_2$”	5	wh. powd., ins. in NH_3 (liq.)	-	313

$[Pb(\mu\text{-}OBu^t)_2]_3$, linear chain of Pb oct. in the center and 2 $[:PbO_3]$ ψ-tetrah. sharing $(\mu\text{-}OR)_3$ faces ↓ t; H_2O	4, 5, 6	colrl. cr., 219 (m., dec.), $95/10^{-2}$ (subl.), s. in hc., stab. in b. tol. s. (110°, 48 h.),α=2.6; t→$Pb+ROH+CH_4+$....	IR, ^1H, ^{13}C, ^{207}Pb,ESR, cryosc., m-s, X-r	649, 1135, 1254, 1565, 1681, 1684
$[Pb_4O(OBu^t)_6]$ H_2O →**$[Pb_6O_4(OBu^t)_4]$** isostr. with its OPr^i -analog	4, 5	colrl. cr., $130/10^{-4}$ (subl.) wh. powd., s. in THF		
$Pb(OC_2H_4Pr^i)_2$	5	wh. powd., ins. in NH_3 (liq.)	-	252, 313
$Pb(OC_5H_{11}{}^t)_2$	4, 6	colrl. cr., $105/10^{-4}$ (subl.), s. in org. solv., α= 3.5	IR, ^1H, ^{13}C, cryosc.	649, 1135
$Pb(OC_6H_{11}{}^c)_2$, $Pb(OCH_2Ph)_2$	5	wh. powd., s.i n ROH	-	1271
$[Pb(OCEt_3)_2]_4 \cdot Et_3COH$	4	visc. liq., $160/10^{-4}$ (subl.), α=4	IR, ^1H,^{13}C	649
$Pb(OCBu^t{}_3)_2 \cdot Bu^t{}_3COH$	4	yel.cr.,s in C_5H_{12},0°→Pb-coll.		1254
$Pb(OPh)_2$↓	4	wh. powd.	-	1095
$Pb(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2$	4, 5	red cr., 170 (m.), s. in ArH, α=1	^1H, m-s, X-r	311
$[Pb[OCH(CF_3)_2]_2(4\text{-}Me_2NPy)]_2$ 2 trig. bipyr. with a common $(\mu\text{-}OR)_2$ edge		-	IR,^1H, ^{13}C, X-r	1543
$Pb[OC(CF_3)_3]_2$	7	light tan sld.	IR, ^{19}F	294
$[Pb(OSiMe_3)_2]_n$ ↓	5	wh. powd., 110 (dec.→R_2O), s. in $CHCl_3$, THF, α=3→1	^1H, ebul.	608, 1417

$[Pb_7O_2(OSiMe_3)_{10}]$, $[Pb_4(\mu_4\text{-}O)(OR)_6]$ connected with a $[Pb_3(\mu_3\text{-}O)(OR)_4]$ chain			^1H, ^{13}C, ^{207}Pb, X-r	1724
$[Pb_4(\mu_4\text{-}O)(\mu\text{-}OSiPh_3)_6]\cdot C_7H_8$ $[OM_4]$ tetrah., edges capped with 6 (μ-OR), $[:PbO_4]$ - ψ- trig. bipyr.	4	colrl. cr., s. in eth., bz., 212 (m., dec)	IR, X-r	608
$Pb[OSi(OBu^t)_3]_2\cdot{}^tBuOH\cdot MeCN$	6	colrl. cr., s. in bz.	IR, ^1H	1571
$[Pb(OC_2H_4OMe)_2]\downarrow$, linear chains of $[Pb(\mu\text{-}OR)_4]$ tetrah.	4	colrl. cr., s. in ROH, $95/10^{-2}$ (subl. with dec.)	IR, ^1H, X-r	649
$[Pb(OCMe_2CH_2OMe)_2]$ isostr. with $[Pb(OC_2H_4OMe)_2]$		$95/10^{-2}$ (quantitatively subl.), $\alpha=2$ (m-s)	m-s	732
$Pb(C_2H_4O_2)\downarrow$	5	wh. powd.	-	63, 313, 1271
$[Pb(\eta^2,\mu\text{-}OCH_2CHOCH_2OH)]_\infty$ zigzag chains of $[PbO_6]$ oct.	3, 4	colrl. cr., hν→ blk., 120(dec.)	X-r	564, 896, 1215
$Pb_2Hal(OMe)_3$, Hal= F,Cl,Br, I		wh. powd., ins. in org. solv.	-	34
$[MPb(OBu^t)_3]_2$, M=Li, Na, isostr. with $[Li_2Sn_2(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4]$,		colrl. cr., s. in ArH, THF, **Na:** 178 (m., dec.), $\alpha=1$	^1H, X-r	1565, 1681
$NaPb[\mu\text{-}OSi(OBu^t)_3]_3$, 6-coord. $[Na(OSi)_3(OBu^t)_3]$ and ψ-tetrahs. $[:PbO_3]$		colrl. cr., s. in C_5H_{12}	IR, ^1H, ^{13}C, ^{29}Si, TGA, X-r	1571
$TlPb(OBu^t)_3$, ψ-tetrahs. $[:PbO_3]$ and $[:TlO_3]$ sharing $(\mu\text{-}OR)_3$ face		colrl. cr., s. in ArH, 73 (m.)	^1H, X-r	1695

$M^{II}Pb_2(OBu^t)_6$ = $[Pb(\mu\text{-}OR)_3M^{II}(\mu\text{-}OR)_3Pb]$, M^{II}=Ca, Sr, Ba, Zn, Cd, Ge, Mn, Zn linear chains	colrl. cr., s. in ArH, vol., $\alpha=1$; m., dec.: 220, 250, 265, 312, 203, 323, 84; $t \rightarrow Pb+M^{II}PbO_3+CH_4+ROH+CH_2CMe_2+\ldots$	IR, ^1H, ^{13}C, ^{207}Pb, ESP, m-s, X-r	1681, 1683, 1684
$PbLa_3(OBu^t)_{11}$ $=[PbLa_3(\mu_3\text{-}OR)_3(\mu OR)_4(OR)_4]_2$	colrl. cr., s. in tol.	^{207}Pb, X-r	782.
$Co_2Pb_2(OBu^t)_8$ $=[Co_2Pb_2(\mu\text{-}OBu^t)_6(OBu^t)_2]$, linear chain with 2 central Co tetrah. in and 2 peripheral Pb ψ- tetrah.	colrl. cr., s. in ArH, 210 (m.., dec.), vol.	X-r	1683
$[Me_2NH_2]^+_2\{[Pb[OCH(CF_3)_2]_3\}^-_2$ anion - 2 trig. bipyr. sharing $(\mu\text{-}OR)_2$ edge	-	IR, ^1H, ^{13}C, X-r	1543

$Pb_3M^{IV}O(OPr^i)_8$, M^{IV}=Sn, Ti, Zr [1565]; **$Pb_2Ti_2O(OPr^i)_{10}$** [447]; **$[NaPb_2Ti_2O(OPr^i)_{10}]^+Cl^-$** [782]; **$PbZr(OBu^t)_6$; $Pb_4Zr_2(OPr^i)_{16}$; $Pb_2Zr_4(OPr^i)_{20}$** [1565]; **$PbIM^{IV}_2(OPr^i)_9$**, M^{IV}=Ti, Zr [1688]; **$Pb[Sb(OR)_4]_2$** [74]; **$Pb_6Nb_4O_4(OEt)_{24}$** [1253]

lications are devoted to the reaction products of the oxide, hydroxide, and acetate of lead with glycols or glycerine and found their application in pharmacology and also as protecting coverings. The product of polycondensation of PbO with glycerine is a polymer having special rigidity after being heated to 120°C, due, apparently, to a net-like structure containing CH_2–O–Pb–O–CH_2– fragments [144].

12.11. Titanium alkoxides

This class of compounds is the most represented and most thoroughly studied compared with the alkoxides of other metals and even with other organometallic derivatives of titanium (as alkoxides appear to be the most stable and easiest to approach among them). The preparation of $Ti(OEt)_4$ was first reported by Demarcay (1875) [473] on the reaction of $TiCl_4$ with NaOEt. In 1892 Levy reported the preparation of a number of phenoxides and naphtoxides. The interest in the alkoxides of titanium is connected with the growing areas of their application. A great contribution to the chemistry of titanium alkoxides was made by D. C. Bradley in the 1950s and 1960s. [224, 223]. He has prepared and systematically studied all the homologous series of $Ti(OAlk)_4$ derivatives, which allowed the tracing of general trends in the variation of physicochemical properties in homologous series, possibilities of separation from the derivatives of other rare metals; he has also carried out the thermochemical and hydrolytic studies of these compounds. Nesmeyanov, Freidlina *et al.* [1204, 1208, 1209] have made fundamental studies in the synthesis of alkoxides and alkoxide halides of titanium, and Andrianov studied the siloxides of titanium and derived polymers [48, 49].

At present researchers are focused on the studies of bimetallic derivatives in connection with the obtaining of complex oxide materials (see also Section 10.1 and 12.12).

The number of articles and especially patent publications devoted to $Ti(OR)_4$ is increasing continuosly (while the peak of their number was observed in 1950-70-es). The properties and synthetic approaches to $Ti(OR)_4$ and their derivatives have been summarized in the capital review by Suvorov and Spasskiy [1547], included in a reduced version in the book by Feld and Cowe [560]; more recent publications were summarized in the book by Reetz [1346].

12.11.1. $Ti(OR)_3$

Numerous attempts have been made to reduce $Ti(OR)_4$, and the isolation of $Ti(OR)_3$ ($R = Pr, Bu^n$) was achieved first in 1954 by Nesmeyanov *et al.* [1209] on the interaction of $Ti(OR)_4$ with K metal in alcohol. In continuation for the reduction of $Ti(OR)_4$ were applied such agents as $(R'O)_3SiH$ ($R = Et, Bu^n, Ph$) [21], Mg/Hg in Et_2O or THF ($R = Bu^n, C_2H_4OEt$), and Na/Hg (in the synthesis of $[NaTHF_2Ti(OC_6H_3Pr^i_2\text{-}2,6)_4]$) [509]. The application of $LiAlH_4$ led to such complexes as $Ti_4O(OPr^i)_{12}$ and $Ti_4H(OEt)_{13}$, containing both Ti(III) and Ti(IV) atoms [1378].

Except the reduction of $Ti(OR)_4$ in the synthesis of $Ti(OR)_3$ were used such approaches as alcoholysis of $TiCp_n(NMe_2)_{3-n}$ ($R = Et, Ph, C_6H_4/2$) [991] and $Ti[N(SiMe_3)_2]_3$ ($R = C_6H_3Me_2\text{-}2,6$) [1155] (method 4) and also the metathesis reactions of $TiCl_3$ with NaOPh [1155] or $NaOC_2H_4OEt$ [1422] (method 5).

All the derivatives of Ti(III) are strong reducive agents and are immediately oxidized in air with the formation of titanium (IV) oxoalkoxides. $Ti(OAlk)_3$ are green or pinkish violet solids, poorly soluble in organic solvents; they are diamagnetic and supposedly polymeric (the X-ray patterns of methoxide and ethoxide are very close to those of the corresponding derivatives of Cr (III) [1366]). The phenoxides are bluish green crystalline substances; they are paramagnetic oligomeric and soluble in hydrocarbon solvents.

On the action of an excess of a reducive agent (K or Na/Hg) on $Ti(OAr)_4$ there are formed the derivatives of formally divalent titanium. They contain, however, a hydride ligand as is shown by their reactions ($+ CCl_4 \rightarrow CHCl_3$), while the magnetic and ESR data indicate the presence of a single unpaired strongly delocalized electron per each Ti atom. The electrochemical study of the $[Ti(OC_6H_3Pr^i\text{-}2,6)_2Dipy_2]$ complex permitted the consideration of one of the Dipy ligands as an anion [510]. The compounds presented at the beginning of the Table 12.12 should be considered supposedly as containing Ti(III).

The derivatives from this series are suitable for the fixation of molecular nitrogen and can be used for the preparation of NH_3 with rather high yields [1706, 1673].

12.11.2. $Ti(OR)_4$

12.11.2.1. Synthesis

See also Chapter 2. The reaction of the chloride with sodium alkoxide proposed by Demarcay (method 5) has for a long time served as the major synthetic approach to $Ti(OAlk)_4$. Its numerous studies, however, have indicated (in case of the ethoxide) rather huge variations in the yield of the final product — from 25 to 80%. Different ways have been studied for the introduction of the components (NaOR or Na metal, preliminary heating of $TiCl_4$ with ROH or its introduction in the reaction avoiding the preliminary contact with alcohol), separation of the products (distillation of $Ti(OR)_4$ or centrifugation of NaCl), different temperatures, solvents, and so on. The optimal turned out to be the technique proposed by Andreev and Nikolsky [47], who introduced $TiCl_4$ slowly into the solution of NaOEt in EtOH at –20°C and then heated it for 3 hours at 60 to 65°C (to decompose the intermediate bimetallic alkoxide chlorides). These conditions exclude the preliminary alcoholysis of $TiCl_4$, accompanied by formation of water and alkoxide chlorides and then polymeric oxoalkoxides. This method was used for the preparation of $Ti(OR)_4$ other than ethoxide ($R = Me, Pr^i, Bu^n, Bu^s$) [8, 153, 1515]. The major disadvantage of this technique is the necessity for using sodium alkoxide and also the decrease in the yield of $Ti(OR)_4$ with the increase in the R size; in case of $NaOR^t$ no reaction takes place at all [472].

In 1940 Nelles patented the application of ammoniac instead of NaOR in the metathesis of $TiCl_4$, which permitted the increase of the yields of alkoxides and the application of the reaction for all R [1275]. At present this method has become the major industrial and laboratory route to $Ti(OR)_4$ [185, 215, 433, 1217, 1547, *etc.*]. Benzene, toluene, or CCl_4, favoring the precipitation of NH_4Cl, were recommended as solvents by Boyd [185]. The best solution has been achieved by the application of the $TiCl_4{\bullet}8NH_3$ solid adduct as reactant and by bubbling the EtOH vapor via its solution [47, 1800] or by its refluxing with ROH ($R = Bu^t, C_5H_{11}{}^t, C_3H_5$) [1660, 560]. Py can be used instead of NH_3 in the case of ^nBuOH, while in EtOH a very stable $TiCl(OEt)_3$ permit the increase of the yield [1217]. In the case of ^sBuOH, ^tBuOH, and $^tC_5H_{11}OH$ the application of En, Et_3N, Bu^tNH_2, and $Bu^t{}_2NH$ permits to increase the yield of the products, while that of Py, $Bu^t{}_3N$, and $PhNH_2$ hinders completely the reaction [1800].

The greatest number of $Ti(OR)_4$ homologs was obtained using the alcohol interchange reaction (method 6), the isopropoxide being usually applied as reactant [225, 224, 235]. This reaction has also been reported to lead to numerous $Ti(OR)_n(OR')_{4-n}$. Application of esters as alkoxylating agents has also been reported Mehrotra [1111, 1800].

The alcoholysis of other derivatives than alkoxides themselves (method 4) has not found any broad application in the case of titanium derivatives; however, the use of $Ti(NMe_2)_4$ for this purpose has been reported [1579]. Phenoxides can often be prepared simply by the formation of $TiCl_4$ with phenols [599], while in the case of sterically hindered ligands this reaction is often complicated by formation of phenoxide chlorides (for example, $[TiCl_2(OC_6H_3Ph_2\text{-}2,6)_2]$ is formed not only on alcoholysis with corresponding phenol but even on the reaction of $TiCl_4$ with LiOAr [480]).

At present the most perspective and ecologically pure route appears to be the anodic oxidation of metal in alcohols in the presence of a conductive additive (method 2), and industrial technology has been developed in Russia for $Ti(OBu^n)_4$ [948].

12.11.2.2. Properties

$Ti(OAlk)_4$ are mainly colorless or light yellow liquids (even the t-butoxide, being crystalline for nearly all other metals). The boiling points increase nearly linearly with the molecular weights in the n-, s-, and t-R series considered, starting with the ethoxide (Fig. 3.2). The increase in the evaporation enthropies and decrease in d^{25} and n_D^{25} along the same series are connected with the effect on the entanglement of hydrocarbon chains [224]. In the $Ti(OR^n)_4$ series (R = Et, Pr, Bu) the molecular complexity is 3 [220]; in the $Ti(OR^s)_4$ series 1.4 to 1; all $Ti(OR^t)_4$ are monomeric. The influence of the ramification of R on the evaporation temperature is demonstrated by the scheme in Fig. 3.3, showing the boiling points for isomeric amylates for a number of metals (the derivatives of titanium being most volatile). In spite of all the amylates being monomeric ($\alpha = 1.4$ only for R^n), the boiling point turns to be more sensitive to the increase in ramification.

It is quite surprising that the dipole moments in the $Ti(OR^n)_4$ series – from trimeric butoxide to monomeric nonanoxide — are practically the same (1.60 to 1.68 D) and do not differ from the theoretical values calculated for a tetrahedral monomer with freely rotating OR- groups [61].

The only solid $Ti(OR^n)_4$ derivative with a high melting point is the methoxide. It is known in 2 modifications — polymeric (“A-form”) obtained on alcohol interchange or on reaction of $TiCl_4$ with NaOMe, and oligomeric (“B-form”), obtained from the reaction with NH_3. The first one is insoluble in organic solvents; the second is soluble in toluene on refluxing. It melts at 216°C and is tetrameric in both solution and gas phases [8, 866]. Its structure is also built up of tetrameric centrosymmetric molecules (Fig. 4.7 *a*) [1759]. The analogous molecules were also discovered in the structures of $Ti(OEt)_4$ and $Ti(OMe)(OEt)_3$ [800, 1757]. At the same time the determinations of molecular complexity for $Ti(OEt)_4$ in solution (reported independently in at least 15 different publications) is close to 3 (the maximal observed value — 3.21 was reported in [1208]). Having compared the results obtained by anisotropic relay scattering on $Ti(OEt)_4$ (in solutions in cyclohexane and CCl_4) with those of IR, Raman, and ^1H NMR spectra, Russo and Nelson [1376] confirmed the presence of trimers in them and not a mixture of tetramers and dimers as it was supposed by Martin and Winter [1064].* It is supposed now that in the trimeric molecule the octahedrally coordinated central atom is sharing edges with the coordination polyhedra of 2 peripheric pentacoordinated Ti atoms — $(RO)_2Ti[(\mu\text{-}OR)_2Ti(OR)_3]_2$. The same structure is characteristic supposedly for the trimers of n-propoxide and n-butoxide in solution, as a very quick exchange between the terminal and the bridging groups has been discovered for them by ^1HNMR even at –90°C [220]. This situation with the existence of 2 types of structures — a trimer and a tetramer — is very close to that described for the solid and the liqud $[Al(OPr^i)_3]_n$. Both trimeric molecules contain 5-coordinated metal atoms that become octahedrally coordinated in tetramers (see Chapter 6 and Section 12.5).

12.11.2.3. Oxoalkoxides, $Ti_nO_m(OR)_{4n-2m}$

The only other known crystalline alkoxide complexes of titanium are the oxoalkoxides, $Ti_nO_m(OR)_{4n-2m}$— representatives of a new series of condensed molecules. They originated from the controlled hydrolysis of $Ti(OR)_4$. The complexes described recently mainly by Day *et al.* and Mosset contain from 3 to 18 Ti atoms and polydentate μ_4-, μ_3-, μ-O, and OR ligands. The long known "first crystalline hydrolysis product of titanium ethoxide" — $Ti_7O_4(OEt)_{20}$ — was found as a precipitate formed on storage of the solution of alkoxide in ethanol and on introduction of 0.5 to 0.67 M H_2O per mol of $Ti(OEt)_4$ into them [1719, 214] (Fig. 5.1 *a*). Another product isolated under the same conditions along with $Ti_7O_4(OEt)_{20}$ is $[Ti_{16}O_{16}(OEt)_{32}]$ [1177] (see also Section 4.7.2).

The $Ti_3O(OPr^i)_{10}$ molecule is, according to the NMR data, formed in solution on hydrolysis at h = 0.05–0.2, but only a heteroleptic complex of $Ti(\mu_3\text{-}O)(\mu_3\text{-}OMe)(OPr^i)_9$ composition could be obtained in the crystalline form [454].

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* This conclusion is also supported by the fact that the molecular complexity of $Ti(OEt)_4$ is not dependent on the concentration of solutions but decreases in the presence of the traces of water ($\sim 4\cdot 10^{-3}$ M) [220]).

The ^{13}C NMR studies of $Ti(OEt)_4$ solutions indicated the existence of an octanuclear $Ti_8O_6(OEt)_{20}$ molecule, but the crystalline complex with a $[Ti_8O_6]$ core was successfully isolated only for the benzylate $[Ti_8O_6(OCH_2Ph)_{20}]\cdot Et_2O$ [457] (see Section 4.7.2). From the solutions of oxoethoxides in toluene there has also been isolated a decanuclear $[Ti_{10}O_8(OEt)_{24}]\cdot PhMe$ complex. The hydrolysis of $Ti(OPr^i)_4$ at 100°C (in an autoclave) provides a mixture of two isomers of $[Ti_{12}O_{16}(OPr^i)_{16}]$ composition. A solvate of this complex with CH_2Cl_2 ia also one of the products of interaction of the isopropoxide with acetic acid [1532].

The treatment of this complex with EtOH gives crystalline $[Ti_{12}O_{16}(OPr^i)_{10}(OEt)_6]$. Its spherical molecule consists of 3 layers of Ti atoms (3 in both the upper and lower layers and 6 in the middle one) connected by O groups; the CN for Ti is 5 in the middle layer and 6 in the peripheric ones. On hydrolysis at room temperature, the $[Ti_{11}O_{13}(OPr^i)_{18}]$ complex is formed in solution and can be crystallized in the presence of EtOH as $[Ti_{11}O_{13}(OPr^i)_{13}(OEt)_5]$ [457].

The biggest molecule of this kind, $[Ti_{18}O_{28}(OBu^t)_{16}(^tBuOH)]$, is formed on hydrolysis of $Ti(OBu^t)_4$. It is considered to be the first example of Keggin structure built up of Ti atoms [291] (see also Section 4.7.2).

While the formation of solvates is not characteristic of $Ti(OR)_4$, Bains has obtained stable orange complexes of ethoxide and isopropoxide with such strong donors as En, N_2H_4 [92]. The study of the solubility polytherm in the $Ti(OEt)_4$–EtOH system indicated the formation of a solvent with 1:1 composition [1615]. $Ti(OBu^n)_4$ forms in solution the complexes with certain esters (for example, in 1:1 composition with dibutilphtalate) [1310].

12.11.2.4. Aryloxides

Aryloxides are crystalline yellowish orange substances soluble in nonpolar organic solvents and usually can be sublimed *in vacuo*. Their color appears presumably due to the charge transfer from the phenyl radical to the metal atom. Their structures demonstrate the decrease in the coordination numbers of Ti atoms with the increase in ramification. Thus the molecule of $[Ti(OPh)_4(PhOH)]_2$ is built up of 2 octahedra sharing a common edge [1550]; $[TiO(OC_6H_3Pr^i_2\text{-}2,6)_2L_2]$ is a trigonal bipyramid [748] (the latter molecule demonstrates a rather rare example of terminal oxoligand at Ti atom). The presence of bulky 2,6-substituted phenyl rings in the structures of $[Ti(OC_6H_3Pr^i_2\text{-}2,6)_4]$ and $[Ti(OC_6HMe_4\text{-}2,3,5,6)_4]$ leads to tetrahedral coordination of the metal and rather short Ti–O bond lengths (1.78 Å).

12.11.2.5. Siloxides, $Ti(OSiR_3)_4$

An important area in the chemistry of titanium alkoxides is with the siloxides, $Ti(OSiR_3)_4$and their derivatives containing Hal, OR, oxoligands and the related polymers. The latter find rather broad applications as dielectric and isolation materials. They are briefly considered in the book by Feld and Cowe [560], a detailed review being included in the monograph by Andrianov [48]. Table 12.12 presents the properties of only certain simplest derivatives.

12.11.2.6. Titanium alkoxide halides

The literature data on titanium alkoxide halides — $TiHal_n(OR)_{4-n}$ — are as numerous as those on homoleptic alkoxides. Described are the derivatives of all R from Me to naphtolates and those of polyols where Hal varies from F to I, all the steps in substitution (n = 1, 2, 3) having apparently their individual representatives. The alcoholysis products of $TiCl_4$ have different composition depending on the reaction conditions, the solutions obtained containing often mixtures of derivatives, the special techniques being developed to separate individual components. The preparation of $TiCl_3(OR)$ requires the reaction to be carried out in the excess of $TiCl_4$ at 0°C or in an inert media like CCl_4 [1205, 1337]. Andrianov *et al.* have used the reaction of $TiCl_4$ with Me_3SiOR in this purpose [49]. The excess of alcohols at room temperature leads mainly to $TiCl_2(OR)_2{\bullet}ROH$, which can then be used for the preparation of derivatives of less stable alcohols via alcohol interchange or transesterification. Dialkoxide halides are formed also on action of free halogenes or HHal on solutions of $Ti(OR)_4$ in benzene [1205].

$TiCl(OR)_3$ can be most conveniently prepared via alcohol interchange from $TiCl(OEt)_3$ — a very stable product of $TiCl_4$ interaction with ethanol in the presence of Py (see above). It is possible to insert one Cl atom in the molecule of $Ti(OR)_4$ with the aid of [PyH]Cl [1217].

The most universal and facile techniques for the preparation of the derivatives of all three types of complexes are reactions of co-proportionation of $TiHal_4$ with $Ti(OR)_4$ [1204, 1199] and also of action of AcOHal on $Ti(OR)_4$ (in 1:1, 1:2 and 1:3 ratios). In the latter case the crystallization of solvates of $TiCl_n(OR)_{4-n}{\bullet}AcOR$ composition is observed [215]. The preparation of alkoxofluorides has been achieved also with the use of SbF_3 instead of AcOF [259]. The vacuum distillation of alkoxide chlorides is often accompanied by their disproportionation, and the separation in the form of adducts with pipyridine $C_5H_{10}NH$ has been therefore proposed as an alternative [1204].

At room temperature the phenol substitutes only one chlorine atom in **$TiCl_4$** producing **$TiCl_3(OPh)$,** while **β-naphtol** replaces – 2 Cl atoms.

Alkoxide halides, **$TiHal_n(OAlk)_{4-n}$ $(n > 1)$,** are colorless crystalline matters (in contrast to liquid **$Ti(OR)_4$**) with low m.p. and b.p. and are soluble in most of the common organic solvents. **$TiHal(OR)_3$,** are usually viscous liquids. The derivatives of *s*- and *t*-alcohols decompose easily on storage and/or heating with formation of **$TiOCl_2$**, HCl, RCl, and the products of olefine polymerization. **$TiHal_n(OAr)_{4-n}$** are crystalline yellowish orange substances.

In contrast to the alkoxides, the **$TiHal_n(OAlk)_{4-n}$** are very prone to the formation of rather stable adducts with ROH, **RCOOR', $C_5H_{10}NH$,** and so on. The stability of the latter increases with the number of Hal atoms in the molecule. The alkoxide halides are usually aggregated via **μ-OR** groups. Among the exclusions can be named **$[TiCl_3(OPh)]$,** containing the infinite chains with Cl-bridging atoms **[*cis*-$Ti(\mu\text{-}Cl)_2Cl(OPh)$]** [1600]. The molecules of **$[TiCl_3(OAr)THF_2]$, $[TiCl_2(OAr)_2THF_2]$, Ar = $C_6H_3Me_2$-2,6** [876, 1789], and **$[TiCl_3(OPr^i)L_2]$** [1799] are isolated octahedra with *cis*-arrangement of solvating molecules. Alkoxide dichlorides, containing one solvating alcohol molecule, form dimers of 2 octahedra sharing a common edge — **$[TiCl_2(OPr^i)_2(Pr^iOH)]_2$** [624], **$[TiCl_2(\eta^2,\mu\text{-}O(CH_2)_3O)THF]_2$-*trans*** [777]. In the absence of solvating molecules the **$[TiCl_2(OR)_2]_2$ (R = Et, Ph)** dimers are built up of 2 polyhedra with 5 vertexes sharing common edge. Only the presence of more than one bulky OAr-group leads to monomeric tetrahedral molecules. The only complex with a Ti:Cl = 2:1 ratio exists as a **$[Ti_4Cl_2(OMe)_{14}]$** tetramer — an analog of **$[Ti_4(OMe)_{16}]$**.

12.11.2.7. Bimetallic titanium alkoxides

The study of bimetallic titanium alkoxides during recent years has been urged by the prospect of their application in the sol-gel technology of perovskite-related materials, and therefore attention has been paid to the derivatives of divalent metals (mainly barium and strontium). Comparison with analogous derivatives of zirconium reveals much lower stability of titanium complexes, none of them displaying volatility. The composition and structure of the known alkoxotitanates and -zirconates (determined in particular on study of the **$Ba(OR)_2$–$M^{IV}(OR)_4$–L system**) in the main do coincide, however [1631, 1609, 1686]). Only a few of the described complexes possesss 1:1 composition, permitting them to be used as molecular precursors of **$M^{II}TiO_3$**. Among

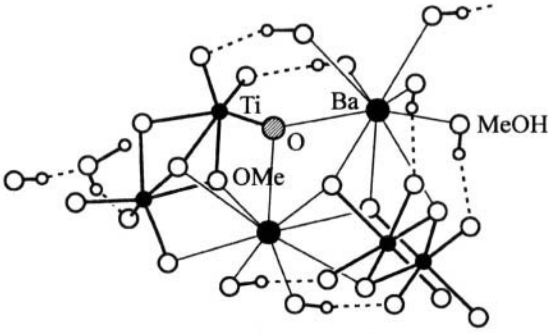

Fig. 12.2. The metal-oxygen core in structures of [$Ba_2Ti_4O(OMe)_{18}(MeOH)_7$]. MeOH [1523]. The presence of a μ_3-O ligand in the molecule is connected apparently with the trend of the Ba atom to increase its CN to 9 on coordination of small ligands as MeO [1523]. Concerning the trimetallic [$M^ICdTi_2(OPr^i)_{12}$]$_2$, see Sections 12.12 and 4.7.3.

them can be mentioned [$BaTiO(OPr^i)_4(^iPrOH)_{7/8}$]$_4$ [1787, 1631] (see Section 4.7.1), $Pb_2Ti_2(\mu_4\text{-}O)(OPr^i)_{10}$ [447], and $(BaDmfa)_2Ti_2(OPh)_{12}$ [456].

The more typical structure arrangement for alkoxotitanates contains usually a [$Ti_2(OR)_9$]-group (of 2 octahedra with a common face), which is connected with a M^{II} via two μ_3-O and two μ-O groups. The coordination of two such groups by a Ba atom leads to the highly symmetric $Ba[Ti_2(OR)_9]_2$ molecule with a CN = 8 for Ba (Fig. 4.9 *b).* The Ba:Ti = 1:2 ratio leads to a [M_3] triangle, containing the same kind [$Ti_2(OR)_9$] fragment, connected to the Ba atom. Quite an original structure is demonstrated by [$Ba_2Ti_4O(OMe)_{18}(MeOH)_7$]•MeOH, where in addition to the [$Ti_2(OR)_9$] group, the molecule contains also a [$Ti_2(OR)_{10}$] group (of 2 octahedra sharing a common edge) [1523] (Fig. 12.2).

The mechanism of the hydrolysis and nature of its products for bimetallic titanium alkoxides are discussed in Chpters 9 and 10.

The application of $Ti(OR)_4$ in different areas of technology has been reported in a tremendous number of articles and patents. We cannot discuss this question in detail, so we only refer to 2 detailed review articles — in the book by Harwood [715] and Feld, Cowe [560]. We list below only the major aspects of application of $Ti(OR)_4$ and their derivatives:

- As catalysts of different reactions and components in catalytical compositions (initially of the Ziegler type, applied not only in the polymerization processes but even in nitrogen fixation),

Table 12.12. Titanium alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
«Ti(II)»				
$[Ti(OPh)_2]_3(H)$	7	grey sld., α=1, μ_{eff}=0.69	IR, Raman, ^1H, ESR m-s, magn. prop.	570
$[Ti(OPh)_2]_2(N_2)(H)$		purple cr., α=1, μ_{eff}=0.76		
$[Ti_3Cl(OPh)_2(THF)_2]_2(H)$		yel. sld., μ_{eff}=0.90		
$Ti_5Cl_2(OPh)_8$		or. sld.		
$[Ti(OC_6H_3Pr^i-2,6)_2Dipy_2]$-*cis*, oct.	7	deep bl. cr.	^1H, ^{13}C, X-r X-r powd.	510
$[Ti(OC_6H_3Pr^i-2,6)_2Py_3]_2$		grn. sld.		
$Ti(OC_6H_3Pr^i-2,6)_2(\eta^2\text{-}Bu^t{=}C(CH_2Ph)_2$ $\cdot L$, L=Py, PhPy		red-brn. sld.		
$(TiC_6H_4O_2\text{-}1,2)_2(N_2)(H)THF$	7	brn. sld., μ_{eff}=0.79	magn. prop.	570
$K_{11}Ti_3(OPh)_7$	7	grey sld., α=0.63	ESR	570
Ti(III)				
$Ti(OMe)_3$	4, 5, 7	light grn. cr., diamagn.	electr. sp.,magn. prop., X-r powd.	6, 21, 32, 991
$Ti(OEt)_3$	4, 7	grn.cr., 236 (93-?m.), α=4, diamagn.	IR, ^{13}C, magn. prop., X-r powd.	21, 32, 991, 1209

$Ti(OPr^n)_3$, $\cdot{}^nPrOH$	7	pink-vlt. sld., low s. in org. solv.		1209
$Ti(OMe)(OPr^i)_2$		-	fotoel. sp.	119
$Ti(OBu^n)_3$, $\cdot{}^nBuOH$	7	pink cr., 226 (dec.), diamagn.	IR, ^{13}C, magn. prop., X-r powd.	21, 1209
$Ti(OPh)_3$, **$\cdot Me_2NH$**	7	grn.cr., 265 (m., dec.) yel.-or. cr., 152 (m.), diamagn..	IR, ^{13}C, magn. prop., X-r powd.	21, 991
$[Ti_3(OPh)_9(Tmeda)_2]$, angular mol., central tetragon. pyr. $[TiO_5]$ sharing a $(\mu\text{-}OR)_2$ edge 2 oct. $[TiO_4N_2]$	5, 7	light grn. cr., s. in tol., μ_{eff} =1.69	magn. prop., X-r	1155
$[Ti(OC_6H_3Me_2\text{-}2,6)_3]_2$ 2 tetrahs. sharing a$(\mu\text{-}OR)_2$ edge	4	grn.-bl. cr., s. in tol., μ_{eff} =0.64	magn. prop., X-r	1155
$[Ti(OC_6H_3Pr_2^i\text{-}2,6)_3]\cdot Py$	7	puple cr., s. in tol.	electr. sp	509
$Ti(OC_6H_3Bu^t_2\text{-}2.6)_3$	5	bl. cr., s. in hex., α=1	ESP, electr. sp.	322, 994
$Ti(OC_2H_4OEt)_3$	5	sld., s. in eth., bz., hex., α=2	^1H, ^{13}C, electr. sp., cryosc.	1422
$Ti_2(C_6H_4O_2\text{-}1,2)_3\cdot 2Me_2NH$	4	brn. sld., diamagn.	magn. prop.	991
$TiCl(OR)_2$, R=Me, Et, Bu^n **$TiCl_2(OEt)\cdot 0.5\ HCOOEt$**	slds., **Me:** brn., 290 (dec.); **Et:** yel.-brn., 270 (dec.); **Bu^n:** brn., μ_{eff}=1.27		IR, magn. prop., X-r powd.	636
$TiHal_2(OR)\cdot 2ROH$, R=Me, Et; Hal=Cl, Br	cr., red (Me, Cl), brn. (Me, Br), mauve (Et, Cl), lilac (Et, Br), diamagn.		IR, electr.sp., magn. prop., conduct.	423
$[TiCl(OCBu^t_3)_2]$	$+CCl_4 \rightarrow TiCl_2(OR)_2$		ESR	1030

$[TiCl_2(OC_6H_3Bu^t_2\text{-}2,6)THF_2]$, trig. bipyr., 2 THF-ax., 2 Cl- equ.	-	X-r	1086
$[TiCl(OC_6H_3Bu^t_2\text{-}3,5)_2Tmeda]_2$	pink cr., s. in tol., μ_{eff} =0.75	magn. prop.	1155
$[TiCl(OC_6H_3Ph_2\text{-}2,6)_2]_2$, 2 tetrah. sharing a $(\mu\text{-}Cl)_2$ edge, Ti-Ti 2.98	dark purple cr.	^1H, ESR, X-r	749
$[TiCl(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2]_n$	grn. sld., 130 (dec.)	^1H, ^{13}C	504
$LiTi(OBu^t)_4$, **·THF**	grn. sld., s. in THF bl. cr., 65 (dec.), paramagn.	ESR, conduct.	1704
$LiTi(OC_6H_3Pr^i_2\text{-}2,6)_4(Tmeda)_2$ **·PhMe**	or. cr., s. in tol., μ_{eff} =1.67	magn. prop.	1155
$[Na_2Ti_2(\mu\text{-}OC_6H_3Me_2\text{-}2.6)_8Py_2]$ in cycle $-[Ti(\mu\text{-}OR)_2(OR)_2N]$- trig. bipyr., $[Na(\mu\text{-}OR)_2(\eta^6\text{-}Ph)_2]$	vlt. cr.	^1H, ESR, X-r	509
$[NaTHF_2Ti(OC_6H_3Pr^i_2\text{-}2,6)_4]$ 2 tetrahs. sharing a $(\mu\text{-}OR)_2$ edge	light bl. cr., s. in tol.	ESR, electr. sp, X-r	509
$[NaTmeda_2THF]^+$ **$[TiCl_2(OC_6H_3Bu^t_2\text{-}3,5)_2\ Tmeda]^-$** **$[HTmeda]^+[TiCl_2(OC_6H_3Bu^t_2\text{-}3,5)_2$ $Tmeda]^-$**, anion- oct., 2 O-ax.	or.-red cr., s. in tol., μ_{eff} =1.79 bright-yel. cr., s. in tol., μ_{eff} =1.93	magn. prop. X-r	1155
$NaTHF_2Ti(OC_6HMe_4\text{-}2,3,5,6)_4$	bl. sld., s. in THF	^1H, ^{13}C	1594
$LiTi(OSiMe_3)_4$	bl. sld., s. in hc.	ESR, conduct.	1704
$AlTi(OBu^t)_6$	grn.-bl. cr., 100/0.1 (subl.)	IR, ESR	1704
Ti (III,IV)			

$Ti_4O(OPr^i)_{12}$	7	purple cr., s. in hc., diamagn.	ESR	1378
$Ti_4H(OEt)_{13}\downarrow$; $+CCl_4 \rightarrow Ti_4Cl(OEt)_{13}$	7	vlt. cr.	^1H, cryosc.	1378
Ti(IV)				
$[Ti(OMe)_4]_4$ («B form») $=[Ti_4(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_{10}]$ rhombus $[Ti_4]$, 2 oct. $[Ti^2(\mu_3\text{-}OR)(\mu\text{-}OR)(OR)_3]$ and 2 oct. $[Ti^1(\mu_3\text{-}OR)_2(\mu\text{-}OR)_2(OR)_2]$	5 (tol., t)	colrl. cr., 216 (m.), 140/0.01, 170/0.1 (subl.), s. in tol., α=4 (m-s, in s.)	IR, Raman, X-r powd., X-r	508, 1759, 1567, 215, 472
$[Ti(OMe)_4]_\infty$ («A form»)	5, 6 (ROH, t)	wt. powd., ins. in org. solv.	IR, X-r powd.	866, 8, 153, 961
$Ti(OMe)_n(OBu)_{4-n}$, n=1, 2, 3	6	40 (m.), 153/0.4 (b.), n_D^{20} 1.5068 (n=1); 157/0.3, 1.5184 (n=2); 165/0.6, 1.5362 (n=3)		560, 508
$[Ti(OEt)_4]_4$ struct. type of $Ti_4(OMe)_{16}$,	2, 4, 5, 6	clrl. liq., 38 (m.), 103/0.1 (b.), d^0 1.1321, d_4^{25}1.1066, n_D^{25}1,5082; s. in ROH 84% (25°C), polytherm; α=3, μ=1.50, $\Delta H^\circ_{form.}$ = -352,7 (349.0) (sld.), -372,0 (liq.)	IR, Raman, ^1H, ^{13}C, cryosc., XANES, EXAFS, magn.prop. X-r powd., X-r	47, 85, 92, 153, 185, 215, 218, 220, 224, 230, 301, 433, 634, 765, 800, 866, 961, 1064, 1217, 1376, 1467, 1436, 1599, 1615, 1757

$\cdot$L, L=EtOH, En/2, $N_2H_4/2$		-10 (dec.)		1615
$Ti_7O_4(OEt)_{20}]$ **(~ «$Ti_6O_4(OEt)_{16}$»)** =$[Ti_7(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2(\mu\text{-}OR)_8(OR)_{12}]$ (Chapt. 4.7)	hydrol.	colrl. cr.	^{17}O, X-r	457, 153, 214, 1177, 1414, 1719
$Ti_8O_6(OEt)_{20}$ (Chapt. 4.8)	hydrol.	colrl. cr.	^{13}C, ^{17}O, X-r	457
$[Ti_{10}O_8(OEt)_{24}]\cdot PhMe$= $[Ti_{10}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_2(\mu\text{-}O)_2(\mu\text{-}OR)_{10}(OR)_{14}]\cdot PhMe$ (Chapt. 4.10)	hydrol.	colrl. cr.		
$[Ti_{16}O_{16}(OEt)_{32}]$ (2 forms) =$[Ti_8(\mu_4\text{-}O)_2(\mu_3\text{-}O)_4(\mu\text{-}O)_2(\mu\text{-}OR)_8(OR)_8]_2$ (Chapt. 4.11)		colrl. cr.	X-r	1177, 1414
$[Ti(OEt)_3(OMe)]_4$, struct. type of $Ti_4(OMe)_{16}$,	-	-	X-r	1757
$Ti(OEt)_n(OBu)_{4-n}$, n=1, 2, 3	6	liq., b.: 180/17 (n=1); 176/ 16 (n=2); 164/18 (n=3)	-	472
$Ti(OEt)_n(OR)_{4-n}$, R= C_5H_{11}, $C_6H_{11}{}^c$, C_7H_{15}, $C_4H_6Cl_3$, n=1, 2, 3	6	liq., b.: 152/3, $n_D{}^{20}$ 1,4910 (n=1, R=C_5H_{11}); 228/15 (n=1), 182/16 (n=3, $C_6H_{11}{}^c$); 208/6 (n=1, C_7H_{15})	-	560, 472
$Ti(OPr^n)_4$	6	colrl. liq., 124/0.1(b.), d^o 1.0564; $d_4{}^{25}$ 1.0329; $n_D{}^{35}$ 1,4803; α=3; μ=1,20(1,47); p-T (polytherm); $\Delta H^o{}_{form.}$= -372(liq.), -354 (gas)	Raman, ^1H, ^{13}C, cryosc., magn.prop, visc.	224, 230, 220, 218, 301, 433, 560, 634, 765, 1111, 1580, 1757

$Ti(OPr^n)_3(OPr^i)$	6	liq., 132/0.6 (b.)	-	560
$Ti(OPr^i)_4$	2, 4	colrl. cr., 20 (m.), 49/0.1 (b.), d_4^{20} 0.9711; n_D^{35}1,4568, *p-T* (polytherm); α=1.0, ΔH^o_{form}= -372 (-390) (liq.); -360 (gas)	Raman, ^1H, ^{13}C, cryosc., ebul., visc., electr. sp., magn.prop. XANES, EXAFS	92, 85, 153, 225, 215, 218, 220, 411, 479, 560, 765, 961, 991, 1171, 1436, 1467, 1580
·**L**, L= N_2H_4, Me_2NH, $EtNH_2$, En, En/2		yel-or. cr., 152 (m.), 60/0.05 (subl.)		
$[Ti_3O(OPr^i)_9(OMe)]$= $[Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OMe)(\mu\text{-}OR)_3(OR)_6]$, trian. $[M_3]$	hydrol.	colrl. cr.	^1H, ^{13}C ^{17}O, X-r	454
$Ti_3O(OPr^i)_{10}$		colrl. cr	^1H, ^{13}C, ^{17}O	454
$Ti_{11}O_{13}(OPr^i)_{18}$ **$[Ti_{11}O_{13}(OPr^i)_{13}(OEt)_5]$** = $[Ti_{11}(\mu_3\text{-}O)_{10}(\mu\text{-}O)_3(\mu\text{-}OR)_7(OR)_6(OEt)_5]$ **$[Ti_{12}O_{16}(OPr^i)_{16}]$** (2 forms) =$[Ti_{12}(\mu_3\text{-}O)_{14}(\mu\text{-}O)_2(\mu\text{-}OR)_4(OR)_{12}]$ **$[Ti_{12}O_{16}(OPr^i)_{10}(OEt)_6]$** (2 forms) =$[Ti_{12}(\mu_3\text{-}O)_{14}(\mu\text{-}O)_2(\mu\text{-}OPr^i)_4(OPr^i)_6(OEt)_6]$	hydrol., 6	colrl. cr.	$^{13}C\{^1H\}$, ^{17}O, X-r	457, 1532
$Ti(OPr^i)_2(OR)_2$, R= $C_{12}H_{25}$, $C_{18}H_{37}$	6	sld., 44 (m.), 246/0.2 (b.)	-	560
$[Ti(OPr^i)_3(OC_6H_2Me_3\text{-}2,4,6)]_2$ 2 trig. bipyrs. sharing a $(\mu\text{-}OPr^i)_2$ edge	6	or. cr.	X-r	820

$[Ti_2(OPr^i)_4X_2]$, X=1,2,5,6 – $(OR)_4$ D-mannit, R=Me, Pr^i etc.	5	-	^1H,^{13}C	1311
$Ti(OBu^n)_4$	4, 6	liq., 142/0.1 (b.), d_0^{20} 1.0051; d_4^{25}0.9932; n_D^{20}1.4925, α=3; μ=1.68 (1.15); p-T (polytherm); $\Delta H°_{form.}$= - 392,7 (-399) (liq.), -377 (gas)	Raman, ^1H, ^{13}C, electr. sp., XANES, EXAFS, cryosc., m-s, visc., thermochem., magn. prop.	61, 85, 153, 185, 215, 224, 230, 220, **218**, 278, 301, 433, 634, 765, 822, 961, 1064, 1111, 1217, 1467, 1579, 1580, 1757
$Ti(OBu^n)_3(OR)$, R=Et, C_nH_{2n-1}	6	liq., 180/17 (b.)	IR, ^1H	472, 487
$Ti(OBu^i)_4$, **$\cdot{}^iBuOH$**		cr., 30-40 (m.), 141/1 (b.), d_4^{25} 0.9601; n_D^{54}1,4749; α=1.8-2.7; $\Delta H°_{form}$= - 403 (liq.); -381 (gas)	^1H, ^{13}C, visc., cryosc., thermochem., X-r parametrs	218, 220, 433, 560, 765, 801, 1580
$Ti(OBu^s)_4$	5, 6	liq., 81/0.1 (b.), d_4^{35} 0.9196; n_D^{20}1.4436, α=1; p-T (polytherm); $\Delta H°_{form}$= - 404 (liq.), -382 (gas)	visc., thermochem., magn. prop.	218, 225, 634, 1111, 1515, 1580, 560
$Ti(OBu^t)_4$	6	liq., 60/0.3 (b.), d^o 0.9060; n_D^{35}1.4429, α=1; μ=1,85; p-T (polytherm); $\Delta H°_{form}$= -395	IR, ^1H, ^{13}C, cryosc., ebul., visc., thermochem., magn. prop.	109, 218, 220, 225, 230, 433, 634, 765, 1111, 1580, 1757

$[Ti_{18}O_{28}(OBu^t)_{16}L]$, (Chapt. 4.11) $[Ti_{18}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_{20}(\mu\text{-}O)_4(OR)_{16}(ROH)]$ L= ^tBuOH, 0.25 MePh,	hyd-rol.	colrl. cr.	IR, ^{17}O, ^{13}C $\{^1H\}$, X-r	291
$Ti(OC_5H_{11}{}^n)_4$	5, 6	liq., 158/0.1 (b.), $n_D{}^{35}$1.4813; $d_4{}^{25}$0.9735, α=1.4; ΔH°_{form}= - 428 (liq.), - 403 (gas)	ebul., visc., thermochem., magn. prop.	218, 225,224, 433, 472,560, 634, 1580
$Ti(OC_2H_4Pr^i)_4$	5, 6	liq., 148/0.1 (b.), $d_4{}^{25}$ 0.9648; α=1.2	ebul., magn.prop.	225, 433, 634, 1207
$Ti(OC_2H_4Pr^i)_3(OR)$, R= Et, Pr^i, Pr^n,C_3H_5 **$Ti(OC_2H_4Pr^i)_2(OC_3H_5)_2$** **$Ti(OC_2H_4Pr^i)(OPr^n)_3$** **$Ti(OC_2H_4Pr^i)(OC_3H_5)_3$**	6	colrl. liqs., 150/1.5 (b.), $n_D{}^{20}$ 1.4870-1.4910; 128/1 (b.), $n_D{}^{20}$ 1.4950; 150/1 (b.), $n_D{}^{20}$ 1.5222	-	
$Ti(OCH_2CHMeEt)_4$	6	liq., 140/0.1 (b.), α=1.1; opt. isomers	ebul.	225, 556
$[Ti(OC_5H_{11}{}^{neo})_4]_2$ 2 oct. sharing a $(\mu\text{-}OR)_2$ edge	6, 4	cr., 64 (m.), 130/1, 105/0.05(b.), s. in tol., α=1.1	^1H, ^{13}C, ^{17}O, $^{47,49}Ti$, ebul., X-r	186, 191,187, 225, 437,765, 1132
$Ti(OCHEt_2)_4$	6	liq., 112/0.1 (b.), α=1; p-T (polytherm)	ebul.	225

$Ti(OCHMePr^n)_4$	6	liq., 115/0.1 (b.), α=1	ebul.	225
$Ti(OCHMePr^i)_4$	6	liq., 117/0.1 (b.), α=1	ebul.	225
$Ti(OC_5H_{11}{}^t)_4$	5, 6	liq., 98/0.1(b.), d_4^{20} 0.9188, n_D^{20}1.4543, α=1; p-T (polytherm), $\Delta H^o{}_{form.}$ = - 457 (liq.), - 438 (gas)	^1H, ebul., XANES, EXAFS, magn.prop., thermochem	85, 225, 215, 230, 218, 560, 634
$Ti(OC_5H_9{}^c)_4$		cr., 45 (m.), 159/0.4 (b.) ; 230 (dec.)	-	440, 560
$Ti(OC_6H_{13}{}^n)_4$	6	liq., 176/0.1 (b.); n_D^{20} 1,4830; d_0^{20} 0.9573 μ=1,62; p-T (polytherm)	ebul., cryosc.	61, 224, 433, 472
$Ti(OCHMeBu^n)_4$, **$Ti(OCHMeBu^t)_4$**	6	liq., 126/0.1 (b.)	ebul.	225
$Ti(OCMeEt_2)_4$	6	154/2 (b.), d^o 0.9437; α=1; p-T (polytherm)	ebul.	225, 230
$Ti(OCMe_2Pr^n)_4$	6	liq., 167/5 (b.), d^o 0.9085; α=1; p-T (polytherm)	ebul.	225, 230
$Ti(OCMe_2Pr^i)_4$	6	liq., 147/0.5 (b.)	-	225
$Ti(OC_6H_{11}{}^c)_4$	5	liq.,190/1 (b.); n_D^{35} 1.5155, d^{35} 1.0589	-	472, 1217
$Ti(OC_6H_{11}{}^c)_3(OEt)$	6	liq., 228/15 (b.)		472
$Ti(OC_7H_{15}{}^n)_4$	5, 6	liq., 201/0.1 (b.), d_0^{20} 0.8963, n_D^{20} 1,4610; μ=1.64	ebul.	61, 224, 472
$Ti(OCHPr^n{}_2)_4$, **$Ti(OCHPr^i{}_2)_4$**	6	cr., 160 (m.), 156/0.1(b.), liq., 162/0.1(b.), α=1	ebul.	225

Ti(OCMeEtPr^i)$_4$	6	liq., 197/0.1, α=1, p-T (polytherm)	ebul.	225
Ti(OCMe$_2$Bu^t)$_4$, Ti(OCEt$_3$)$_4$	6	liq., 163/; 180/0.5 (b.), α=1; p-T (polytherm)	ebul.	225
Ti(OCH$_2$Ph)$_4$	6	liq., 250/2 (dec.)	-	560
Ti(OC$_6$H$_{10}$^{c}Me)$_4$	6	liq., 193/0.1 (b.)	-	560
Ti(OC$_8$H$_{17}$^{n})$_4$	6	liq., n_D^{20}1,4810; α=1.4, μ=1.67	ebul.	61, 224
Ti(OCH$_2$CHEtBu)$_4$	6	liq., < -25 (m.),248/11 (b.), n_D^{35} 1.4750	-	560
Ti[OCHMe(C$_6$H$_{13}$)]$_4$	6	liq., 182/0.1(b.), n_D^{35} 1.4601	-	225, 560
Ti(OC$_9$H$_{19}$^{n})$_4$	6	liq., 264/1.5 (b.), n_D^{20} 1.4785, d^{20} 0.9241, μ=1.68		61
Ti(OCHBu^n$_2$)$_4$	6	liq., 195/0.1 (b.)	ebul.	225
Ti(C$_{10}$H$_{21}$^{n})$_4$	6	sld., 68 (m.), 265/0.2 (b.), d^{25} 0.87, μ=1.6		61, 560
Ti(OC$_{10}$H$_{17}$^{i})$_4$ (i-bornil)		[α_D] (4.0 in bz.) = -1.48		560
Ti(OC$_{10}$H$_{17}$)$_4$		[α_D] (5.0 in bz.) = -99.5		560
Ti(OAd-1)$_4$,Ti(OAd-2)$_4$, **Ti(OCH$_2$Ad-1)$_4$** Ad=adamantyl (C$_{10}$H$_{15}$)	6	colrl. cr., >350 (m.), s. in org. solv., α=1	IR, ^{1}H, m-s, cryosc.	166
Ti(OCHMeC$_2$H$_4$CHEtBu)$_4$		liq., 255/1 (b.), d^{25} 0.9012	-	560
Ti(OC$_{18}$H$_{37}$)$_4$ **Ti(OC$_{18}$H$_{35}$)$_4$**		sld., 64 (m.), 305/1 (b.); liq., 288/0.1 (b.), d^{20} 0.87	-	560
Ti(OCH$_2$Ph)$_4$	6	-		1205

[Ti$_8$O$_6$(OCH$_2$Ph)$_{20}$]·Et$_2$O = [Ti$_8$(μ_3-O)$_4$(μ-O)$_2$(μ-OR)$_8$ (OR)$_{12}$] Et$_2$O	hyd-rol.	-	^{17}O, ^{13}C, X-r	457
Ti(OCHPh$_2$)$_4$		sld., 58 (m.),	-	560
Ti[OCPh$_3$]$_4$		sld., 195 (m.)	-	560
Ti(OPh)$_4$	4, 5, 6	or. cr., 153 (m.), 230 /0.8 (b.), s. in hex.,α=1	IR, ^{1}H, electr. sp., cryosc.	479, 532,570, 584, 598,706, 991, 1421, 1800, 1712
·**L**, L= C$_6$H$_4$OMe (2, 3 ,4), NR$_3$, R$_2$NH, NH$_3$, R$_2$CO		yel.-or. cr., s. in eth., hex.		
[Ti(OPh)$_4$(PhOH)]$_2$ 2 oct. sharing a(μ-OR)$_2$ edge	4	or. cr., 159 (m.), s. in bz., CCl$_4$, CS$_2$	X-r	1550, 599, 1297, 1675
Ti(OPh)$_3$(OPr^i)·PhOH, Ti(OPh)$_2$(OBu^n)$_2$	6	-	-	
Ti(OC$_6$H$_4$Me-2)$_4$	6	slds., 104(m.), 235/0.08(b.)		584, 706, 1800
Ti(OC$_6$H$_4$Me-3)$_4$		324/3(b.), α=1		
Ti(OC$_6$H$_4$Me-4)$_4$		50 (m.), 240/0.07 (b.), α=1		
[Ti(OC$_6$H$_4$Bu^t-2)$_4$, tetrah.	5	yel. cr., s. in hex., bz	^{1}H, ^{13}C, X-r	1594
[Ti(OC$_6$H$_3$Me$_2$-2,6)$_4$]	5	bright-yel. cr., 460/3 (b.), s. in tol., α=1	^{1}H, ^{13}C, electr. sp.	509, 706
[Ti(OC$_6$H$_3$Pr$^i_2$-2,6)$_4$] tetrah.	5	golden-yel. cr., >330 (m.), s. in tol., hex. α=1	IR, ^{1}H, ^{13}C, electr. sp.	509, 504
[TiO(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$L$_2$], trig. bipyr., Ti=O 1.66	hyd-rol.	cr.	m-s, voltamet.	748

$[TiO(OC_6H_3Pr^i{}_2\text{-}2,6)_2L]_2$, L=$NC_5H_4\text{-}4\text{-}NC_4H_8$ 2 trig. bipyr. sharing a $(\mu\text{-}O)_2$ edge		yel. cr.	X-r	
$Ti(OC_6H_2Me_3\text{-}2,4,6)_4 \cdot L$, L= THF, Py, Dipy	4	-	^1H, m-s, cryosc.	1463
$Ti(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)(OMe)_2$	6	yel. sld., 170 (m.), s. in eth., hc.	^1H, ^{13}C	504
$[Ti(OC_6HMe_4\text{-}2,3,5,6)_4]$, tetrah.	5	yel. cr., s. in hex., bz	^1H, ^{13}C, X-r	1594
$Ti(OC_{10}H_7)_4$ - α, -β	4	brn. sld., 60 (m.), invol., α=1	IR, TGA	706, 1055, 599
$Ti(OBinoMe_2)(OPr^i)_2$ (Bino = binaphtholat)	6		X-r	189
$Ti(OCH_2CH{=}CH_2)_4$	5, 5	liq., 141/1 (b.), d^{25} 1.1138	-	1217, 433, 655
$Ti(OCH_2CH{=}CHMe)_4$	6	or. liq., n_D^{25} 1.5413, α=2	IR, ^1H, ebul.	
$Ti(OCHMeCH_2CH{=}CH_2)_4$		colrl. liq., 98/0.4 (b.), n_D^{20} 1.491		
$Ti(OCMe_2CH{=}CH_2)_4$		112/0.1 (b.), n_D^{25} 1.464		
$Ti(OC_2H_6CH{=}CH_2)_4$		α=1.5		
$Ti[OCH(CF_3)_2]_4$	5, 6	colrl. liq. (cr.?), 35/ 0.15 (b.), s. in tol., ROH, α=1 - 1.5 (bz.)	IR, ^1H, ^{19}F, m-s, TGA, X-r	880, 1085, 292
$[Ti(OCH(CF_3)_2)_4(MeCN)_2]$-*cis*, oct.		colrl. cr., vol.		
$[Ti[OCH(CF_3)_2]_2(OEt)_2(EtOH)]_2$ 2 oct. sharing a$(\mu\text{-}OEt)_2$ edge		colrl. cr.		
$[Ti[OCH(CF_3)_2]_2(OPr^i)_2]_2$ 2 trig. bipyr. sharing a $(\mu\text{-}OPr^i)_2$ edge		α=1 (m-s, in s.)		566

$Ti[OC(CF_3)_3]_4$	7	wh. sld.,126(m.), 50/vac.(subl.)		294
$[Ti(OC_6H_3F_2\text{-}2,6)_3(OPr^i)]_2$ 2 trig. bipyr. sharing a $(\mu\text{-}OPr^i)_2$ edge	6	or. cr.	X-r	292
$Ti[O(CH_2)_nCl]_4$, n=2, 3 **$Ti(OCH_2CCl_3)_4$, $Ti(OCMe_2CCl_3)_4$** **$Ti(OCMe_2CCl_3)_3(OEt)$**	4, 6	visc. liq. colrl. cr., 150/0.15 (subl.), α=1	-	233, 531, 1283
$[Ti(OC_6H_3F_2\text{-}2,6)_3(OPr^i)]_2$ 2 tetragon. pyr. sharing a$(\mu\text{-}OR)_2$ edge **$[Ti(OC_6F_5)_3(OPr^i)(^iPrOH)]_2{\cdot}C_7H_8$** 2 oct. sharing a $(\mu\text{-}OPr^i)_2$ edge	6	or. cr. yel. cr.	IR, ^1H, ^{19}F, X-r	292
$Ti(OSiMe_3)_4$	6	liq., 60/0.1 (b.), d^{20}_4 0.9051, n_D^{20}1,4278, α=1.2	IR, Raman, ebul.	49,235, 441, 491, 961
$Ti(OSiEtMe_2)_4$	6	colrl. liq., 86/0.1 (b.), d^{20}_4 0.9237, n_D^{20}1,4461, α=1	ebul.	235
$Ti(OSiEt_2Me)_4$	6	colrl. liq., 120/0.1 (b.), d^{20}_4 0.9248, n_D^{20}1,4545, α=1	ebul.	235, 491
$Ti(OSiEt_3)_4$	6	cr., 110 (m.), 150/0.1(b.), d^{20}_4 0.9408, n_D^{20}1,4689, α=1	ebul.	49, 235, 491, 1579
$Ti(OSiMe_2Pr^n)_4$	6	colrl. liq., 112/0.2 (b.), α=1.0	ebul.	235
$Ti(OSiMePr_2{}^n)_4$	6	colrl. liq., 190/3.5, d^{20}_4 0.9056, n_D^{20}1,4582	-	491
$Ti(OSiMe_2Pr^i)_4$	6	colrl. liq., 115/0.2 (b.), α=1.0	ebul.	235

$Ti(OSiPh_3)_4$	5, 6	colrl. sld., 480 (502 ? m), 360/10^{-4} (b.), d^{20}_4 1.215, n_D^{20}1,6488, low s. in tol.	-	491, 690, 1810
$Ti(OC_2H_4OMe)_4$ **$Ti(OC_2H_4OEt)_4$**	6	liqs., 183/3(b.), d^{18}_4 1.1910, n_D^{18}1,5077 n_D^{21}1,4920, d^{21}_4 1.1106	^{13}C -	293, 1205
$Ti[O(CH_2)_nO]_2$, n=2, 3 n=4-6	6	n=3, liq.,51/0.1(b.); yel. gl.	IR	438, 472, 1323
$Ti(CH_2O)_2(OR)_2$, R=Et, Pr^i, Bu^i, Bu^t	6	sld., m.: 145 (Et), 101(Pr^i)	-	1323, 1347
$Ti[CH_2(CHMeO)_2]_2 \cdot CH_2(CHMeOH)_2$	6			1768
$[Ti_4(\eta^2\text{-}C_2H_4O_2)_5(\mu\text{-}OR)(OR)_6Ti(OR)_3]$, R=$Pr^i$, struct. type of $Ti_4(OMe)_{16}$ CN 3 at. Ti 5, 1 at. Ti - 6 and 1 at. Ti 7	6	cr., s. in hex., α=2	^1H, X-r	1249
$Ti[CH_2(CHMeO)_2](OEt)_2$	6	liq., 140/0.06 (b.), n_D^{25} 1.5100, α=1		438
$[Ti_4(\eta^2,\mu_3,\mu\text{-}[RC(CH_2O)_3]_2)_2(OPr^i)_{10}]$, R= Me, Et , struct. type of $Ti_4(OMe)_{16}$, 1 of 3 at. O of RO_3- μ-$_3$, 2 at. μ-O, OPr^i-term.	6	colrl. cr., s. in tol., dec.: 88 (Me), 93 (Et)	IR, ^1H, ^{13}C, TGA, X-r	193
$Ti(C_6H_4O_2)_2 \cdot 2R(OH)_2$	4	-	-	605
$Ti(C_6H_4O_2\text{-}1,2)(OR)_2$ R=Et, Pr^i etc.	6	slds., red, yel., m.: 85, 112, s. in bz., α=1	cryosc.	438
$[Ti_2(O_2Ar)_2(OArOH)_4]_\infty$, Ar=$C_6H_4$-1,4 **$[Ti_2(O_2Ar')_2(OAr'OH)_2(OPr^i)_2]_\infty$**, Ar'=2,7-$C_{10}H_6$, networks of oct.	6	or. cr., s. in eth.	IR, X-r	1699

TiF$_n$(OEt)$_{4-n}$, n=1, 2, 3; **TiF(OPr^i)$_3$**	**n=1, 2**: cr., 143, 115 (m.); α=1, 4; **n=3:** gl., 125 (dec.), α=6	IR	259, 1199
TiCl$_3$(OMe)	cr., 185 (m.), 90/0.1$\rightarrow$ TiCl$_2$(OR)$_2$	-	49, 215, 623, 799, 1283
TiCl$_2$(OMe)$_2$ $\cdot$**L,** L=MeOH, N$_2$H$_4$, Hmpa, etc.	cr., 85 (m., dec.), d^{20}=1.582, s. in MeOH, CHCl$_3$, Me$_2$CO, α=1	IR, ^{1}H, m-s, cryosc.	
[Ti$_4$Cl$_2$(OMe)$_{14}$], struct. type of Ti$_4$(OMe)$_{16}$, Ti^2-Cl	cr., s. in tol.	X-r	
TiCl$_3$(OEt), $\cdot$**nL,** L=MeCO$_2$Et (n=1), MeCN(n=2), Diox (n=1.5)	yel. cr., 283 (m.), 185/atm., α=1.2-1.5, s. in hc., CH$_2$Cl$_2$	^{1}H, magn. prop.	215, 217, 253, 301, 472, 537, 561, 634, 693
[TiCl$_2$(OEt)$_2$]2, 2 5-vertex polyhedron sharing a (μ-OR)$_2$ edge $\cdot$**nL,** L=EtOH, MeCN, Diox, C$_5$H$_{10}$NH (n=1)	cr., 45 (m., dec.), 142/1(b.), α=2 105(m.), α=1.5 (EtOH)	X-r	
TiCl(OEt)$_3$, $\cdot$**C$_5$H$_{10}$NH**	oil, 136/2 (b.), α=3, μ=2.51	cryosc., magn.prop.	1217, 1205, 1204, 1725
TiCl$_3$(OPr^n)$_3$, $\cdot$**C$_5$H$_{10}$NH** **TiCl$_2$(OPr^n)$_2$,** $\cdot$**L,** L=2Py, C$_5$H$_{10}$NH, ROH	yel. cr., 66 (m.), 100/23 (b.) liq., 159/18 (b.), wh. sld.	-	560, 634, 1205, 1204,
TiCl(OPr^n)$_3$, $\cdot$**C$_5$H$_{10}$NH**	liq., 136/1 (b.), d^{25}1,1348, α=3	cryosc.	1283
TiCl$_3$(OPr^i), $\cdot$**L,** L=CO(NH$_2$)$_2$, RCONH$_2$, R$_2$CO **[TiCl$_3$(OPr^i)L]$_2$,** L=ROH, THF, PhCOOMe 2 octs. sharing a (μ-Cl)$_2$ edge	yel. sld., 85 (m.), 65/1 (b.), t$\rightarrow$TiOCl$_2$+RCl+polymer	IR, ^{1}H, ^{13}C electr. sp., magn. prop., X-r	49, 88, 215, 479, 624, 634, 1283, 1337

$[TiCl_3(OPr^i)L_2]$, oct.	colrl. cr.	IR, ^1H, ^{13}C, X-r	
L= Diox/2, [PhCHO, Et_2O]	yel. cr., Et_2O: 70/0.1 (b.)		
$[TiCl_2(OPr^i)_2(Pr^iOH)]_2$			1337, 1762, 1799
2 oct. sharing a $(\mu\text{-}OR)_2$ edge	yel. sld. 42 (m.), 70 (dec.)	electr. sp.	
$TiCl_2(OPr^i)_2 \cdot L$, L=Py, $CO(NH_2)_2$, $RCONH_2$			
$TiCl(OPr^i)_3$, $\cdot nNH_3$, n=1, 3	liq., α=1-2	cryosc.	
$TiCl_3(OBu^n)$. **nL,** L=NH_3 (n=3, 5), Py, Diox, MeCOOEt, (n=1), THF (n=2), BuOH (n=1, 2, 6)	cr., 71 (m.), 93/3 (b.), 150/0.5→ $TiCl_2(OR)_2$; α=1, syst. $TiCl_3(OR)$ - ROH (d, η, conduct.)	IR, ^1H, magn. prop.	49, 62, 215, 253, 472, 508, 560, 634, 1064
$TiCl_2(OBu^n)_2$, **$\cdot L$,** L= BuOH, THF, Diox, $C_5H_{10}NH$	liq., 130/4 (b.), α=2, 1 sld.	IR,^1H,X-r - parameters	1205, 1217, 1204, 1799
$TiCl(OBu^n)_3$, **$\cdot n\ NH_3$**	liq., 154/2 (b.), d^{20} 1.0985, n_D^{20} 1.5169, α=3	cryosc.	
$TiCl_3(OBu^i)$	sld., 82 (m.), 93/9 (b.), 138 (dec.)	-	1205, 1217, 1337
$TiCl_2(OBu^i)_2$, $\cdot$ROH, R= Me, Et, Bu^i	cr., 184/16 (b.)		
$TiCl(OBu^i)_3$	liq., 147/5 (b.), d^{20}1.1043, n_D^{20}1.5158	-	
$TiCl_3(OBu^s)$	bright yel. sld., 54 (m.)	-	1800, 1337
$TiCl(OBu^s)_3$	18 (m.), 128/2.5 (b.), n_D^{28}1.4636	cryosc.	
$TiCl_3(OBu^t)$	-		1132, 1337, 1800
$TiCl(OBu^t)_3$	liq., 79/1.5 (b.), n_D^{29}1,4543, α=1-2	cryosc.	
$TiCl_3(OC_5H_{11}{}^n)\cdot {}^nC_5H_{11}OH$	sld., 105/0,5 (b.)		433, 560
$TiCl(OC_5H_{11}{}^n)_3$	liq., 214/20 (b.)		
$TiCl_3(OC_5H_{11}{}^i)\cdot {}^iC_5H_{11}OH$	sld., 55 (m.), 110/17 (b.)		556, 1205, 1217, 1799

$TiCl_2(OC_5H_{11}{}^i)_2$	liq., 155/5 (b.), opt. isomers		
$TiCl(OC_5H_{11}{}^i)_3$	liq., 174/2 (b.), d^{20} 1.0600; $n_D{}^{20}$1,5092		
$[Ti_3(\mu_3\text{-}O)(\mu_3\text{-}Cl)(OC_5H_{11}{}^{neo})_9]$, trian.	cr., s. in tol., ins. in hex.	X-r	186
$TiCl_3(OC_5H_{11}{}^t)$	-		215, 1800
$TiCl(OC_5H_{11}{}^t)_3$	liq.,131/1(b.), $n_D{}^{29}$1,54634, α=1-2	cryosc.	
$TiCl_3(OC_6H_{13}{}^n)$	48 (m.), 120/8 (b.), $n_D{}^{20}$1.5092		472, 1205, 1217
$TiCl(OC_6H_{13}{}^n)_3$	liq., 182/1 (b.), $n_D{}^{20}$ 1.5060, d^{20} 1.0039		
$TiCl_3(OC_6H_{11}{}^c)$	bright yel. sld., 76 (m.)		1337
$TiCl(OC_7H_{15}{}^n)_3$	liq., 206/4 (b.)		472
$[TiCl_2(OCBu^t{}_3)_2]$	colrl. sld, s. in hex.	-	1030
$[Ti(\mu\text{-}Cl)_2Cl(OPh)]$ zigzag chains of oct., term. gr. *cis*-, **·PhOH**	yel. cr., α=3.0, μ=2,97	IR, Raman, ^1H, ^{31}P, electr.sp, m-s, X-r	479, 570, 584, 664, 706, 1035, 1055,1047, 1600
$[TiCl_2(OPh)_2]_2$ 2 trig. bipyr. sharing a $(\mu\text{-}OR)_2$ edge $\uparrow$>120°	red cr., α=1 (in s., m-s)		1719
2L, L=PMe_3, PPh_3, $(Ph_2P)_2(CH_2)_2$			1675, 1719
$TiCl(OPh)_3$	265/4 (b.)		
$TiCl_2(OAr)_2$, Ar=C_6H_4Me-2, -3 or –4, C_6H_4OR', R'=Me, Et	sld., s. in $CHCl_3$, CCl_4	IR, electr.sp.	706, 1047
***cis*-$[TiCl_3(OC_6H_3Me_2\text{-}2,6)THF_2]$**, oct.	red cr., 122 (m.), s. in THF-hex.	IR, ^1H, m-s,	504, 706, 876, 994, 1789

***cis*-, *cis*-**$[\mathbf{TiCl_2(OAr)_2THF_2}]$, oct., 2 Cl-ax $[\mathbf{TiCl_2(OAr)_2THF_3}]$ $[\mathbf{TiHal_2(OAr)_2}]_n$, Hal=Cl, Br $\mathbf{TiCl(OAr)_3}$	red cr., 85 (m.), s. in hex., α=1; red. sld. red cr., 64 (m.), exeption. s. in hc. liq., 480/2 (b.)	culonom., cryosc. X-r	
$[\mathbf{TiCl_3(OC_6H_3Bu^t_2\text{-}2,6)}]$, tetrah. $[\mathbf{TiHal(OAr)_3}]$, Hal=Cl, Br, I, tetrah. (I)	deep red cr., subl./vac., s. in C_5H_{12} colrl. cr., α=1	^{1}H culonom., X-r	994, 1079
$[\mathbf{TiCl_2(OC_6H_3Ph_2\text{-}2,6)_2}]$, tetrah. $[\mathbf{TiCl_2(OC_6H_3Ph_2\text{-}2,6)_2THF_2}]$, oct.	red cr., s. in tol., hex.	X-r	480, 876
$\mathbf{TiCl_{4-n}(OC_6H_2Me_3\text{-}2,4,6)\cdot mL}$, L=Py, RNH_2, THF etc. (m=2) L=Py, Dipy etc (m=1)	sld., α=1	IR, ^{1}H, DTA cryosc., m-s	1463
$[\mathbf{TiCl_2(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2}]$ $[\mathbf{TiCl(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(OR)}]$ R=Et, Bu^t	red-brn. sld., 176 (m.) or. sld.,121 (m.) **-Et,** yel.-or. sld., 183 (m.)**-Bu^t**	-	504
$[\mathbf{TiCl_2(OC_6H_2Bu^t_3\text{-}2,4,6)_2}$	cr., 288 (m.)	^{1}H	854
$[\mathbf{TiCl_2(OC_{10}H_7\text{-}\beta)_2}$	blk.cr., s. in $CHCl_3$, CCl_4	IR, electr.sp	599, 1047
$\mathbf{TiCl_n(OCH_2CF_2CHF_2)_{4-n}}$, n=1 n=2; 3 $[\mathbf{TiCl_2(OC_2H_4Cl)_2(ClC_2H_4OH)}]_2$ – ***cis*,** 2 octs. sharing a (μ-OR)$_2$ edge, · **nL,** L=Hmpa,Ph_3PO $[\mathbf{TiCl_2(OC_2H_4Hal)_2(HalC_2H_4OH)_2}$, Hal=Br, I	yel. oil, 145/12 (b.) cr., 84 (m.),126/12 (b.); oil, 145/12 cr., s. in CH_2Cl_2 wt. sld.	- IR, ^{1}H, ^{13}C {^{1}H}, conduct.	690, 1217, 1283, 1754
$\mathbf{TiCl(OCMe_2CCl_3)_3}$	-	-	233

$TiCl_n(OSiMe_3)_{4-n}$, n=1 n=2; 3	sld., 32 (m.), 67/9 (b.), d^{20}_4 1.305 liq., 72/3 (b.), d^{20}_4 1.155.;103/10 (b.)		49
$TiCl_3(OC_2H_4OMe)$ **$TiCl(OC_2H_4OEt)_3$**	sld., 166 (m.), 170/5 (subl.) liq., 182/1 (b.), d^{20} 1.2035, n_D^{20} 1.5178,	-	1205, 1217
$[TiCl_2(\eta^2,\mu\text{-}RO_2)THF]_2$-*trans* 2 octs. sharing a $(\mu\text{-}OR)_2$ edge **$[TiCl(\eta^2,\mu\text{-}RO_2)]_2(\eta^2\text{-}OROH)]_2$**, R=$[CH_2]_3$, 2 octs. sharing a $(\mu\text{-}OR)_2$ edge	cr. cr.	^1H, ^{13}C $\{^1H\}$, X-r	777
$(TiCl_3)_2(3\text{-}MeC_6H_9{}^cO_2\text{-}1,2)$ **$(TiCl_3)_2(C_5H_8{}^cO_2\text{-}1,2)$, · R_2CO** **$TiCl_2(C_6H_4O_2\text{-}1,2)$** **·2L**, L=Py, THF	slds.. 133 (m.) blk. sld. sld., red (Py), brn. (THF)	IR, ^1H, ^{13}C IR, Raman, ^1H, m-s.	570, 88
$TiBr_n(OR)_{4-n}$ · L, L=ROH, R'COOR R=Et, Pr^n, Pr^i,Bu^n, Bu^s, $C_{10}H_7$; n=1, 2, 3;	yel.-brn. slds. or liq., ~100/2 (b.), vol. in vac.	-	253, 532, 1205, 1204, 1675
$[LiTi(OR)_5]_2$, R=Pr^i, $C_5H_{11}{}^{neo}$, struct. type of $Ti_4(OMe)_{16}$, trig. bipyr. $[Ti^2]$, tetrah. $[Li^1]$	wh.cr.,low s. in tol., α=2 (in bz.), 1(gas)	IR,^1H,^7Li, ^{13}C, ^{17}O, DTA, X-r, cryosc.	187, 187, 703
$[LiTiO(OPr^i)_3]_4$ = $[Li_4Ti_4(\mu_5\text{-}O)_2(\mu_3\text{-}O)_2(OR)_4]$, in centre -2 cubes $[Li_2Ti_2O_4]$ sharing a face $[Ti_2(\mu_5\text{-}O)_2]$, 2 trig. bipyr. $[Ti(\mu_5\text{-}O)_2(\mu\text{-}OR)_3(OR)]$	clrl. cr., s. in THF, hex.	IR, ^1H, $^{13}C\{^1H\}$, X-r	970

$[NaTi(OR)_5]_\infty$, $R=Pr^i$, $C_5H_{11}{}^{neo}$, zigzag chains of tetrah. $[Na(\mu\text{-}OR)_4]$ and trig. bipyr. $[Ti(\mu\text{-}OR)_4(OR)]$	colrl. cr., s. in ROH	IR, ^1H, ^{13}C, ^{17}O, ^{23}Na, DGA, X-r	187, 187, 703, 1691
$[KTi(OR)_5]_\infty$, $R=Pr^i$, $C_5H_{11}{}^{neo}$, zigzag chains of trig. bipyr.$[K(\mu_3\text{-}OR)_2(\mu\text{-}OR)_3]$ and $[Ti(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)]$ **$KTi_2(OPr^i)_9$**	colrl. cr., s in bz., tol., $\alpha=2$ (Pr^i), 1 ($C_5H_{11}{}^{neo}$) s. in bz.,	IR, ^1H, ^{13}C, ^{17}O, DGA, X-r	187, 187, 1688, 1691
$Na_2Ti(C_2H_4O_2)_3 \cdot 4C_2H_4(OH)_2$ **$K_2[Ti(C_2H_4O_2)_3] \cdot 2.5\ C_2H_4(OH)_2$** $=\{K[R(OH)_2]_2\}_2{}^+[Ti(\eta\text{-}RO_2)_3]^{2-} \cdot 0.5\ R(OH)_2$, anion - oct.	cr., s. in MeOH, MeCN	IR, ^1H, ^{13}C, X-r	610
$[NH_4]_2[Ti(\eta^2\text{-}C_6H_4O_2\text{-}1,2)_3] \cdot 2H_2O$	red.cr.	IR	170
$K_4[TiO(\eta^2\text{-}C_6H_4O_2\text{-}1,2)_2]_2 \cdot nH_2O$, n=9, 2; anion $[Ti_2(\mu\text{-}O)_2(RO_2)_4]$ -2 octs.	yel. cr., red	IR, X-r	170
$[CuClTi_2(OPr^i)_9]$, isostr. with its Zr-analog	grn. cr., s. in s. in tol.-hex., $\alpha=1$	IR, ^1H, ^{13}C, X-r	1664, 1686, 1690
$[Mg_nTi_{4-n}(OEt)_{16-2n}(EtOH)_{2n}]$= $[Mg_nTi_{4-n}(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_{10-2n}(ROH)_{2n}]$, n=0-2, struct. type of $Ti_4(OMe)_{16}$	colrl. cr., ins. in EtOH, s. in system (20°)	X-r	1773
$[MgTi_2(OEt)_8Cl_2]_2$ gr. $[Ti_2(\mu\text{-}OR)_3(OR)_5Cl]$ - 2 octs., oct. $[Mg(\mu_3\text{-}OR)_2(\mu\text{-}OR)(\mu\text{-}Cl)_3]$, in the centre- gr.$[Mg_2Cl_2]$	colrl. cr., 214(m), s. in C_7H_{16}, $\alpha=1$	IR, ^1H, cryosc., X-r	1061
$M_2Ti(OEt)_8(EtOH)_5$, M=Sr,Ba	colrl. cr., 65 (m. dec., Sr), 125 (m., Ba)	IR, ^1H, ^{13}C, TGA	125

$[Sr_2Ti(OPr^i)_8(^iPrOH)_3]\cdot 2^iPrOH$ isostruct with $[Ba_2Zr(OR)_8(ROH)_3]\cdot 2ROH$	colrl. cr., 52 (m.), s. in common solvs.	IR, ^1H, ^{13}C, TGA, X-r	125, 306
$Sr(^iPrOH)_2[Ti_2O(OPr^i)_7]_2$, 2 trian. $[SrTi_2]$, gr. $[Ti_2O(OR)_7]$ -2 trig. bipyr. sharing a $[(\mu_3\text{-}O)(\mu\text{-}OR)]$ edge -connected with Sr oct.	colrl. cr.	X-r.	1519
$[Sr_6Ti_4(\mu_4\text{-}O)_4(OPr^i)_{20}]$, on 8 faces of oct. $[Sr_6]$-4 μ_3-OR and 4 $[OTi(OR)_4]$, $[SrO_6]$ - oct.	colrl. cr.	X-r	1519
$[Ba_2Ti_4O(OMe)_{18}(MeOH)_7]\cdot MeOH$, gr.- $[Ti_2O(OR)_8]$, $[Ti_2(OR)_{10}]$, $[Ba(ROH)_2]$, $[Ba(ROH)_5]$, CN Ba 9	colrl. cr., s. in system .$M(OR)_2$-$Ti(OR)_2$-ROH (20°)	X-r	946, 1523
$M[Ti_2(OEt)_9]_2$, M=Ca, Sr, Ba, isostruct with its Zr-analog	colrl. cr., 125 (m., Sr) 129 (m., Ba), s. in ROH 12%, s.$M(OR)_2$-$Ti(OR)_2$- ROH (20°)	IR, ^1H, ^{13}C, TGA, X-r	125, 1611, 1626, 1631, 1783
$MTi_2(OEt)_{10}(EtOH)_5$, M=Ba,Sr **$[BaTi_2(OEt)_9(EtOH)_4]^+[H(OEt)_2]^-$**	colrl. cr. , m.: 85 (Sr), 40 (Ba), s. in ROH 14% (Ba)	IR, ^1H, ^{13}C, TGA, X-r	125,1783
$Ba_4Ti_2O(OEt)_{14}\cdot 8EtOH$ isostr. with its Zr-analog	colrl. cr., s. in ROH 24%	IR, m-s	1631
$Ba[Ti_2(OPr^i)_9]_2$	colrl. cr., high s. in hc.	IR, ^1H, ^{13}C, cryosc., X-r	1686
$[BaTi_2(OPr^i)_{10}]_2$, isostr. with its Zr-analogs	colrl. cr., s. in hc., α=1		
$[BaTi_3(OPr^i)_{14}]$ 2 oct. $[Ti_2(OR)_9]$ and trig. bipyr. $[Ti(OR)_5]$ shares 3 $(\mu\text{-}OR)_2$ edge with at. Ba, CN Ba 6	colrl. cr., high s. in ArH, hex, THF, α=1; t/vac $\rightarrow Ti(OR)_4\uparrow$		

$[BaTiO(OPr^i)_4(^iPrOH)_{7/8}]_4$ in the centre – cube $[Ba_4O_4]$, 2 gr. $[TiO(\mu_3\text{-}OR)(\mu\text{-}OR)(OR)_2]$ - tetragon. pyr., CN Ba 6; 2 gr. $[TiO(\mu\text{-}OR)_3(OR)]$ trig. bipyr., CN Ba 7	colrl. cr.	X-r	619, 1783, 1787
$[BaClTi_2(OPr^i)_9(^iPrOH)]$ trian. $[M_3]$, 2 oct. Ti and oct. $[Ba(OR)_4Cl(ROH)]$		X-r	306
$[BaITi_2(OPr^i)_9]_2$, isostr. with its Zr-analog		X-r	1691
$[BaTi_2(OC_5H_{11}{}^{neo})_{10}Py_2]$, angular mol., oct. *cis*-$[BaPy_2(\mu\text{-}OR)_2]$	cr., s. in hex., tol., THF, Py	X-r	191
$[(BaDmfa)_2Ti_2(OPh)_{12}]$ struct. type of $Ti_4(OMe)_{16}$, 2 oct. $[Ti^2O_6]$ and 2 8-vertex polyhedrons $[Ba^1O_8]$ sharing a face	brn. cr., s. in Et_20	X-r	456
$BaTi(OC_2H_4OMe)_6$ (?), $+H_2O\rightarrow$ **$[Ba_4Ti_{13}(\mu_5\text{-}O)_6(\mu_3\text{-}O)_{12}(OC_2H_4OMe)_{24}]$** spheric mol. - 1 central and 12 peripheric $[TiO_6]$ oct., $[BaO_9]$ - gr. on the surface of the sphere	wh. sld. colrl. cr., s. in ROH	^{13}C IR, ^1H, ^{13}C, X-r	293
$[CdITi_2(OPr^i)_9]$, isostr. with its Zr-analog	colrl. cr., high s. in tol.	^1H, ^{13}C, ^{113}Cd, X-r	1686, 1688, 1687
$[CdM^{II}Ti_2(OPr^i)_{12}]_2$, M^{II}= Ba, Sr, Ca, isostr. with its Zr-analogs	colrl. cr., high s. in tol.-ROH, α=1	^1H, ^{13}C, ^{113}Cd, X-r	1687, 1686, 1690, 1691
$[YCl_2Ti_2(OPr^i)_9]$, isostr. with its Zr-analog **$YCl[Ti_2(OPr^i)_9]_2$**	colrl. cr., high s. in tol.-ROH, α=1	^1H, ^{13}C, X-r	1686, 1691

$ErTi_2O(OEt)_9(EtOH)]_2$, below and over the planar $[Ti_2Er_2]$ cycle - 2 $[Ti(\mu_4\text{-}O)(\mu_3\text{-}OR)(\mu\text{-}OR)_2(OR)]$ gr., Ti oct., CN Er =8	colrl. cr., 102 (m.), s. in tol., hex.	IR, electr. sp, DTG, X-r	1735
$[Ln_4TiO(OPr^i)_{14}]$, Ln=Sm, La, Pr, Nd	-	-	444, 442
$SnI_2[Ti(OPr^i)_5]_2$, angular mol, in the centrum – *cis*-$[SnI_2(\mu\text{-}OR)_4]$ oct., CN Ti 5			
$\{SnI[Ti_2(OPr^i)_9]\}_2$	yel. flakes, s. in tol.	^1H, ^{13}C, ^{119}Sn	1688
$[Pb_2Ti_2O(OPr^i)_{10}]$ $=[Pb_2Ti_2(\mu_4\text{-}O)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_4]$ in tetrah. $[OPb_2Ti_2]$ - ψ-oct. $[:PbO_5]$, oct. Ti	colrl. cr., s. in tol., low s. in ROH	IR, ^1H, ^{13}C, ^{207}Pb, X-r	447
$[NaPb_2Ti_2O(OPr^i)_{10}]^+Cl$	-	-	782
$[BiTi_2O(OPr^i)_9]$, trian. $[M_3]$, 2 oct. Ti sharing a $[O(OR)_2]$ face and $[O(OR)]$ edge with ψ- 5-vertex polyhedron $[BiO_4]$	colrl. crs., s. common org. solvs.	IR, ^1H, X-r	1258
$[BiTi_2O(OEt)_9]$, **$[Bi_4Ti_3O_4(OPr^i)_{16}]$**			
$[Ti_3(OEt)_{11}]^+[Mn(CO)_5]^-$, cation - trian. $[Ti_3(\mu_3\text{-}OR)_2(\mu\text{-}OR)_3(OR)_6]^+$, 3 oct. Ti	or. cr., s. in bz., THF, eth., MeCN	X-r	135
$[(COD)Rh]_2[Ti(OPr^n)_6]$ linear mol., oct. $[Ti(\mu\text{-}OR)_4(OR)_2]$-*cis*	yel. cr., s. in tol.	^1H, X-r	455
$M_2[Ti(\eta^2\text{-}C_6H_4O_2\text{-}1,2)_3]$, M=$NH_4$, Et_3NH, Na ($7H_2O$), Mg, Ba, Zn, Ni, anion - oct.	red or yel. cr.	IR, X-r	170, 605
$[Et_3NH]_2[Ti(ArO_2)_2[ArO(OH)]_2 \cdot 2CHCl_3$, Ar=3,5-$Bu^t_2C_6H_2$-1,2	red cr.	IR, X-r	170

$M_2[TiCl_5(OR)]$, M= PyH, Et_3NH, R=Et, Pr^i **$M[TiCl_4(OEt)(MeCN)]$**, **$[Et_3NH]^+[TiCl_4(OPr^i)THF]^-$**, anions - oct.	grn. or yel. cr., in MeCN, ins. in ROH	^1H, ^{13}C, X-r	561, 624
$TiZrCl_4(OPh)_4$	yel. sld., ins. in hc.	IR, cryosc.	1712

- In the technology of refractory coatings,
- As additives to pigments, promoting their drying,
- As binding and modifying (providing hydrophobic properties) agents for cellulose,
- As additives to motor fuels,
- leaching agents on cloth painting,
- in the cosmetic industries,
- in the production of dielectric and protective coatings based on polyorganotitanoxanes and -siloxytitanoxanes; and recently
- In the production of TiO_2 and titanate-based inorganic materials (films, coatings, powders, and ceramics).

12.12. Zirconium and hafnium alkoxides

The synthesis of zirconium and hafnium alkoxides was first carried out by Meerwein and Bersin [1101] in 1929. They found out that the formation of $Zr(OR)_4$ on metathesis of $ZrCl_4$ with NaOR is hindered by the rather high stability of the bimetallic complexes formed. To achieve decomposition they introduced steicheiometric amounts of dry HC1. All the major $M(OR)_4$ derivatives for both metals were prepared and investigated by Bradley at the beginning of the 1950s [223]. The practical aspect of these works was connected with the search for the separation and purification routes for the derivatives of zirconium and hafnium — products of nuclear reactions, components in mineral raw materials, and so on. Application of zirconates and also titanate-zirconates in modern electronics stimulated the studies of bimetallic derivatives of Zr and alkaline earth metals and also lead, copper, and so on that were carried out at the beginning of the 1990s by Caulton *et al.* [970, 1385, 1387, 1389, 1565,1662–1664]. Of considerable interest are also the recent studies by Veith *et al.* on alkoxohalogenozirconates of Ba, Cd, Pb, and Bi — precursors of trimetallic complexes with peculiar structure [1686–1689, 1691].

12.12.1. Synthesis.

That was in fact for zirconium alkoxides that Bradley developed all the major synthetic approaches to the alkoxides of high-valent metals—metathesis of $ZrCl_4$ or (more preferably $[PyH]_2ZrCl_6$) with ammonia [201]* (method 5), alcoholysis of $Zr(NR_2)_4$ [1579] (method 4), alcohol interchange reactions

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* Application of alkali alkoxides is impossible in this reaction because of formation of rather stable alkoxozirconates [115].

starting from isopropoxide [224] (method 6, see also Section 2.6). The preparation of $Zr(OR)_4$ and $Hf(OR)_4$ was also very efficiently carried out by anodic dissolution of metals in alcohols (method 2). The samples purified from LiCl by extraction with hexane, usually still contain about 0,5% Cl in the form of alkoxide chlorides, volatile and soluble in hydrocarbons. The solubility of $M(OPr^i)_4 \cdot {}^iPrOH$ in ^iPrOH increases rapidly with the increased temperature, and therefore, the Li and Cl impurities can easily be diminished to < 0.1% values by recrystallization [1612]. This result is fairly good as the purification of the majority of these derivatives by distillation or sublimation is impossible in contrast to the data published earlier in literature (see below).

12.12.2. Properties

The majority of "$Zr(OAlk)_4$" and "$Hf(OAlk)_4$" described in literature are amorphous solids or viscous liquids. In contrast to the traditional concepts these are not individual compounds. According to the mass-spectrometry and proton NMR data they contain big amounts of oxocomplexes like $M_3O(OR)_{10}$, $M_4O(OR)_{14}$ along with $M(OR)_4$ in their composition. The same concerns the desolvation products of $M(OR)_4 \cdot ROH$ ($R = Pr^i, Bu^i$), having the "$M(OR)_4$" average composition that contain according to IR and X-ray powder data the residual quantities of nondecomposed solvates [1612]. It is especially interesting that the data on molecular complexity of many "$M(OR)_4$" in benzene solutions reported by many authors practically coincide with the data on "stability" of the corresponding aggregates in thir mass-spectra. ("Stability" is the ratio of the intensity of an individual ion to the total intensity for all ions observed.) The average for the molecular complexity is observed at 3.1 to 3.6 for the majority of derivatives, which corresponds to the presence of tri- and tetranuclear oxocomplexes. The same situation takes place supposedly for a number of alkoxides, for which the data on molecular complexity are missing (isomeric amyloxides, n-octyloxide, and so on). Their compositions are therefore placed in citation signs in Table 12.13.

The triangular molecules of $Zr_3O(OR)_9X$, (X = Cl, OH, OR) type, centered by two groups — μ_3-O and μ_3-X — have been discovered in the structures of products crystallizing in the syntheses of "$Zr(OR)_4$". Thus crystalline oxocomplexes of $Zr_3O(OBu^t)_9(OH)$ and $Zr_3O(OC_5H_{11}^{neo})_9Cl$ compositions [543] are formed in the metathesis of $ZrCl_4$ with the alkali alkoxides in 1:4 ratio (and proper protection against moisture), while a prolonged storage of an electrolyte obtained by anodic oxidation of metal in ^tBuOH gave $Zr_3O(OBu^t)_{10}$

Table 12.13. Zirconium and hafnium alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
Zr				
"Zr(OMe)$_4$↓"	6	sld. wh.	-	236
«Zr(OMe)$_3$(OBu^t)»		sld. wh., invol.	-	225
Zr$_{13}$O$_8$(OMe)$_{36}$= $[Zr_{13}(\mu_4\text{-}O)_4(\mu\text{-}O)_4(\mu\text{-}OR)_{24}(OR)_{12}]$, dist. central [$[ZrO_8]$ cube connected to 12 $[ZrO_2(\mu\text{-}OR)_4(OR)]$	hyd-rol.	colrl. cr., s. in MeOH	X-r	1173
"Zr(OEt)$_4$"	2,5,6	wh. sld., amor., 180/0,1 (subl.), s. in hex.> bz.,CCl_4, α=3,6 (bz); 2,5 (ROH), in m-s $[M_4O(OR)_{13}]^+$	IR, m-s, ebul., thermolysis	38, 236, 201, 225, 213, 1111, 1599, 1612
"Zr(OPr^n)$_4$"	5, 6	liq., 208/0,1 (b.)		236, 224, 1111
"Zr(OPr^i)$_4$" ↑- ROH(120°/0.1)	5, 6	visc. liq. or gl., 105-120(m.), 160/0.1(b.); in IR- ν OH; p-T (polytherm); α= 3.6 (bz.), 2 (ROH)	IR, ebul., cryosc.,m-s, DTG, X-r powd.	201, 213, 220 225, 235, 236 494, 1612

$[Zr(OPr^i)_4 \cdot {}^iPrOH]_2$ (2 forms ?) [193, 1665] 2 oct. sharing a(μ-OR)$_2$ edge, 2 bonds ROH...OR between 2 pairs of ax. gr.	2, 4, 5, 6	colrl. cr., ~140 (m.), 90/0.1→ ROH +R_2O + $Zr_3O(OR)_{10}^+$.., s. in THF, hex, bz., s. in ROH (polytherm), 1.5% (20°)	IR, ^{1}H, m-s, tensim., X-r, X-r powd.	193, 201,915, 951, 801, 143 1612, 1665
$[TiZr(OPr^i)_8({}^iPrOH)_2]$, statist. distrib. of Ti and Zr at.		-	X-r	1689
$[Zr(OPr^i)_4 \cdot L]_2$, L=Py, THF, N_2H_4,En/2,		colrl. cr.		92
"$Zr(OBu^n)_4$"	2, 5, 6	visc. colrl. liq., slowly→ gl., s. in inorg.s. in, ~100 (m. in 5 monts), 260(243)/0.1 (b.), α =3.4, in m-s $[M_4O(OR)_{13}]^+$	IR, ebul., m-s	236, 201, 225, 224, 1111, 1612
$Zr(OBu^i)_4 \cdot {}^iBuOH$	2, 6	wh. sld.,145 (m.,dec.),100°/vac. →ROH; in m-s $[M_4O(OR)_{13}]^+$	IR, m-s, X-r powd.	1612
«$Zr(OBu^s)_4$» (·**ROH** - does not exist)	2, 5, 6	visc. colrl. liq., slowly→gl., ~100 (m. in 5 monts), 164/0,1 (b.), α= 2,4 (ROH), in m-s - $[M_3O(OR)_9]^+$	IR, ebul., m-s	201, 236, 1111, 1612
$Zr(OBu^t)_4$	2, 4,5, 6	colrl. liq., d° 0.9845, 55/0.2 (b.); 96 (dec.), α= 1, p-T (polytherm)	ebul., m-s, tensim., surface tens., TGA	213, 236,201, 225, 230,234, 235, 1111, 1565, 1386, 1579

«$Zr(OBu^t)_3(OMe)$», «$Zr(OBu^t)_2(OMe)_2$»	6	cr., α=2.16 (bz.), 4.53 (bz.)	ebul.	1113
$Zr(OBu^t)_2(OEt)_2$	6	liq., 175/0.5 (b.)	ebul.	1113
$Zr_3O(OBu^t)_{10}$, trian. [M_3], 3 oct.	2	colrl. cr.	X-r	1520
$Zr_3O(OBu^t)_9(OH)$, trian. [M_3]	5	colrl. cr., s. in tol., hex.	^1H, ^{13}C , X-r	543
$Zr(OMe)(OBu^t)_3$	6	colrl. cr.,60-70 (m.)	-	201
«$Zr(OEt)(OBu^t)_3$»	5	colrl.cr., 110-130(m.); t/vac→ $Zr(OBu^t)_4\uparrow$	-	201
«$Zr(OC_5H_{11}{}^n)_4$»	6	colrl. liq.,256/0.01(b.); α= 3.2	ebul.	236, 225
«$Zr(OC_2H_4Pr^i)_4$»	6	colrl. gl., 247/0.1 (b.); α=3.3	ebul.	225
«$Zr(OCH_2CHMeEt)_4$»	6	gl., 238/0.1 (b.); α=3.7	ebul.	225
«$Zr(OC_5H_{11}{}^{neo})_4$»	6	colrl. cr., 150 (m.), 176/0.05 (b.); α=2.4	ebul.	225
«$Zr(OCHEt_2)_4$»	6	gl. liq., 181/0.1 (b.); α= 2	ebul.	225
«$Zr(OCHMePr^n)_4$»	6	liq., 175/0.08 (b.); α= 2	ebul.	225, 230
«$Zr(OCHMePr^i)_4$»	6	sld., 156/0.01 (b.); α= 2	ebul.	225
$Zr(OC_5H_{11}{}^t)_4$	6	colrl. liq.; d^0 0.9960; 95/0.1(b.); stab.<220; p-T (polytherm); α=1.0	ebul.,tensim, surface electr.sp.	225, 230, 234, 213, 1261
$Zr(OC_5H_{11}{}^t)_3(OMe)$	6	liq., -80° - gl., 180°→ $Zr(OC_5H_{11}{}^t)_4\uparrow$	ebul.	1113
»$Zr(OC_6H_{13}{}^n)_4$»	4, 6	visc liq., b./10^{-5}, 310/0.5 (dec.)	-	225, 239
$Zr(OCHMeBu^n)_4$	6	liq., 190/0,1(b.)		225

$Zr(OCHMeBu^t)_4$		liq. (sld.-78),128/0.1(b.); α=1	ebul.	225, 1261
$Zr(OCMeEt_2)_4$	6	colrl. liq., d^o 1.0092; α=1, 150/1.2 (b.); p-T (polytherm)	tensim.,ebul. electr. sp.	225, 230, 1261
$Zr(OCMe_2Pr^n)_4$	6	yel. liq., d^o 0.9719; 133/0.7(b), p-T (polytherm); α=1	tensim.,ebul. surface tens.	225, 230
$Zr(OCMe_2Pr^i)_4$	6	pale yel. liq.,133/0.1(b.);α=1	ebul.	225,
»$Zr(OC_7H_{15}{}^n)_4$»	4	visc. liq., b. /10^{-5}	-	239, 224
$Zr(OCHPr^n{}_2)_4$; $Zr(OCHPr^i{}_2)_4$	6	liq., 163/; 158/0.1 (b.); α=1	ebul.	225
$Zr(OCEt_3)_4$	6	colrl. gl., 180/0.4 (b.); α=1	ebul., electr.sp	225, 1261
$Zr(OCMe_2Bu^t)_4$	6	yel. sld., 168/0.5 (b.); α=1	ebul.	225
$Zr(OCMeEtPr^i)_4$	6	colrl. liq., 194/0.7(b.); α=1	ebul.	225
»$Zr(OC_8H_{17}{}^n)_4$»	4, 6	visc. liq., b. /10^{-5} , α= 3.4	ebul.	224, 239
$Zr(OCHMeC_6H_{13})_4$	6	liq., 212/0.1 (dec.), α= 1.7	ebul.	236, 225
»$Zr(OC_9H_{19}{}^n)_4$»	4	mobil liq., b. /10^{-5}	-	239
$Zr(OCHBu^n{}_2)_4$	6	gl., 198/0.1(b.)	-	225
»$Zr(OCH_2Ph)_4$»	4	visc. liq., t/10^{-4} →ROH	-	585
$Zr(OPh)_4 \cdot nL$, L=Py, Dipy, Phen, n=2, 1	4	colrl. cr., s. in bz.	IR, ebul.	1057, 824
$Zr(OC_6H_3Pr^i{}_2\text{-}2,6)_4$	4	wh. sld.,s. in hex.	^1H	509
$Zr(OC_6H_2Me_3\text{-}2,4,6)_4$, **$Zr(OC_6H_3Bu^t{}_2)_4$,** **$Zr(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_4$**	4	colrl. cr., s. in in ArH (t), α= 1	IR,^1H, cryosc., m-s, TGA	1463
$Zr(OCMeEtCH{=}CH_2)_4$	6	colrl. liq., α=1	IR, ^1H,ebul.	655

$Zr[OCMe_2(CF_3)]_4$	6	liq., $60/10^{-2}$ (b.), 106 (dec.), s. in hc., v. s. in C_6F_6	^1H, ^{19}F,	1386
$Zr[OCH(CF_3)_2]_4$	5, 6	wh. sld., 111(m.), $70/10^{-2}$ (subl.), 82(dec.), s. in hc., C_6F_6, α=1 (m-s),1.8 (bz.)	IR, ^1H, ^{19}F, m-s, TGA	1387, 1386, 880, 1085
$Zr[OCMe(CF_3)_2]_4$ tetrah.+3 bonds Zr...F	6	wh. sld., $40/10^{-2}$(subl.), 98 (dec.), s. in hc., v. s. in C_6F_6	IR, ^1H, ^{19}F, X-r	1387, 1386
$Zr[OC(CF_3)_3]_4$	6	wh. sld., $35/10^{-2}$(subl.), 96 (dec.), s. in hc., v. s. in C_6F_6	^1H, ^{19}F	1386
$Zr(OC_2H_4Cl)_4$, $Zr(OC_3H_6Cl)_4$, **$Zr(OCH_2CCl_3)_4 \cdot 2Me_2CO$,** **$Zr(OCMe_2CCl_3)_4$**	4, 6	-	-	233, 531
$Zr(OSiMe_nEt_{3-n})_4$, n=0-3	6	wt.sld., s.in ArH; α=1 (2, n=3), m: 152,105, 30, liq.; subl./0.1; 135, 105,120,147	-	235
$Zr(OSiMe_2Pr^n)_4$, $Zr(OSiMe_2Pr^i)_4$	6	60 (m.), liq., 110 /0.1(subl.)		235
$Zr(OSiPh_3)_4$	5	410(m.), $360/10^{-4}$ (subl.)		690
$Zr[OSi(OBu^t)_3]_4$, **$\cdot\cdot H_2O$**, trig. bipyr., H_2O-ax.	6	150(dec.), s. in hex., α=2, 100° $\rightarrow ZrSiO_4$(amor.) +SiO_2	IR, ^1H, TGA, X-r	2, 1571, 1032
$Zr(OC_2H_4OMe)_4$, **$Zr[O(CH_2)_nOR]_4$**	2, 6	colrl. liq., in m-s -$[M_3(OR)_7]^+$,	IR, m-s	825, 1612, 1652
$Zr[(OCH_2\text{-})_2]_2$, **$Zr[(OCHMe\text{-})_2]_2$,** **$Zr[(OCMe_2\text{-})_2]_2 \cdot R(OH)_2$**	6	wh. sld., s. in $R(OH)_2$	IR, ebul.	1408
$[Zr(C_6H_4O_2H)_2(C_6H_4O_2\text{-}1,2)] \downarrow$ **$[Zr(C_{10}H_6O_2\text{-}\alpha,\alpha)_2]_2$, $\cdot 2Am$,** **$Zr(OC_6H_4\text{-}C_6H_4O)_2$**	4	s. in in Me_2CO, THF, ins. in hc.	-	46

$\{[Zr_4[RC(CH_2O)_3]_2(OPr^i)_{10}\}$, R=Me,Et, 4 oct .$[Zr(\mu\text{-}O)_4(OPr^i)_2]$ joined in a cycle	6	colrl. cr, 90 (dec.), s. in tol.	IR, ^1H, ^{13}C, TGA, X-r	193
$ZrCl_n(OMe)_{4-n}$, n=1, 2		s. in CCl_4, bz.	-	201
$ZrCl_3(OEt)$, ·L, L=EtOH, AcCl		cr.,100/1 (b.), s. in ROH, bz.	-	201, 1113
$ZrCl(OPr^n)_3$		visc. liq., b. /10^{-4}	-	239
$ZrCl_n(OPr^i)_{4-n}\cdot{}^iPrOH$, n=1, 2, $[ZrCl_3(OPr^i)L_2]$, L=^{i}PrOH, THF, $[ZrBr_2(OPr^i)_2]$		colrl.cr., s. in CH_2Cl_2, hex.	^1H	201, 613, 915, 881
$ZrCl(OBu^n)_3$		visc. liq., b. /10^{-3}	-	239
$ZrCl(OBu^t)_3$, ·2Py		does not react with NaOR	-	201, 1131
$ZrCl(OC_5H_{11}{}^t)_3$		-	-	201
$Zr_3OCl(OC_5H_{11}{}^{neo})_9$= $[Zr_3(\mu_3\text{-}O)(\mu_3\text{-}Cl)(\mu\text{-}OR)_3(OR)_6]$ trian. $[M_3]$, 3 oct. $[ZrOCl(OR)_4]$		colrl. cr., s. in tol., hex., THF	^1H, ^{13}C, X-r	543
$ZrCl(OR^n)_3$, R=C_6H_{13} - C_9H_{20}		visc. liq., b. /10^{-5}	-	239
$ZrCl_2(OCBu^t{}_3)_2$		colrl. cr., s. in hex.	-	1030
$ZrCl(OPh)_3$, $ZrCl_2(OAr)_2$, Ar=Ph, C_6H_4-1, -2		wh. sld., ins. in hc.	IR, conduct.	824, 1057, 1395
$[ZrCl_2(OC_6H_3Me_2\text{-}2,6)_2THF_2]$, oct., 2 Cl -ax. $[ZrCl_3(OC_6H_3Me_2\text{-}2,6)THF_2]$		colrl. cr., 153 (m.,dec) colrl. cr., 142 (m.,dec)	^1H, m-s, X-r	876, 1789
$[ZrCl(OC_6H_3Bu^t{}_2\text{-}2,6)_3]$		yel. cr., s. in ArH (t), t→ MCl_4+$M(OAr)_4$	IR, ^1H,	322, 994

$ZrCl_n(OC_6H_2Me_3\text{-}2,4,6)_{4-n}$, n=1-3, ·**2L,** L=Py, Am, THF	colrl. cr., s. in ArH decreases with «n», α=1	IR, ^1H, ebul., cryos. in, TGA	1463
$[ZrCl_2(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2]$	colrl.cr.,185(m.), s.in eth.,hc.	IR, ^1H, ^{13}C	504
$[ZrCl_2(OC_6H_2Bu^t_3\text{-}2,4,6)_2$	-	^1H	854
$ZrCl(OCMe_2CCl_3)_3$	-	-	233
$[ZrCl_2(OSiPh_3)_2Dme]\cdot 2C_6H_6$-*cis,cis*,, oct.	colrl. cr., 350(m.), s. in tol.	^1H, ^{13}C, X-r	84
$[ZrCl_2(3\text{-}Me\text{-}C_6H_9{}^cO_2\text{-}1,2)THF_2]$, oct.	-	X-r	1789
$[(ZrCl_3THF_2)_2({}^cC_6H_{10}O_2\text{-}1,2)]\cdot CH_2Cl_2$ 2 oct.. sharing a $(\mu\text{-}OR)_2$ edge	colrl. cr., 86 (m), s. in C_5H_{12}, +THF→$ZrCl_4\cdot 2THF$	IR, X-r	613
$LiZr_2(OR)_9$, R=Et, Pr^n, Pr^i, Bu^n, Bu^s	gl., subl.: 260/0.2 (Et), 226/0.3 (Pr^n), 220/0.3(Pr^i); 221/0.3 (Bu^n); 200/0.2 (Bu^s); m: 204(Et), α=2 (R^n),1 (R^s)	ebul.	115, 1116
$[LiZr_2(OPr^i)_9({}^iPrOH)]$= trian. $[M_3]$, tetrah. $[Li(\mu_3\text{-}OR)_2(\mu\text{-}OR)(ROH)]$, 1 oct. $[Zr(\mu_3\text{-}OR)_2(\mu\text{-}OR)(OR)_3]$, 1 oct. $[Zr(\mu_3\text{-}OR)_2(\mu\text{-}OR)_2(OR)_2]$	cr., 206 (m.), s. in THF, ROH, hc., α=1 (bz., ROH)	$^{13}C\{^1H\}$, ebul., X-r	115, 1662
$NaZr_2(OR)_9$, R=Me, Et, Pr^n, Pr^i, Bu^n	subl.: 290/0.02 (Me), 230/0.1 (Et), 218/0.37 (Bu^n), α=1	ebul.	115
$Li_2Zr_3(OR)_{14}$, R=Me, Et, Pr^i, Bu^s	**Pr^i:** 200/0.5 (subl.), α=1	ebul.	1116
$[Na_2Zr_3O(OEt)_{12}]_2$, 2 trig. bipyr. $[(\mu_5\text{-}O)Na_2Zr_3]$ sharing a $[Na_2(\mu_3\text{-}O)_4]$ face **$Na_2Zr_3O(OPr^n)_{12}$**	cr., non vol., s. in THF, tol. s. in bz. (b.)	IR, ^1H, ^{13}C X-r	115, 543

$MZr_2(OPr^i)_9$, M=K, Rb, Cs **$KZr_2(OBu^n)_9$**	cr., s. in THF, C_5H_{12}, $\alpha=1$; struct.analog of the Dme comp	^1H, ebul.	115, 1137
$KZr_2(OPr^i)_9 \cdot Dme$= $[(\eta\text{-}L)KZr_2(\mu_3\text{-}OR)_2(\mu\text{-}OR)_3(OR)_4]$, trian. $[M_3]$ of oct. Zr and K	-	^1H, ^{13}C, X-r	1666
↓H_2O **$[K_4Zr_2O(OPr^i)_{10}]$** $=[K_4Zr_2(\mu_6\text{-}O)(\mu_3OR)_8(OR)_2]$, oct. *trans* - $[K_4Zr_2]$, 2 oct.. $[ZrO(\mu_3OR)_4(OR)]$ - 4 tetragon. pyr.. -$[KO(\mu_3\text{-}OR)_4]$ -	subl. vac., 260°→$K_4Zr_2O_5(OR)_2$	^1H, X-r	1385, 1666
$KZr_2(OBu^t)_9$ $Zr(OR)_4$↑↓t, vac (-$Zr(OR)_4$↑) **$K_2Zr_2(OBu^t)_{10}$=** $K_2[Zr_2(\mu_3\text{-}OR)_3(\mu\text{-}OR)_4(OR)_3]$, struct tye of $Ti_4(OMe)_{16}$, in asymmetr. mol. 2 trig. bipyr. $[Zr^2O_5]$ and 2 gr. $[K^1O_5]$	colrl. cr., s. in tol. colrl. cr., 130/0.2 (subl.), s. in C_5H_{12}, $\alpha=1.4$	^1H, ^{13}C, TGA ^1H, ^{13}C, ebul., X-r	1564 1116, 1564
$TlZr_2(OPr^i)_9$	220/0.5 (subl.), s. in ROH	-	115
$[Cu^I_2Zr_2(OPr^i)_{10}]$ $= [Cu^I_2Zr_2(\mu\text{-}OR)_6(OR)_4]$, in cycle -2 oct. sharing a $(\mu\text{-}OR)_3$ face $[Zr_2(\mu\text{-}OR)_3(\mu\text{-}OR)_2(OR)_4]$, gr. $[Cu_2(\mu\text{-}OR)_3]$ of linear $[CuO_2]$ $+H_2O$→**$[Cu^I_4Zr_4O(OPr^i)_{18}]$** 2 8-membered cycles $[OCu_2(\mu\text{-}OR)_2Zr_2(\mu\text{-}OR)_3(OR)_4]$ with common μ_4-O vertex	cr., ~200 (dec.); $+O_2 \rightarrow Cu_4Zr_4O_3(OR)_{18}$ + +ROH+Me_2CO cr., s. in eth., tol., ~200 (dec.); $\alpha=1$;160°→$Cu+ZrO_2+H_2+Me_2CO$;$+O_2 \rightarrow Cu_4Zr_4O_3(OR)_{18}$	^1H, TGA, X-r IR, ^1H, ^{13}C, TGA, X-r, cryosc.	1385, 1664 1385

$+O_2 \rightarrow$ **$[Cu^{II}_4Zr_4O_3(OPr^i)_{18}]$**, band struc. with $[Cu_4O(\mu\text{-}OR)_2]$ square in the center, sharing 2 edges with 2 $[Cu_2Zr_2O(\mu\text{-}OR)_4(OR)_4]$ tetrah.	cobalt-bl. dichroic cr., s. in THF, C_5H_{12}, $\mu_{eff.}=1.1$; $>200 \rightarrow Cu+ZrO_2+H_2+Me_2CO$	IR, ^1H, ^{13}C, magn., prop., X-r	1385
$[Cu^{II}ClZr_2(OPr^i)_9]$= $[CuClZr_2(\mu_3\text{-}OR)_2(\mu\text{-}OR)_3(OR)_4]$, trian. $[M_3]$, 2 oct. $[ZrO_6]$ and trig. bipyr. $[CuClO_4]$	grn. cr., 165(dec.), v. s.in C_5H_{12},	^1H, X-r	1385, 1664
$M^{II}[Zr_2(OR)_9]_2$, M^{II}=Mg,Ca,Sr, R=Et, Pr^i,	colrl. cr., s. in ROH (t); **Mg**: 190/0.1 (subl.), $\alpha=1$; **Ca:** $\alpha=2$	ebul.	115,668, 1112
$M^{II}[Zr_2(OBu^t)_5(OPr^i)_4]_2$, M^{II}=Mg, Ca, Sr, Ba,	-	ebul.	1112
$Ba[Zr_2(OEt)_9]_2$, 2 trian. $[ZrTi_2]$, gr.$[Zr_2(OR)_9]$, CN M 8 **$Ba_4Zr_2O(OEt)_{14}\cdot 8EtOH$**, in the centre - oct. $[Zr_2Ba_4(\mu_6\text{-}O)]]$-*trans*	colrl. cr., s.in system $Ba(OR)_2$-$Zr(OR)_4$- ROH(20°)	IR, m-s	1609
$Ba[Zr_2(OPr^i)_9]_2$ $\downarrow H_2O$ **$Ba[Zr_4(OH)(OPr^i)_{17}]$**, X=R, H 2 trian. $[BaZr_2]$ sharing a $(\mu\text{-}OR)$ vertex Ba, gr. $[Zr_2(OR)_9]$ -2 oct. sharing a $(\mu\text{-}OR)_3$ face, CN Ba 8	colrl. cr., s. in C_5H_{12}, THF (24), ROH (3%),; t,vac. $\rightarrow$ $Zr(OR)_4+BaZr_2(OR)_{10}$; s. in systems $Ba(OR)_2$-$Zr(OR)_4$-ROH (THF) (20°)	IR, ^1H, $^{13}C\{^1H\}$, m-s, X-r, X-r powd.	970, 1609, 1662
$[BaZr(\mu_3\text{-}OH)(OPr^i)_5(^iPrOH)_3]$, struct. type of $Ti_4(OMe)_{16}$, $[Ba^1O_7]$–capped trig.prism, $[Zr^2O_6]$ –oct.	colrl.cr, v. s. in ^iPrOH	^1H, ^{13}C, X-r	1689

$[BaZr_2(OPr^i)_{10}]_2$ $=[BaZr_2(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_4]_2$, 2 trian. $[BaZr_2(OR)_9]$, linked by central $[Ba_2(OR)_2]$, CN M 6 **$[BaTiZr(OPr^i)_{10}]_2$** **$Ba_2Zr(OPr^i)_8 \cdot 5ROH$** $=[Ba_2Zr(\mu_3\text{-}OR)_2(\mu\text{-}OR)_3(OR)_3(ROH)_3] \cdot 2ROH$, trian. $[M_3]$, 3 oct. $[MO_6]$	colrl.cr., 278 (m.); s. in C_5H_{12}, THF (19),ROH (4%), s. in system (20°) s. in ROH ~4%	IR, ^1H, ^{13}C, m-s, X-r, X-r powd.	1609, 1662, 1691 1609
$[BaZr_2(OBu^t)_{10}]$ $= Ba[(\mu\text{-}OR)_3Zr(OR)_2]_2$, angular mol. **$[Ba_2Zr(OBu^t)_8(^tBuOH)THF_2]$**, trian. $[M_3(\mu_3\text{-}OR)_2]$ **$[BaZr(OBu^t)_6THF_2]$**	colrl.cr., s. in THF, ROH	^1H, ^{13}C, X-r	1689
$[BaIZr_2(OPr^i)_9]_2$, 2 trian. $[M_3]$, chain of 2 oct. $[Ti_2(OR)_9]$, oct Ba, linked by central . $[Ba_2(\mu\text{-}I)_2]$ 4-member cycle	-	-	1691
$[CdClZr_2(OPr^i)_9]_2$, 2 trian. $[CdZr_2(OR)_9]$, linked by central $[Cd_2Cl_2]$ gr.	colrl. needles, s. in hc., 162/0.01 (subl.)	X-r	1508
$[CdIZr_2(OPr^i)_9]$ $=[ICd(\mu_3\text{-}OR)_2(\mu\text{-}OR)_3(OR)_4]$ trian. $[M_3]$, trig. bipyr. $[CdIO_4]$ and 2 oct. $[ZrO_6]$	colrl. cr., $140/10^{-2}$ (subl.), s. in tol., hex., $\alpha=1$	H, ^{13}C, ^{113}Cd, X-r, cryosc.	1686 - 1688
$[CdM^{II}Zr_2(OPr^i)_{12}]_2$, M^{II}= Ca, Sr,Ba, in trian. $[Zr_2Ba]$ - 2 oct. $[Zr_2(OR)_9]$, oct. $[Ba(\mu_3\text{-}OR)_2(\mu\text{-}OR)_2]$ and tetrah. $[Cd(OR)_4]$, central linear chain $[Ba(\mu\text{-}OR)_2Cd(\mu\text{-}OR)_2Cd(\mu OR)_2Ba]$	colrl. square plates, high s. in tol., C_5H_{12}, $\alpha=2$	H, $^{13}C\{^1H\}$, ^{113}Cd, X-r, cryosc	1687, 1691

$\mathbf{[YCl_2Zr_2(OPr^i)_9]}$ trian. $[M_3]$, 2 oct. $[ZrO_6]$ and $[YCl_2O_4]$	-	-	1691
$\mathbf{[La_2Zr_3O(OPr^i)_{16}]}$, tetrah. $[La_2Zr_2(\mu_4\text{-}O)]$ connected with gr. $[Zr(\mu_3\text{-}OR)_2(\mu\text{-}OR)_2(OR)_2]$	colrl. cr., 135 (m., dec.), s. in ROH, in m-s - $La_2Zr_2O(OR)_{10}^+$	m-s, X-r	898
$\mathbf{[Sn^{II}Zr_2(OPr^i)_9]_2Hal_2}$, Hal=Cl, I, 2 trian. $[SnZr_2(OR)_9]$, linked by central. *cis*-$[Zr_2(\mu\text{-}Hal)_2]$, $[ZrO_6]$-oct., $[SnI_2O_3]$ -ψ-oct.	yel. (Hal=I) cr., s. in tol., α=1.6	^1H, ^{13}C, cryosc., X-r	1688, 1690
$\mathbf{Sn^{II}Zr(OPr^i)_6}$	colrl.cr., s. in eth., hc., $55/10^{-2}$ (subl.); 315° → $Sn+ZrO_2+$...	^1H, ^{13}C, ^{119}Sn	1565
$\mathbf{Sn^{IV}I_3Zr(OPr^i)_5(^iPrOH)}$, 2 oct. sharing a $(\mu\text{-}OR)_3$ face	or. cr., s. in hex.-ROH	IR, ^1H, ^{13}C, ^{119}Sn	1690
$\mathbf{PbI[Zr_2(OPr^i)_9]}$	waxy sld., s. in tol.-hex.	^1H, ^{13}C, ^{207}Pb	1688
$\mathbf{PbZr(OBu^t)_6}$	cr.,s.in eth., $120/10^{-2}$ (subl.)	^1H, ^{13}C, ^{207}Pb	1565, 1663
$\mathbf{[PbZr_2(OPr^i)_{10}]_2}$, 2 trian. $[PbZr_2(OR)_9]$ of 2 oct. Zr, tetrah. Pb in the zigzag chain, 4-membered $[Pb_2O_2]$ cycle in the centre	colrl. cr., s. in eth.	^1H, $^{13}C\{^1H\}$	1565
$\mathbf{[Pb_2Zr(OPr^i)_8]_2}$= $[Pb_2Zr(\mu\text{-}OR)_4(OR)_4]_2$, 2 gr. $[(RO)_3Zr(\mu OR)_3\,Pb(\mu\text{-}OR)]$ in the zigzag chain connected via μ-OR with the central $[Pb_2(\mu OR)_2]$	wh. sld., s. in eth., bz.	^1H, $^{13}C\{^1H\}$, ^{207}Pb	1565, 1663

$[Pb_3ZrO(OPr^i)_8]$ $= [Pb_3Zr(\mu_4\text{-}O)(\mu_3\text{-}OR)(\mu\text{-}OR)_5(OR)_2]$ $[OM_4]$ -tetrah., oct. Zr and 1ψ-tetrah. $[PbO(\mu\text{-}OR)_2]$ bound only by μ_4-O, 2 ψ-oct. $[PbO(\mu_3\text{-}OR)(\mu\text{-}OR)_3]$ sharing a $[O(\mu_3\text{-}OR)(\mu\text{-}OR)]$ face	colrl. cr., s. in tol., $125/10^{-2}$ (subl.), 325° $\rightarrow Pb+ZrO_2+ROH+C_3H_6+Me_2CO$...	^1H, $^{13}C\{^1H\}$, ^{207}Pb, ^{17}O, m-s, X-r	1565
$[BiCl_2Zr_2(OPr^i)_9]_2$, 2 trian. $[BiZr_2]$, linked by central $[Bi_2(\mu\text{-}Cl)_2]$ cycle, CN Bi and Zr 6	-	-	1691
$Na_2Zr[OCH(CF_3)_2]_6(C_6H_6)_2$ linear mol., $[ZrO_6]$ sharing a $(\mu\text{-}OR)_2$ edge with 2 $[NaO_2F_4]$ gr., Na-F	cr., s. in ArH., $80/10^{-2}$ (subl.), $110°/10^{-2}$(8 h.) $\rightarrow$ **$Na_2Zr(OR)_6$**	IR, ^1H, ^{19}F, X-r	1387
$[Na_2Zr[\mu\text{-}OCH(CF_3)_2]_6(C_6H_6)]_\infty$, $[ZrO_6]$ sharing a $(\mu\text{-}OR)_3$ face with 2 $[NaO_3F_3]$ gr., linear chain is formed via $(\eta^6\text{-}C_6H_6)$, perpendic. to the chain, Na-F 2.72-3.4	-	-	
$[Tl_2Zr[\mu\text{-}OCH(CF_3)_2]_6]$, linear chain, oct. $[ZrO_6]$ sharing faces with 2 ψ-tetrah. $[:TlO_3]$, Tl...F contacs	colrl. cr., s. in tol., $120/10^{-2}$ (subl.)	IR, ^1H, ^{205}Tl, ^{13}C, X-r	1389, 1387
$[Me_3NH]_2^+[ZrCl_4(OMe)(MeOH)]^-Cl^-$ - *trans*,	cr., 241(m., dec.), s. in ROH	X-r	885
$[PyH]_2[ZrCl_5(OEt)]$ ↓ **$[PyH]_2[ZrCl_4(OR)_2]$**, R=Me, Et; **$[PyH]_2[ZrCl_2(OEt)_4]$**	wh. cr., s. in ROH, 135 (dec.)	IR, X-r powd.	75, 201, 1592
$[PyH]_2[ZrCl_4(OCH_2CHal_3)_2]$, Hal=F, Cl	wh. slds, s. in MeCN	IR	75

$[Li(Et_2O)_2ZrCl_3(OCBu^t{}_3)_2]$ tetrah. Li and trig bipyr. Zr sharing a (μ-Cl)$_2$ edge		colrl. cr., s. in eth., + hex.$\rightarrow ZrCl_2(OR)_2$	X-r	1030
$Al_2Zr(OPr^i)_{10}$ [1116, 1608]				
Hf				
"$Hf(OMe)_4$"$\downarrow$	6	wh. sld.	-	225
"$Hf(OEt)_4$"	2, 5	wh. amor. sld., 180 (m.), 180-200/ 0.1 (b.); α=3.6 (bz.), 2.5 (ROH), in m-s $[M_4O(OR)_{13}]^+$, s. in hex., bz., CCl_4	IR, m-s, ebul.	38, 225, 1520, 1612
$Hf_6O_2(OEt)_{20}$-2EtOH = $Hf_3(\mu_3\text{-}O)(\mu\text{-}OEt)_4(OR)_6(ROH)]_2$, 2 trian.	hydro-.	colrl. cr.	X-r	1520
"$Hf(OPr^n)_4$"	5	wh. sld.	-	38
"$Hf(OPr^i)_4$" $\uparrow$- ROH(120°/0.5)	5	wh. sld.; 170/0.35 (b.), α=3.3-3.6	^1H,cryosc., thermochem	38, 220, 225, 1797
$[Hf(OPr^i)_4\cdot{}^iPrOH]_2$ isostr. to its Zr-analog	2, 5	colrl. cr., 150(m.), 120/0.1 $\rightarrow$ ROH+R_2O+..., s. in THF, hex, bz., ROH 1.9% (20°), polytherm - ROH	IR,^1H,m-s, X-r, X-r powd.	1612, 1665, 1690
$[Hf_2(OPr^i)_8\cdot{}^iPrOH\cdot L]$, **L=Py** [2 oct. sharing a (μ-OR)$_2$ edge; 2 L-ax. - at the same side], **Diox**		colrl. cr., s. in in tol.-L , α=1	IR,^1H, $^{13}C\{^1H\}$,	1690
"$Hf(OBu^n)_4$", "$Hf(OBu^i)_4$"	2, 5	-		38

$Hf(OBu^t)_4$	6	colrl. liq., d^{20} 1.159; 88/6 (b.); p-T (polytherm)		225, 234, 1111
"$Hf(OMe)(OBu^t)_3$"	6	wh. sld.	-	225
«$Hf(OC_5H_{11}{}^n)_4$»	6	colrl. liq., 90/6.5 (b.)	-	225
$Hf(OC_5H_{11}{}^t)_4$	6	colrl.liq., 92/0.1 (b.); p-T (polytherm)		225, 234
$Hf[OCH(CF_3)_2]_4$	5	sld., 110 (m.), subl./ vac, s. in tol., ROH, α=1	IR, ^1H, ^{19}F, m-s, TGA	1085
$Hf(OSiPh_3)_4$	5	cr., 383 (m.), 360/10^{-4} (dec.)	-	690, 1032
$Hf(OC_2H_4OMe)_4$	2	liq., in m-s -$[M_3(OR)_7]^+$	IR, m-s	1612, 1652
$HfCl_n(OPr^i)_{4-n}\cdot{}^iPrOH$, n=1, 2, 3 **$\cdot$Dmfa**, n=2, 3		cr., m: 142 (n=1), 149 (n=2), b.: 144/1(1)		1797
$[HfCl_2(OC_6H_3Me_2\text{-}2,6)_2THF_2]$ **$[HfCl_3(OC_6H_3Me_2\text{-}2,6)THF_2]$**		colrl. cr., 153 (m.) colrl. cr.,161 (m.,dec.)	^1H, m-s	876, 1789
$[HfCl(OC_6H_3Bu^t{}_2\text{-}2,6)_3]$ tetrah.		colrl.cr., s. in ArH(t), t$\rightarrow$$MCl_4$+$M(OAr)_4$	X-r	322, 994
$[Li_2Hf_2(OPr^i)_{10}]$ $=Li_2[Hf_2(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_4]$, struct. type of $Ti_4(OMe)_{16}$, Hf^1 oct., Li^2 -trig. pyr.		colrl. cr., 200/0.7 (subl.), s. in tol., α=1	^1H, $^{13}C\{^1H\}$, ^7Li, ebul., X-r	1690, 1112
$MHf_2(OPr^i)_9$, M=Li, Na, K, Cs		colrl. cr., s. in bz., ROH, α=1 **Li** 200/0.7 (b.), **Na** 170/0.1, **K** 180/0.2, **Cs** 230/0.1 (subl.)	^1H, $^{13}C\{^1H\}$	1686, 1137, 1112
$Li_2Hf_3(OPr^i)_{14}$		liq., 200/0.5 (b.), α=1	ebul.	1112
$KHf(OBu^t)_5$		178/0.5 (subl.), α=1.4	ebul.	1112

$[Cu^{II}ClHf_2(OPr^i)_9]$= $[ClCuHf_2(\mu_3\text{-}OR)_2(\mu\text{-}OR)_3(OR)_4]$, trian. $[M_3]$ of 2 Hf oct. and $[CuClO_4]$ trig. bipyr.	grn. cr., s. in C_5H_{12}, $\alpha=1$, paramagn.	^1H, ^{13}C, magn. prop., X-r	1690
$M^{II}[Hf_2(OPr)_9]_2$, M^{II} =Mg, Ca, Sr, Ba	colrl. cr., s. in org. solvs., **Mg:**165/0.1 (subl.), $\alpha=1$	^1H, ebul.	669, 1112
$[BaIHf_2(OPr^i)_9]_2$, isostr. with its Zr- analog	-	-	1691
$[CdIHf_2(OPr^i)_9]$, isostr. with its Zr- analog $\downarrow KM^{II}(OR)_3$	colrl. transparent cr., v. s. in hc., $\alpha=1$	^1H, ^{13}C, ^{113}Cd, X-r, cryosc.	1686, 1690
$[CdM^{II}Hf_2(OPr^i)_{12}]_2$, M^{II}=Sr, Ba isostr. to its Zr- analog	colrl. plates, s. in tol.-C_5H_{12}	^1H, ^{13}C,X-r, cryosc.	1686, 1690, 1691
$[SnHf_2(OPr^i)_9]_2Hal_2$ Hal=Cl, I, isostr. with its Zr- analog	yel. (Hal=I) cr., s. in tol., $\alpha=1.6$	"	1688, 1690
$[Me_3NH]_2^+[Hf(OMe)Cl_4(MeOH)]^-$ ***-trans,*** isomorph. with its Zr-analog	colrl. cr., s. in MeOH	X-r	885
$[PyH]_2[Hf(OMe)_2Cl_4]$	-	IR, X-r powd.	1592

$[Al_2Hf(OEt)_{10}]$, $[Al_2Hf(OPr^i)_{10}]$ [1608]

[1520]. The molecular structure of hafnium "ethoxide", $Hf_6O_2(OEt)_{20}\cdot 2EtOH$, can be considered as a dimer of $M_3(\mu_3\text{-}O)(\mu\text{-}OR)_3(OR)_6$ units [1520]. The molecule of $Zr_4O(OPr^i)_{10}(acac)_4$ can even be considered to be a structural analog of the $M_4O(OR)_{14}$ [1590].

At the same time the crystalline $[Zr(OR)_4\cdot ROH]_2$, where $R = Pr^i, Bu^i$ [1665] (Fig.4.1 *b*) and also the liquid $Zr(OR^t)_4$, $Zr(OR^s)_4$ ($R^s = C_6H_{13}, C_7H_{15}$) containing monomeric molecules, are individual compounds. The mass-spectra of $M(OC_2H_4OMe)_4$ ($M = Zr, Hf$) contain only the ions corresponding to fragmentation of aggregated molecules of homoleptic 2-methoxyethoxides [1612]. The same group includes obviously also the crystalline phenoxides and in particular the monomeric $Zr(OC_6H_2R_3\text{-}2,4,6)_4$ [1463], glycerates [193], and derivatives of fluorinated alcohols such as $Zr[OCMe_n(CF_3)_{3-n}]_4$ [1386]. The formation of $Zr(OBu^t)_4$ on distillation of the crude product of the synthesis, containing oxoadmixtures, is associated apparently with the low thermal stability of the latter and high volatility of the homoleptic t-butoxide. This explains also the low yield of distillation in this case.

12.12.3. Bimetallic complexes

An important role in the chemistry of zirconium alkoxides is played by the bimetallic complexes, which have much higher stability than the corresponding alkoxotitanates and -thorates. The compositions of the derivatives of alkaline metals — $MZr_2(OR)_9$ ($M = Li\text{–}Cs, Tl$), $Na_2Zr_3O(OR)_{12}$, $MZr(OBu)_5$, described first by Bartley and Wardlaw [115], and also those of alkaline earth metals $M^{II}[Zr_2(OR)_9]_2$, prepared by Mehrotra *et al.* [1112], — were later confirmed by the X-ray data [543, 1385, 1564, 1662, 1666]. However, the existence of derivatives of some other compositions as, for example, $M^{II}Zr_3(OR)_{14}$ [1112], $LaZr_4(OR)_{19}$, numerous derivatives of 3*d*-transition metals [306, 1138, 1116], was not confirmed by further studies. The repeated attempts to reproduce the data dealing with the bimetallic complexes of Fe, Co, Ni, Cr (in the case of alkoxoniobates, -tantalates, *etc.*) [1561, 1365, 1622,], and also the results of X-ray single crystal studies of alkoxozirconates (and other alkoxometallates) of transition metals indicate that these products usually are oxocomplexes — $M_nM'_mO_p(OR)_q$ (and not $M_nM'_m(OR)_q$, as they were described by Mehrotra [501]). The only exclusions known so far are homoleptic alkoxozirconate of copper (I) — $Cu_2Zr_2(OPr^i)_{10}$ [1664, 1385] — and alkoxoantimonates of Ni and Mn(II) [140]. The developed synthetic approach — a metathesis reaction of halides with stepwise replacement of Hal in reaction with different $KM(OR)_n$

(containing different metal atoms) permitted Mehrotra *et al.* to describe different tri- and even tetrametallic complexes such as $AlCuZr_2(OR)_{13}$, $GaCuZr_2(OR)_{13}$, $TaCuZr_2(OR)_{15}$, $AlMgZr_2(OR)_{13}$, and $FeZr_2TaAl(OR)_{19}$. The lack of the individuality proof for the corresponding bimetallic complexes gives reason to doubt concerning these more complex compositions (see also Section 12.16). Taking this fact into consideration, we included into the Table 12.13 only the heterometallic derivatives, whose composition is confirmed by X-ray single-crystal data and their analogs.

The presence of halide ligands in the molecules of bimetallic alkoxide complexes hinders apparently their decomposition with formation of oxoalkoxoderivatives. Examples are $Cu^{II}ClZr_2(OPr^i)_9$ [1664], $CdHalZr_2(OPr^i)_9$ [1508, 1687]. Veith *et al.* [1687,1691] used the the stepwise replacement of Cl and I atoms for preparation of trimetallic zirconates, $[M^{II}CdZr_2(OPr^i)_{12}]_2$, $M^{II} = Ca$, Sr, Ba. These octanuclear aggregates contain linear $[Ba(\mu\text{-}OR)_2Cd(\mu\text{-}OR)_2Cd(\mu\text{-}OR)_2Ba]$ chains in the center and $[Zr_2Ba]$ triangles at the ends of each molecule (see also Section 4.7.3).

The structures of the majority of alkoxozirconates (and isomorphous -hafniates) contain the $[Zr_2(OR)_9]$ fragments, which form via two μ-OR-bridges, connecting them to the heteroatom, the $[Zr_2M]$ triangles. The latter are centered by two μ_3-OR-groups (Section 4.5). The molecules of bimetallic oxoalkoxides contain polydentate oxoligands. Thus the structure of $Pb_3ZrO(OPr^i)_8$ containsa μ_4-O atom in the center of $[Pb_3Zr]$ tetrahedron [1565] (Section 4.4.1), and that of $Cu^I_4Zr_4O_3(OPr^i)_{18}$ in the center of a $[Cu_4]$ square [1385]. The $[Na_2Zr_3O(OEt)_{12}]_2$ molecules are trigonal bipyramids $[(\mu_5\text{-}O)Na_2Zr_3]$ [543] (Section 4.5), and $[K_4Zr_2O(OPr^i)_{10}]$ are *trans*-$[K_4Zr_2]$ octahedra with a hexandentate O-atom in the center [1385, 1666] (Section 4.6.1).

Practically all the known structures of zirconium and hafnium alkoxides contain the atoms ofthese atoms in octahedral coordination. Only the presence of such 2 ramified ligands as tritox, as in the molecule of $[Li(Et_2O)_2ZrCl_3(OCBu^t_3)_2]$, leads to the decrease in coordination number to 5 trigonal bipyramid) [1030]. The presence of 3 sterically crowded aryloxide ligands in the molecule of $[HfCl(OC_6H_3Bu^t_2\text{-}2,6)_3]$ leads to tetrahedral coordination [322, 994]. The rather small size ofthe ligands permitts the existence of $[ZrO_2(\mu\text{-}OR)_4(OR)]$ 7-vertex polyhedron in the spherical molecule of $Zr_{13}O_8(OMe)_{36}$ [1173] (Fig. 5.1 c).

The prospects for the application of mono- and bimetallic alkoxides in CVD-technology gave special actuality to the studies of their volatility. The coexistence in the gas phase over "$Zr(OR)_4$" of the particles of different size and composition cannot be a hindrance in their application in preparation of ZrO_2. The most convenient are, however, the volatile monomeric "$Zr(OR^t)_4$" and initially t-butoxide and also $Zr[OCMe_n(CF_3)_{3n}]_4$. The sublimation temperatures decrease with the replacement for Me-groups with CF_3 and are higher for the derivatives of Zr than for those of Ti. The thermolysis of $Zr(OBu^t)_4$ and the derivatives of fluorinated alcohols (in He atmosphere) takes place at ~100°C at a temperature much higher than that of their transition into the gas phase [1386]. Concerning the application of"$Zr(OR)_4$" and "$Hf(OR)_4$" ($R = Pr\text{-}C_7H_{15}$) for the preparation of fine powders and crystalline MO_2 films see [1082,1084, 1763].

The alkoxozirconates that sublime in a vacuum include $M[Zr_2(OR)_9]_n$, where M = Li, Na, K, Tl, Mg [115,1116], $K_2Zr_2(OBu^t)_{10}$ [1112, 1564], $M_2Zr[OCH(CF_3)_2]_6$, M = Na, Tl[1387], $MZr(OPr^i)_6$, M = Sn,Pb, $PbZr(OBu^t)_6$, [1565, 1663] and also—quite naturally—oxocomplexes, whose molecules have nearly spherical shapes, such as $K_4Zr_2O(OPr^i)_{10}$ [1385, 1666] and $Pb_3ZrO(OPr^i)_8$ [1565].

Thermolysis of tin and lead alkoxozirconates leads to the formation of metals. The mass-spectral data indicate the presence ofbarium and aluminium derivatives in the gas phase, but no preparative data are accessible for them. The major application ofzirconium and hafnium alkoxides lies now in the sol-gel technology of zirconate-titanate and solid solutions ZrO_2–Y_2O_3 (see Section 10.3), Except in the synthesis ofoxide materials, the alkoxides of zirconium and hafnium are traditionally used in the polymer chemistry, where they are applied as the components in catalysts [1278, 1269] and as additives to polymers, improving their characteristics [825, 1403] and so on. Already in 1930s Meerwein has proposed the use of zirconium alkoxides for the reduction of aldehydes into primary alcohols (Meerwein-Schmidt reaction) [1420].

12.13. Thorium alkoxides

The first studies ofthorium alkoxides were carried out by Bradley [223] in the mid-950s in connection with the problem of the separation of rare elements of Group IV and Ce(IV). They were devoted at the same time to the solution of certain theoretical problems such as the influence of the size of the central atom and the nature of the alkoxide groups on the molecular complexity of $M(OR)_4$ and their physical chemical properties. All the members ofthe homologous series — from the methoxides to heptyloxides have been synthesized and characterized. Recently a number of derivatives of sterically hindered alcohols, in particular phenoxides, were also prepared and characterized structurally by Clark *etal.* from Los Alamos National Laboratory [108, 106, 382, 384].

12.13.1. Synthesis

The basic nature of $Th(OR)_4$ does not permit the use of metathesis reactions with the solutions of ammonia (see Chapter 2). Only M^1OR (stronger bases than $Th(OR)_4$) can be used as reactants in metathesis with $ThCl_4$ or ThI_4. Application ofthis approach is attractive as thorium alkoxides do not form as stable bimetallic intermediates as their zirconium analogs [196] (method 5). Most of the derivatives described by Bradley were obtained by alcohol interchange from $Th(OPr^i)_4$ [232, 206] (method 6). In recent studies the major approach applied was alcoholysis of a silylamide thorim derivative $[(Me_3Si)_2N]_2Th[(CH_2SiMe_2)(NSiMe_3)]$ [106, 387] (method 4).

12.13.2. Properties

All $Th(OAlk)_4$ are solid amorphous or crystalline powders except $Th(OR^t)_4$ — viscous liquids. $Th(OPr^i)_4$ and $Th(OR^t)_4$ can be sublimed or distilled *in vacuo*; they usually are well soluble in organic solvents. The molecular complexities for the distinct derivatives are usually twice as high those for the corresponding $Zr(OR)_4$ and one and a half times as higher as those for $Ce(OR)_4$, which excludes the possibility of the structural analogy (except for $M(OPr^i)_4$, where $\alpha = 3.2–3.8$ for all three metals). Bradley supposed that this situation is due to higher coordination numbers for thorium atoms. To illustrate mis postulate one can compare the monomeric tetrahedral $Zr(OBu^t)_4$ molecule [225] with $Th(OBu^t)_4$, whose molecular complexity was determined to be equal to 3.4 [232]. Among $Th(OR)_4$ only the t-amyloxides were found to be monomeric. The decrease in the coordination number occurs therefore "in advance" for $Zr(OR)_4$ compared with $Th(OR)_4$. The described structures of $Th(OR)_4$ contain octahedral and trigonal pyramidal coordinated atoms (a dodecahedron was observed only in one case — that of the $Na_4[Th(\eta^2\text{-}C_6H_4O_2\text{-}1,2)_4]$ salt anion with long ionic bonds around Th atom [1529]). The difference in the molecular complexity not connected with a change in the coordination number of metal is demonstrated by the structures of two pyridine adducts — $[Zr(OPr^i)_4Py]_2$

Table 12.14. Thorium alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
$Th(OMe)_4$↓	6	wh. sld., invol.	-	232
$Th(OEt)_4$↓	6	wh. sld., poorly s. in bz., ROH.,	-	232
$[Th(OPr^{isS})_4]_n$	4, 5	sld., 210/0.1(subl.), s. in hex., ROH, , α=3.8 (bz.), 1.8(ROH)	IR, ^1H, ebul.	106, 232, 206
$[Th_4(\mu\text{-}OPr^i)_6(OPr^i)_{10}Py_2]$, zigzag chain of 4 oct. sharing a$(\mu\text{-}OR)_2$ edge	5	colrl. cr., s. in hex.+Py	IR, ^1H, X-r	106
$Th(OBu^n)_4$, $Th(OBu^i)_4$,$Th(OBu^s)_4$	6	sld., α=6.4, 4.2	ebul.	206
$Th(OBu^t)_4$	6	sld., 160/0.1(subl.), α=3.4	ebul.	232
$Th_2(OBu^t)_8\cdot{}^tBuOH$,	4, 5	colrl. cr., s. in THF, Py	IR, ^1H, X-r	387
$[Th(OBu^t)_4Py_2]$-*cis* , oct.				
+H_2O →**$Th_3O(OBu^t)_{10}$**	4	wh.fluffy cr., s. in hex., tol.	IR, ^1H	
$Th(OC_5H_{11}{}^n)_4$, $Th(OCHEt_2)_4$	6	wh. sld.,. α=4	ebul.	206
$[Th(OCHEt_2)_4Py]_2$ 2 oct. with a common $(\mu\text{-}OR)_2$ edge	4, 5	wh. cr, s. in hex., poorly - in tol.+Py	IR,^1H, ebul., X-r	106
$Th(OC_5H_{11}{}^t)_4$	6	visc. liq., 208/0.3(b.), α=2.8	ebul.	232
$Th(OCMeEt_2)_4$	6	sld.,.148/ 0.1 (subl.), α=1.8	ebul.	232
$Th(OCMe_2Pr^n)_4$, $Th(OCMe_2Pr^i)_4$	6	visc.liq.,120/0.1(dec.),α=2.6	ebul.	232
$[Th(OCHPr^i{}_2)_4]_2$, 2 trig. bipyr. with a common $(\mu\text{-}OR)_2$ edge	4	colrl. cr.,s. in tol., in s. dimer ↔monomer	^1H, X-r	106

$[Th(OCHPr^i_2)_4L]$, L= Dme, 2 Py, $C_7H_{13}N$ (quinuclidin, trig. pyr., N-ax.)		colrl. cr.,s. in hex., tol..	IR, ^1H, X-r	106
$Th(OCMeEtPr^n)_4$, **$Th(OCMeEtPr^i)_4$**	6	visc. liq., 153/0. (b.), α=1.7 , 1	IR, ^1H, ebul.	232, 106
$Th(OCEt_3)_4$	6	liq., d^o 1.2505;148/0.1(b.),α=1	surface tens.	232, 230
$[Th(OPh)_4(\eta^2\text{-}Dmpe)_2]\cdot C_7H_8$, 12- vertex polyhedra	5	colrl. cr., s. in tol.	^1H,^{13}C,^{13}P, X-r	520
$Th(OC_6H_4Bu^t\text{-}4)_4$, polymer, +Py→monomer, **$\cdot Py_3$**	4	wh. sld., s. in tol.	IR, ^1H, ^{13}C	143
$[Th(OC_6H_3Me_2\text{-}2,6)_4THF_2]$ **$[Th(OC_6H_3Me_2\text{-}2,6)_4Py_2]\cdot PhMe$-*cis*** oct.	5	pale-brh. sld., s. in tol., THF wh. sld	IR, ^1H,^{13}C X-r	143
$Th(OC_6H_3Pr^i_2\text{-}2,6)_4$	5	bl. cr., s. in hc.	-	157
$[Th(OC_6H_3Pr^i_2\text{-}2,6)_4THF_2]$	5	wh. sld., s. in THF	IR, ^1H,^{13}C, X-r	143
$[Th(OC_6H_3Bu^t_2\text{-}2,\ 6)_4]$,, tetrah.	5	colrl. cr., s. in tol.	“	143
$[Th(OCMe_2CCl_3)_4Py_2]$	5 , 6	115/0.1 (dec.)	-	233
$[Th(C_6H_4O_2H)_2(C_6H_4O_2\text{-}1,2)]$ ↓ **$[Th(C_{10}H_6O_2\text{-}\alpha,\alpha)_2]_2$**, **$[Th(OC_6H_4\text{-}C_6H_4O]_2$**	4	s. in Me_2CO,THF	-	46
$[ThH_2(OC_6H_3Bu^t_2\text{-}2,6)_2]_3$ = $[Th_3(\mu_3\text{-}H)_2(\mu\text{-}H)_4(OR)_6]$, trian. $[M_3]$, 1 oct. $[ThH_4O_2]$, two 7- vertex polyhedra $[ThH_5O_2]$		colrl. cr., s. in bz., α=3	IR, ^1H, ^{13}C $\{^1H\}$, X-r	382
$ThCl_n(OR)_{4-n}$, R= Pr^i, Bu^t, n= 1-3		-	-	1133

$[ThI_2(\mu\text{-}OPr^i)_2(^iPrOH)]_2$ **$[ThI(OCHPr^i_2)_3Py_2]$-*cis*,** oct..	colrl. cr., s. in tol., ROH	^1H, X-r	108, 106
$[ThBr_2(OC_6H_3Bu^t_2\text{-}2,6)_2THF_2]$	colrl. cr., s. in tol.	IR, ^1H	382
$[ThCl_2(OC_6H_2Bu^t_3\text{-}2,6\text{-}Me\text{-}4)_2]_n$ **$ThCl(OC_6H_2Bu^t_3\text{-}2,4,6)_3$**	cream cr., s. in hc.	^1H, ^{13}C	759
$[Th_4Cl_8O[(OC_2H_4\text{-})_4O]_3]\cdot 3MeCN$, tetrah. $[(\mu_4\text{-}O)Th_4]$		X-r	1364
$[NaTh_2(OBu^t)_9]$, trian. $[M_3(\mu_3\text{-}OR)_2]$, $[NaO_4]$, 2 oct. Th	colrl. cr., s. in hex., tol.	IR, ^1H, X-r	387
$[LiTHF_4]^+[Th(OC_6H_3Pr^i_2\text{-}2,6)_5]^-$, anion- trig. bipyr.	colrl. cr., s. in hc.	X-r	157
$Na_4[Th(\eta^2\text{-}C_6H_4O_2\text{-}1,2)_4]\cdot 21H_2O$, anion-12- vertex polyhedra	colrl. cr.	X-r	1529

and $[Th_4(OPr^i)_{16}Py_2]$ [106]. The dimeric molecule of the first is evidently composed of 2 octahedra sharing common edge, while that of the second one is a zigzag chain of 4 octahedra sharing common $(\mu\text{-}OR)_2$ edges. At the same time, the dimeric molecule of $[Th(OCHEt_2)_4Py]_2$ [106] with a more branched radical or $[ThI_2(OPr^i)_2(^iPrOH)]_2$ alkoxoiodide [108] were found to be structural analogs of $[Zr(OPr^i)_4{\cdot}{}^iPrOH]_2$ [1665] (Fig. 4.1 *b*). The same is the matter also for the bimetalllic complexes $[NaTh_2(OBu^t)_9]$ [387] and $[MZr_2(OPr^i)_9L]$, where M = Li, K, L = ^iPrOH, Dme [1662, 1666]. All the 3 molecules contain $[M_3]$ triangles connected by three μ-OR along the edges and centered by 2 μ_3-OR-groups, the 2 M^{IV} being octahedrally coordinated.

The majority of $Th(OR)_4$ have been isolated in the crystalline form only as pyridine solvates and $Th(OBu^t)_4$ — as alcohol solvate (with 2:1 composition), the yields of complexes being rather far from quantitative [387]. This fact in combination with the observed molecular complexities (3–4) for unsolvated $Th(OR)_4$ (R = Pr^i, Bu^t, $C_5H_{11}{}^n$, $C_5H_{11}{}^s$, $C_5H_{11}{}^t$) — amorphous solids or viscous liquids — permits to suppose (in analogy with "$Zr(OR)_4$" and "$Hf(OR)_4$", see Section 12.12) the existence in their samples of tri- and tetranuclear oxocomplexes — $M_3O(OR)_{10}$ and $M_4O(OR)_{14}$ — to be supposed. Crystalline $Th_3O(OBu^t)_{10}$ has in fact been isolated on the hydrolysis of $[Th(OBu^t)_4Py_2]$ [387] (Table 12.14).

One of the possible applications of $Th(OR)_4$ has been proposed by Mazdiyasni [1082], who reported the preparation of fine ThO_2 powder on the oxidative pyrolysis of alkoxides in the gas phase.

12.14. Bismuth alkoxides

The study of the bismuth derivatives of polyatomic phenols started in the nineteenth century due to their broad application in dermatology as antiseptic medicines [308, 1575]. Feigl [559] proposed the pyrogallol complex $Bi(O_3C_6H_3)$ as a standard form for the gravimetric determination of bismuth in the presence of lead. The study of bismuth alkoxides has started only in 1966 with the work of Mehrotra [1134], which described the preparation of the first members of the aliphatic homologous series. The discovery of Bi-containing high-temperature superconductors (HTSC) has stimulated the search for new volatile and soluble alkoxides — the derivatives of ramified and functional radicals and also the derivatives of halogenated alcohols. These compounds have usually been characterized by the X-ray single crystal studies.

12.14.1. Synthesis

$Bi(OR)_3$, where R = Me, Et, Pr^i, were first prepared by the exchange reaction of solid $BiCl_3$ with M^IOR (M^I = Li, Na) on prolonged reflux of solutions in benzene-alcohol media (method 5) [1134]. The application of diethylether instead of alcohols in this reaction permitted a noticeably decrease in reaction time and avoided the partial decomposition of $Bi(OR)_3$ [967] (it is preferable to use the freshly sublimed soluble $BiCl_3$ in this reaction). $Bi(OBu^t)_3$ was obtained using $BiBr_3$ in hexane media at room temperature on prolonged stirring (24 h)[1069].

The alkoxides of bismuth have been obtained also using the alcoholysis of $Bi(NMe_2)_3$ (synthesis of $Bi(OPr^i)_3$, $Bi(OC_5H_{11}{}^t)_3$, $Bi(OC_2H_4OMe)_3$ [1074]), $Bi[N(SiMe_3)_2]_3$ (for the preparation of $Bi(OSiPh_3)_3$ and the 2-methoxyethoxide [1069]) and $BiPh_3$ (preparation of $Bi(OC_6F_5)_3$ solvates [851]) (method 4).

The electrochemical route (2) can be applied only for the synthesis of $Bi(OMe)_3$, which is insoluble in the parent alcohol (in the other alcohols it was the electrochemical refinement of metal that took place) [967]. The glycolates and derivatives of polyatomic phenols stable to hydrolysis have been obtained on alcoholysis of Bi_2O_3 [1808, 1352, 684, 559].

12.14.2. Properties

All bismuth alkoxides are white crystalline or amorphous solids; certain phenoxides are yellow. The majority of $Bi(OAlk)_3$ are very unstable even in comparison with the analogous derivatives of other metals: they are tremendously sensitive to the traces of water, oxygen, UV, and X-ray irradiation (which often hinders their X-ray single crystal studies). On storage they slowly decompose getting dark-colored (due probably to their oxidation into Bi(IV) derivatives). The decomposition reactions lead to the formation of oxoalkoxides that are very often easily crystallizable. The latter are exemplified by $Bi_4O_2(OBu^t)_8$ [1405], $Bi_6O_3(OC_6H_3Cl_2\text{-}2,6)_{12}$ [821], $[Bi_6O_3(OC_6F_5)_{12}Thf_2]$ [1742], and $[Bi_9O_7(OC_6F_5)_{13}]\cdot 2L$ [851]. The other route to oxoderivatives is provided by the ether-elimination reaction. Thus the recrystallization of $[NaBi(\mu\text{-}OC_6F_5)_4Thf]$ from toluene gives $[Na_4Bi_2O(OC_6F_5)_8THF_4]$ (the formation of $(C_6F_5)_2O$ was proved by mass spectra) [848].

This high sensitivity of bismuth derivatives to traces of water often leads to a situation where the results of the synthesis are dependent on the origin of the reactants. Thus, Whitmire [1742] has shown that on application of the phenol purchased from Aldrich in the reaction of $BiCl_3$ with $NaOC_6F_5$, the major product is $\mathbf{NaBi_3O(OR)_8{\cdot}THF}$, while when this reactant is purchased from Strem the products obtained are $\mathbf{NaBi_4O_2(OR)_9{\cdot}2THF}$ and $\mathbf{Na_2Bi_4O_2(OR)_{10}}$ (i.e., the products of deeper decomposition). It can be supposed that the reason for such instability lies in the possibility of intramolecular interactions between the oxidant (i.e., Bi(III), and the alkoxide groups being potential reductants). The exclusions are represented by the comparatively stable polymeric methoxide, 2-methoxyethoxides (where the ligands possess a chelate function), and ionic phenoxides.

All $\mathbf{Bi(OAlk)_3}$ derivatives of *n*- and *i*-alcohols are volatile, which permits their purification by distillation, but the yields of the sublimates are low as the processes are accompanied by partial decomposition. A much higher thermal stability is demonstrated by $\mathbf{Bi(OBu^t)_3}$. According to the mass-spectrometry data the first members of the homologous series are dimeric in the gas phase, while $\mathbf{Bi(OR^t)_3}$ and $\mathbf{Bi(OC_2H_4OMe)_3}$ are monomeric [967]. However the solid state structure of the latter contains the polymer chains and its solutions in benzene — the dimeric molecules. The NMR spectra indicate the equilibrium in solution of aggregates with different number of chelated ligands [1069]. This obstacle hinders the crystallization of 2-methoxyethoxide from solutions (Table 12.15).

The coordination of bismuth atoms varies considerably in the structures described in the literature, but as for all other derivatives of Bi(III) these are the geometries with a localized electron pair [Bi:] that are dominating. The minimal CN 3 and 4 (**ψ-tetrahedron** and -trigonal bipyramid) are present in the molecule of $\mathbf{Bi(OBu^t)_3}$ (in the gas phase) and in the polymeric structure of $\mathbf{[KBi(\mu\text{-}OBu^t)_4]_\infty}$. There are also present the structures with 5-coordinated Bi-atom (tetragonal pyramid = **ψ-octahedron**). Its representatives are the structure of $\mathbf{[Bi(OEt)_3{\cdot}\frac{7+x}{8}EtOH]_8}$, 2-methoxyethoxide, $\mathbf{\{Bi[OCH(CF_3)_2]_3THF\}_2}$ and $\mathbf{[NaBi(\mu\text{-}OC_6F_5)_4THF]_\infty}$. The most common coordination for the Bi atoms in the structures of alkoxides is the octahedral one. It is demonstrated by the monomers like $\mathbf{[Bi(\eta^2\text{-}OCMe_2CH_2OMe)_3]}$ and $\mathbf{[Bi(OSiPh_3)_3THF_3]}$, dimers as $\mathbf{[Bi(OC_6F_5)_3THF_2]_2}$ and $\mathbf{(NH_4)_2[Bi_2(\eta^2\text{-}C_6H_4O_2\text{-}1,2)_4]}$, and a tetranuclear $\mathbf{Bi_4O_2(OBu^t)_8}$. The coordination sphere is usually asymmetric and contains 2 or 3 longer bonds with the oxygen atoms of ether functioning (in the pinacolate) or solvating THF molecules or with the bridging OR or O groups. The heptacoordination for Bi (monocapped octahedron) is observed in the $\mathbf{[BiVO(OC_2H_4OMe)_3Cl_3]_2}$ molecule [1290].

Table 12.15. Bismuth alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
$Bi(OMe)_3$↓	2, 5, 6	wh. sld., stab., 180 (dec.), 190/0.08 (subl.), α=2	IR, m-s, X-r powd.	115, 622, 967, 1134, 1743
$Bi(OEt)_3 \cdot \frac{7+x}{8}$ EtOH, $[Bi_8]$-crown of tetragon. pyr. $[Bi(\mu\text{-}OR)_4(OR)]$, ROH…OR	5, 6	wh..cr., darken , $130/10^{-2}$ (subl.), 105-130 (dec.), s. in ROH, eth., stab. in s. by 0°, α=2	IR, Raman, ^1H, $^{13}C\{^1H\}$, m-s , TGA	967, 1069, 1134, 1743, 898
$Bi(OPr^i)_3$	4, 5	wh. cr., darken qickly, s. in ROH, eth., stab. in s. by 0°; 156 (m.), 140/ 0,5 (subl.), 105 (dec.), α=2	IR, ^1H, m-s, X-r powder, TGA	967, 1074, 1134, 1525, 1743
$Bi(OBu^t)_3$ trig. pyr. (ψ-tetrah.) - in gas phase	5	colrl. cr., s. in hc., THF, CH_2Cl_2, 168(m.), $90/10^{-2}$ (subl.), α=1	IR, ^1H, ^{13}C, m-s, gas electronogr.	550, 692, 1069, 1696
$Bi_4O_2(OBu^t)_8$ $=[Bi_4(\mu_3O)_2(\mu OR)_4(OR)_4]$ struct. type of $Ti_4(OMe)_{16}$	4	colrl. cr., s. in hex., bz.,<150/vac. (subl.), 200(dec.)	^1H, X-r	1405
$[Bi(OC_5H_{11}{}^{neo})_3L]_2$, L=ROH, Py, 2 tetragon. pyr. sharing a $(\mu\text{-}OR)_2$ edge	4, 5	colrl. cr., α= 2 (THF)	IR, ^1H, ^{13}C, X-r	192

$Bi(OC_5H_{11}{}^t)_3$	4	wh.sld., 63/10^{-4} (subl.), s. in hc., α=1	IR, ^1H, cryosc.	1074
$[Bi(OC_6H_3Me_2\text{-}2,6)_3]$, trian.	5	yel. cr., s. in hc.	IR, ^1H, ^{13}C, X-r	550
$[Bi(OC_6H_3Pr^i{}_2\text{-}2,6)_3]$	4	colrl. cr., s. in hex., bz., 150/vac.(subl.), 200(dec.)	^1H	1405
$[Bi[OCH(CF_3)_2]_3THF]_2$, 2 tetrag. pyr. with common edge (μ-OR)$_2$, Bi-F 3,14	5	colrl. cr., s. in THF, t→BiOF	IR, ^1H, ^{13}C, X-r	851
$Bi[OC(CF_3)_3]_3$	7	wh. sl.	IR, ^{19}F	294
$[Bi(OC_6F_5)_3THF_2]_2$ (I), C_6H_{14} 2 oct. with common edge (μ-OR)$_2$	**II +** THF	colrl. cr. yel. cr , s. in THF, hex.	IR, ^1H, ^{13}C, X-r	851
$[Bi(OC_6F_5)_3(\eta^6\text{-}PhMe)]_2$ (II) **$[Bi(OC_6F_5)_3(\eta^6\text{-}PhMe)]_2 \cdot 2PhMe$** both -2 ψ-oct. with common edge (μ-OR)$_2$	4	yel. cr., 400°→BiOF	IR, ^1H, ^{13}C, X-r	851
$[Bi_6O_3(OC_6F_5)_{12}THF_2]$ = $[Bi_6(\mu_4\text{-}O)(\mu_3\text{-}O)_2(\mu\text{-}OR)_{12}\,THF_2]$	**II+** NaOAr	colrl. cr.	X-r	1742
$Bi_9O_7(OC_6F_5)_{13} \cdot 2L$, L=THF,PhMe, 7 faces of $[Bi_6]$-oct. capped by (μ_3-O), VIII -(μ_3-OR), 3 of 7 (μ_3-O) coordinate $[Bi(OR)_4]$	**I, II +** H_2O traces	colrl. cr. (L=THF) or yel. (PhMe), cr., s. in tol., THF	X-r	851
$Bi_6O_3(OC_6H_3Cl_2\text{-}2,6)_{12}$ 2 trian. $[Bi_3(\mu_3\text{-}O)(\mu\text{-}OR)_2(OR)_2$, **$\cdot$ArOH**	4	colrl. cr., s. in tol., eth.	X-r	821

$Bi(OSiMe_3)_3$	5	colrl.sld., s. in eth., v. unstab., 0^o dec.	IR, ^1H	1417
$[Bi(OSiPh_3)_3]_n\downarrow$ **$[Bi(OSiPh_3)_3THF_3]$-*fac*,** oct.	4	wt. cr., s. in MePh, CH_2I_2, in s. - exch. THF	IR, ^1H, ^{29}Si, ^{13}C, m-s, TGA, X-r	1069
$Bi[OSi(OBu^t)_3]_3$	5	colrl. cr., s. in C_5H_{12}	IR, ^1H, $^{13}C\{^1H\}$	1571
$[Bi(OC_2H_4OMe)_3]$= $[Bi(\eta^1,\mu\text{-}OR)_4(\eta^1\text{-}OR)]_\infty$, zigzag chains of tetrag. pyr. (Ψ-tetrah..)	4, 5, 6	wt. cr., s. in hex., eth.,45 (m.), vol. α=1(gas),2 (bz.), in s.-isomers with η^1,η^2	IR, ^1H, ^{13}C m-s, X-r, TGA	1074, 1069, 1652
$Bi(OC_2H_4OEt)_3$	6	yel. sld., 39-42 (m.)	IR	1652
$[Bi(\eta^2\text{-}OCMe_2CH_2OMe)_3]$, oct. with 3 cycles	4, 5	cr., $60/10^{-2}$ (subl.), s in eth.	IR,X-r, NMR	739, 732
$Bi_4(C_2H_4O_2H)_2(C_2H_4O_2)_5\downarrow$	3	grey sld.	IR	1808
$[Bi(ArO_2\text{-}1,2)(OH)]$, Ar= Ph, 4-$Bu^t$-$C_6H_3$; 3,5-$Bu^t_2C_6H_2$	3, 5	yel. cr., s. in Dmfa, Dmso, stab. to hydrol.	IR, ^1H, m-s	684, 1352
$[Bi(C_6H_2O_3)]\downarrow$	3	yel. cr., stab. to hydrol.	-	559
$BiCl(OMe)_2\downarrow$		wt. sld., 176 (dec.)	-	622
$[Na_4Bi_2(\mu_6\text{-}O)(\mu_3\text{-}OBu^t)_8]$, oct. [*trans*-$Na_4Bi_2$], M^I and M^{III} positions disordered		colrl. cr., s. in hc., bz., 250 (m., dec.)	^1H, X-r	1696
$[KBi(\mu\text{-}OBu^t)_4]_\infty$, zigzag chains of ψ-trig. bipyr. [:$M(\mu\text{-}OR)_4$] and dist. tetrah. [$K(\mu\text{-}OR)_4$]		colrl. cr., s. in hc., bz., 220 (m., dec.)	^1H, X-r	1696
$[NaBi(\mu\text{-}OC_6F_5)_4THF]_\infty$, zigzag chains of tetrag. pyr.[$Bi(\mu\text{-}OR)_4THF$], [NaO_4F_3]		yel. cr., s. in tol.	IR, X-r	848
$[NaBi_3O(OC_6F_5)_8THF]$ = $NaBi_3(\mu_3\text{-}O)(\mu\text{-}OR)_6(OR)_2THF$		colrl. cr.	X-r	1742

$[NaBi_4O_2(OC_6F_5)_9THF_2]$, 2 $[NaBi_2]$ trian. with a common $[Na(\mu\text{-}OR)]$ side, CN Na and Bi 4	colrl. cr.	X-r	1742
$[Na_2Bi_4(\mu_3\text{-}O)_2(\mu\text{-}OC_6F_5)_{10}THF_2]$, the $Ti_4(OMe)_{16}$-type core with 2 additional (μ-OR), 2 attached [NaTHF]-gr.	colrl. cr.	X-r	1742
$Na_4Bi_2O(OC_6F_5)_8THF_4]$, oct. $[Na_4Bi_2]$-*cis*, 2 μ_3-gr. center the $[Na_3]$-trian., 4 μ - $[Na_2Bi]$ trian, 2 - $[NaBi_2]$ trian.	yel. cr.	IR, X-r	848
$BaBi_2[C_6H_8O_4(OH)_2]_2$↓, (derivative of mannit)	colrl. cr.	-	1596
$(NH_4)_2[Bi_2(\eta^2\text{-}C_6H_4O_2\text{-}1,2)_4]\cdot 2C_6H_4(OH)_2\cdot 2H_2O$, anion- 2 oct. with common edge $(\mu\text{-}O)_2$	colrl. cr.	X-r	1504

$[BiTi_2O(OPr^i)_9]$ [1258]; **$[BiVO(OC_2H_4OMe)_3Cl_3]_2$** [1290]; **$[BiCl_2\{Zr_2(OPr^i)_9\}]_2$** [1691]

Special attention should be paid to the bimetallic alkoxides of bismuth. While the methoxides and ethoxides are unable to build complexes with the alkali metal alkoxides [967], $KBi(OBu^t)_4$ is easily formed on the mixing of the solutions of the components in alcohol. The interaction of bismuth *t*-butoxide with $NaOBu^t$ under the same conditions yields an oxoalkoxide, $Na_4Bi_2O(OBu^t)_8$ [1696]. The interaction of the isopropoxides of bismuth and titanium can be achieved only after the partial hydrolysis of $Bi(OR)_3$. It gave, naturally, an oxocomplex $BiTi_2O(OPr^i)_9$ [1258]. The formation of bimetallic complexes of 3:2 and 1:1 compositions in the $Bi(OEt)_3$–$WO(OEt)_4$–$EtOH$ system and of 2:3 composition in the $Bi(OR)_3$–$MoO_2(OR)_2$–ROH ($R = C_2H_4OMe$) system takes place only in solutions [1638], which were used for the preparation of the powders of oxide ferroelectrics and solid electrolytes [1223].

The most important applications of bismuth alkoxides are connected with the preparation of high-temperature superconductors in the Bi-Sr-Ca-Cu-O system. $Bi(OC_2H_4OMe)_3$ [1619] and $Bi(OPr^i)_3$ (with subsequent exchange with an aminoalcohol) [889] were most frequently used for preparation of solutions for film deposition. The HTSC powder $K_{0.4}Ba_{0.6}BiO_3$ was prepared using bismuth isopropoxide and *t*-butoxide [1525] (see Section 10.5). During recent years considerable attention has been paid to the obtaining of ferroelectric films of bismuth-strontium tantalates and niobates (see Section 10.4) and Bi_2O_3 based oxide solid electrolytes [83]. The application of antiseptic medicines based on Bi(V) pinacolates remains also of importance [1739].

12.15. Vanadium alkoxides

$VO(OR)_3$ — the alkoxides of vanadyl (V) or otherwise the esters of vanadic acid — belong to the most easily available derivatives and can be easily purified by distillation under low vacuum. The synthesis of these derivatives — from ethoxide to t-amyloxide—via alcoholysis of V_2O_5 was first described at the beginning of the twentieth century by Prandtl and Hess [1313, 743]. The same work contained the first description of the hydrolysis of $VO(OR)_3$, which laid basis for the numerous studies of the processes of formation of sols and gels of vanadic acid. The studies of the low-valent derivatives of vanadium that are very sensitive to oxidation were started in the 1960s by the works of Bradley on $V(OR)_4$ and $V(OR)_3$ [226]. The preparation, structure, and magnetic properties of vanadium(II) alkoxides were investigated only quite recently.

12.15.1. Synthesis

The refluxing of V_2O_5 with alcohols (along with the alcoholysis of NH_4VO_3)

provides the simplest access to $VO(OR)_3$ and has remained very important until now. It is especially useful in the case of long-chain alcohols with the boiling points over 100°C, which permits to efficiently remove water from the reaction sphere [1238] (method 3). The reaction time increases for the first derivatives of the homologous series. The yields of different homologs vary from 25 to 90%. The exchange reaction of $VOCl_3$ with alcohols in the presence of ammonia or with NaOR in the benzene-alcohol media (method 5) permitted certain homologs ($R = Me, Et, Bu^n$) to obtained with 50 to 80% yields.* The interaction of $VOCl_3$ with NaOR is complicated according to [1313] by formation of alkoxide chlorides — volatile liquids stable even in the presence of a considerable excess of an alkali alkoxide. For $VO(OR)_3$ ($R = Me, Et, Pr^i$) it has been shown that the stability of $VOCl_n(OR)_{3-n}$ increases in the series $^iPr < Et << Me$ [1613]. The preparation of $VO(OR)_3$ ($R = Et, Pri$) with good yields turned out to be possible in a certain excess of NaOR in comparison with the steichiometry ($[VOCl_3]$: [NaOR] = 1 : 3.09 for $R = {}^iPr$ and 1:3.30 for R = Et). In the case of R = Me, even for $[VOCl_3]$: [NaOR] = 1 : 4.00, the chloride content remained the same as for the 1 : 3.00, and this route appears therefore to be not useful for the synthesis of $VO(OMe)_3$. The 51V NMR study of $VOCl_3$ interaction with KOPri has indicated the formation of the $[VO(OPr^i)_4]^-$ and $[V_2O_2(OPr^i)_7]^-$ ions along with $VO(OPr^i)_3$ in solution [774]. On the attempt to prepare $VO_2(OR)$ via an exchange reaction of VO_2Cl with the solutions of NaOR in alcohols, it turned out that at the first step there occurs alcoholysis yielding $VO(OR)_2Cl$, which in its turn is transformed subsequently into $VO(OR)_3$ [1613]. The majority of the higher $VO(OR)_3$ homologs have been prepared using the alcohol interchange reaction, where in some cases the esters were used as reactants instead of alcohols (method 6). This route provided access to $VO(OPh)_3$, which could not be prepared by alcoholysis of $VOCl_3$ in hexane because of an incomplete substitution of Cl ligands [607].

The major synthetic approach to $V(OR)_4$ is the alcoholysis of $V[NEt_2]_4$ (method 4) [226]. $V(OR)_4$ ($R = Me, Et, Pr^n, Pr^i$) may be also obtained, however, via the interchange reaction of VCl_4 with NaOR [1613].** The same ap-

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*The ^{51}V NMR study of the alcoholysis of $VOCl_3$ in the CCl_4 or MeCN media showed that even in a large excess of alcohol the substitution takes place only for 2 Cl atoms and the equilibrium can be shifted exclusively in the presence of bases — for example, amines [942].

** It is worth noting here that in contradiction to the data published by Bradley [227] on the formation of $VCl_2(OR)_2$ alkoxide chlorides on alcoholysis of VCl_4 his reaction was proved to yield $VOCl_2 \cdot nROH$ as the major products [607, 1634]. To avoid this reaction, the vanadium chloride should be introduced as an ether solution into the reaction with NaOR for the preparation of vanadium (IV) alkoxides.

proach was used also for the preparation of $VO(OR)_2$ (R = Et, Pr^i) [1613]. The synthesis of the polymeric $V(OAlk)_3$ via VCl_3 interaction with LiOR (method 5) demands a very long washing with alcohols to remove LiCl [226]. The application of the same reaction for the preparation of comparably stable $V(OAr)_3$ is more smooth due to the good solubility of the latter in hydrocarbons. The phenoxides of V(II) were obtained on alcoholysis of the metalorganic derivatives of V(II) (method 4) or on interaction of VCl_2•2Tmeda with NaOAr (method 5) [1156].

12.15.2. Properties

The monomeric phenoxides of V(II) (stabilized with the sterically crowded radicals) are red-colored solids with μ_{eff} that practically coincide with the spin-only values (3.88 μB for d^3-configuration); the CN of the V atoms varies from 4 to 6 depending on the size and functionality of the Ar group [1156].

As has already been mentioned, the alkoxides and the alkoxide chlorides of V(III) are green-colored solid polymers, not volatile and insoluble in organic solvents. Their heating *in vacuo* yields $VO(OR)_3$, originating from thermolysis [226]. Their electronic spectra indicate the octahedral coordination of the central atoms, while the low values of μ_{eff} (in comparison with the spin-only value of 2.83 μB for the d^2 configuration) are usually attributed to the exchange interactions. At the same time, the theoretical values are observed for the soluble monomeric phenoxides and phenoxovanadates with trigonal bipyramidal or tetrahedral coordination of the central atom, while the value determined for the binuclear $[[V(OC_6H_3Me_2\text{-}2,6)_3]_2THF]$ molecule was found to be 1.41 μB [614].

$V(OR)_4$ are green or brown liquids except for the solid methoxide and isopropoxide. They are very sensitive to moisture and oxygen. Their molecular complexity decreases in the homologous series from 3 (R = Me) to 2 (Et) and 1 (Bu^t), which permits the supposition that the CN changes for V atoms from 5 to 6 in the molecule of methoxide to 5 in that of the ethoxide and 4 in the molecule of bright blue-colored $V(OBu^t)_4$ (see Table 12.16). These data on coordination were supported by those of IR, electronic, and ESR spectroscopies. Their detailed interpretation is presented in a review by Bradley [198], and also in [1613]. The few known representatives of the $VO(OR)_2$ series are solid brown substances, whose molecules are aggregated via bridging OR-groups to permit the V atoms to achieve octahedral (R = Et) or tetrahedral (Pr^i) coordination.

Special attention should be paid also to the oxoalkoxopolyvanadates (IV) and (IV, V) described recently by Zubieta *et al.* [913, 337]. The single crystals of these compounds demonstrating a considerable stability were grown on their hydrothermal synthesis from vanadium oxides in the presence of alcohols containing a $-C(CH_2OH)_3$-group and basic reagents. Reserches have described 2 major classes of anions—hexa- and decavanadates that possess metal-oxygen cores analogous to the corresponding $[M_6O_{19}]^{n-}$ ("a large octahedron", centered with the μ_6-O, known for M = Nb, Ta, Mo, W) and $[V^V{}_{10}O_{28}]^{6-}$ oxometallate anions. The tridentate $[RO_3]$-bridges are situated on the surface of the anions. It is worth noting that only the hexanuclear complexes have been so far described for V(V) (only the decanuclear structures being known for the oxoanions).

$VO(OR)_3$ are mainly yellow easily distillable liquids. The absence of the color for the derivatives of the branched radicals that are more stable to hydrolysis led to the conclusion that the color of $VO(OR^n)_3$ is due to the presence of polynuclear oxoalkoxides with the structures analogous to those of the orange polyoxovanadates [1313]. As it has been mentioned above, the alkoxohexavanadates (V) have red color (see Table 12.16). Of the lower homologs, solid are only methoxide, *t*-butoxide, and *i*-amyloxide. In the molecular structures of $[VO(OR)_3]_2$, where R = Me and $C_5H_9{}^c$, there are the dimers of two 5-vertex polyhedrons with a common edge [302, 752]. In the case of methoxide they form a weakly connected polymer chain due to formation of longer OR-bridges (connected in the *trans*-position to the doubly bonded O atom of another dimer), completing the coordination arrangement of V atoms to octahedral. From 1970 to 1980 Rehder *et al.* conducted a large cycle of studies devoted to the investigation of the solution structure and behavior (solvation, aggregation, *etc.*) of $VO(OR)_3$, using ^{51}V NMR [1348]. It has been shown that the dimerization in solution takes place for nearly all the homologs, including amyloxides [1284]. The intensity of the dimeric ions in the mass-spectra achieves 2 to 5% for the methoxide and only about 10^{-2}% for other homologs [1613].

The only representative of the $V(OR)_5$ series is the cation in the complex $[V(3,5\text{-}Bu^t{}_2C_6H_2O_2\text{-}1,2)_2Phen]^+[SbCl_6]^-$ [862].

$VO(OR)_3$ are very convenient and easily available precursors for the preparation of a wide range of V(V) derivatives and via their reduction by matallalkyls even for the derivatives of the lower oxidation states. The complete or partial substitution of OR-groups has led to halides, carboxylates, β-diketonates, alkyls, sulfides, azids, complexes with Shiff bases, phenylisocyanate, and so on. Hydrolysis of $VO(OR)_3$ is discussed in Chapter 9.

The thermal decomposition of vanadium alkxoides [24, 983, 1296] and their behavior in the gas phase (with the aid of mass-spectrometry) [11, 1613] were also studied in detail to optimize the CVD-techniques, applying the vanadium alkoxides as precursors.

The alkoxides of vanadium have been tested as substituents for the titanium component in the Ziegler catalysts for about 30 years ago. The most efficient were found to be $VO(OBu^n)_3$ and also $V(OBu^n)_3$, and $V(OBu^n)_4$ (see, for example, [434, 1266]).

One of the most important applications of vanadium alkoxides is connected with their catalytical action on the reactions of oxidation of hydrocarbons and, in particular, alkanes, cycloalkanes, and so on. [645, 172]. Except for $VO(OR)_3$ it was proposed that the complexes already containing the peroxide groups in their composition — such as $VO(OBu^t)_2(OOBu^t)$ [1516], $VO(OR)(OOH)_2$, $VO_2(OOR)$ [172], and $V^{IV}(OPr^i)_3(OOBu^t)$ [25] — be used.

Recently interest has been shown in studies of the biochemical processes, which include the action of enzymes with vanadium-containing centers (like those of serine or tyrosine) that catalyze or inhibiting the redox and phosphorylation reactions, and the alkoxides were investigated as the structural models for the latter [1319, 424]. A bimetallic phenoxide of vanadium (II, III) was found to be an efficient reducive agent for molecular nitrogen in the methanol solutions [1034].

12.16. Niobium and tantalum alkoxides

Studies of niobium and tantalum alkoxides were started by Bradley in the 1950s as a part of the studies of a broad range of derivatives of rare metals for the separation of the elements from the mineral raw materials.

12.16.1. Synthesis

See also Chapter 2. Bradley has used for the preparation of all the homologs of the $M(OR)_5$ alifatic series 2 main reactions — the interaction of

Table 12.16. Vanadium alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
V(II)				
[V(OC$_6$H$_3$Ph$_2$-2,6)$_2$Py$_3$], tetragon pyr.	4, 5	red cr., μ_{eff} =3.72	IR, magn. prop., X-r	1156
[V(OC$_6$H$_3$Ph$_2$-2,6)$_2$Tmeda]-*trans*, saddle shape	5	red cr., μ_{eff} =3.63		
[V(OC$_6$H$_2$Me-4-Bu$^t_2$-2,6)$_2$Py$_2$] ·2C$_7$H$_8$, square planar	4, 5	red-brn. cr., μ_{eff} =3.71	IR, magn. prop., X-r	1156
[V(η^2-OC$_6$H$_4$OMe-2)$_2$Tmeda], oct. with 3 cycles	4	red-or., μ_{eff} =3.83	IR, magn. prop., X-r	1156
[(LiTHF)$_2$V(μ-OC$_6$H$_3$Pr$^i_2$-2,6)$_4$], linear mol., central [VO$_4$] sharing common (μ-OR)$_2$ edges with 2 trian.		yel.-grn. cr., s. in hex., μ_{eff} =3.83	electr.sp., ESR, magn. prop., X-r	1444
LiV(OBu^t)$_3$			ESR, GLC	1338
V(II,III)				
[Na$_2$V$_4$(μ_3-OMe)$_2$(η^2,μ-O$_2$Ar)$_4$(η,μ-OArOH)$_2$ (MeOH)$_8$], Ar(OH)$_2$=Bu$^t_2$C$_6$H$_4$(OH)$_2$-1,2 2 gr. [Na(MeOH)$_2$] are attached to a Ti$_4$(OR)$_{16}$ core of 2 oct. [V^1(μ_3-O)$_2$(μ-OArOH)$_2$ (MeOH)$_2$] and 2 [V^2(μ_3-O)(μ-OArOH)$_2$(O$_2$Ar)$_2$] via μ-OArOH and O$_2$Ar		yel.-brn. cr., +MeOH →H$_2$; +N$_2$+MeOH→ NH$_3$	X-r	1034

V(III)				
V(OMe)$_3$↓	5, 4	sld. grn., 150/10^{-4} → VO(OR)$_3$↑+V^{II}	-	226, 663
V(OEt)$_3$↓	5	sld. grn., 250/10^{-4} → VO(OR)$_3$↑+V^{II}	-	226
V(OBu^t)$_3$	5, 7	-	IR, ESR, GLC	1338
[V(OPh)$_3$Tmeda]	5	grn. cr., μ_{eff} =2.78	IR, magn. prop.	1156
[[V(OC$_6$H$_3$Me$_2$-2,6)$_3$]$_2$THF]·C$_7$H$_8$, tetrah. and trig. bipyr. with common (μ-OR)$_2$-edge, THF$_{ax.}$	4	grn. cr., s. in hex., μ_{eff}= 1.41, in m-s V(OR)$_4^+$	IR, X-r	614
[V(OC$_6$H$_3$Me$_2$-2,6)$_3$Py$_2$] trig. bipyr.	4 ,5	or. cr.,μ_{eff}=2.71, in m-s- V(OR)$_4^+$	IR, m-s, X-r	614, 1156
V(OC$_6$H$_3$Pr$^i_2$-2,6)$_3$L$_2$], L=NH$_2$NMe$_2$, NH$_2$NMePh, trig. bipyr., 2N -ax.	5	red cr., s. in hex.	X-r	1002
V(OCH$_2$CH$_2$Cl)$_3$ ↓,·L, L=Hmpa, Ph$_3$AsO, Dipy, Dmso **·2L,**L=Dmfa, Py, α,β,γ-picolins, Ph$_3$PO	5	μ_{eff} =1.70 μ_{eff} =1.85-2.34	IR , ^{1}H, ^{19}F, m-s, electr.sp., magn. prop., el. conduct.	319
V(OCH$_2$CF$_3$)$_3$, ·L **V(OCH$_2$CCl$_3$)$_3$·Et$_2$O,** **·2L,** L= Dipy, Dmso, Dmfa, Py, Hmpa, THF, Diox, Ph$_3$PO, α,β,γ- picolins	5	s. in MeCN, μ_{eff} =1.43-1.90	IR, magn. prop.	319
V(η^2-OCMe$_2$CH$_2$OMe)$_3$		55/1.5 (subl.)	-	732

$V(OC_6H_4OMe\text{-}2)_3$ = $=[V(\mu,\eta^1\text{-}OR)(\eta^2\text{-}OR)_2]_2$ 2 oct. with a common edge, $(\mu\text{-}OR)_2$	4	or. cr. (cocryst. with $[V(OAr)_3$ $\{NCH(SiMe_3)_2\}_2]$	IR, X-r	1156
$V(OC_2H_4OH)_3\downarrow$; **$V(OCH_2CH(OH)CH_2OH)_3\downarrow$**	4		IR	1502
$VCl(OMe)_2$, ·L, L=MeOH (2 forms), Me_2CO **$VCl_2(OMe)$, ·2MeOH**		grn. cr., μ_{eff}=2.1-2.6; I form - amor., s., α=3; II form - cr., ins., α=4	IR, electr.sp., ebul, magn. prop., X-r powder	636, 868
$VCl_2(OEt)$		grn. cr., 300 (dec.)	IR, X-r powder	636
$VCl(OBu^n)_2$		grn. cr., 270 (dec.)	« magn. prop.	636
$[VCl_2(OC_6H_3Me_2\text{-}2,6)THF_2]$, trig. bipyr., 2 THF-ax.		red cr., s. in hex.	X-r	1086
$VCl(OCH_2CH_2Cl)_2$,·2L **$VCl(OCH_2CCl_3)_2$, ·2L,** Et_2O, Dipy, Dmso, Dmfa, Py, Hmpa, THF, Diox Ph_3PO, $Ph_3AsO\alpha,\beta$, γ- picolins,		grn. oil grn.cr. μ_{eff} =1.60-2.50, oct. at.V	IR, electr.sp., magn. prop., conductance	319
$VCl_2(OCH_2CF_3)$ **$VCl_2(OCH_2CCl_3)$, ·nL,** n=1-2		α=2, antiferromagn.	IR,^1H,^{19}F, m-s, electr.sp., magn.	319
$[VCl(\eta^2\text{-}C_6H_4O_2\text{-}1,2)THF_2]_2$ 2 oct. with a common edge, $[O_2]$ from 2 different RO_2		red cr., s. in hex.	X-r	1086
$\{[Li(\eta^2\text{-}Dme)]_3V(\mu\text{-}OPh)_6\}$, $Al_4(OPr^i)_{12}$ type, central $[VO_6]$ oct. bind 3 tetrah. $[LiO_4]$		grn. cr., s. in hex.., μ_{eff} =2.90	electr.sp., magn. prop., X-r	1746

[LiTHFV(OC$_6$H$_3$Pr$^i_2$-2,6)$_4$] Li trian. and V tetrah. with a common edge, (μ-OR)$_2$		grn. cr., s. in hex.., μ_{eff} =2.75	electr.sp., magn. prop., cyclic voltamet.,X-r	1746
[Li(12-crown-4)]$^+$ [V(OC$_6$H$_3$Pr$^i_2$-2,6)$_4$]$^-$ anion- tetrah.		grn. cr., s. in THF/hex., μ_{eff} =2.72	electr.sp.,magn. prop., cyclic voltamet., X-r	1746
V(IV)				
V(OMe)$_4$	4, 5	brn.amor.sld. , 200/ 0.05 (dec.), μ_{eff} =1.70 -1.79 (123-289 K), α=2.79	IR, m-s, electr. sp., ESR, magn. prop., ebul.	11, 31, 226, 227, 1613
V(OEt)$_4$	4, 5	brn.liq.,100-110/ 0,05(b.), α=2.2, μ_{eff} =1.69	IR, electr.sp., ESR, magn. prop., ebul.	31, 226, 227, 1613
V(OPr^n)$_4$	4, 5	clrl. liq.,140/0.5 (b.),α=1.39	IR, ebul.	226, 1613
V(OPr^i)$_4$	4, 5	grn.sld., , 40 (m.), 70/0.1, 55/0.1 (b.), α=1.17	IR, m-s, ebul.	11, 226, 1579, 1613
V(OBu^n)$_4$	4	brn.liq.,150/0.5 (b.), α=1.31	IR, ebul. TGA	24, 226
V(OBu^i)$_4$	4	brn.liq.,114/ 0.05 (b.),α=1.3	ebul.	24, 226,
V(OBu^s)$_4$	4	brn.liq.,81/0,05 (b.), α=1	ebul.	226
V(OBu^t)$_4$	4, 5, 7	liq. bl.; 90/0.1, 55/ 0.05 (b.), μ_{eff}=1.69, α=1; $\Delta H_{form.}$ =-328 (gas)	IR, ^{1}H, ^{13}C , ^{51}V, electr.sp., ESR, magn. prop., cryosc., calorimetr., X-r	24, 31, 226, 218, 227, 935, 1318, 1338, 1579

V(OC$_5$H$_{11}{}^n$)$_4$, V(OC$_2$H$_4$Pr^i)$_4$ V(OCH$_2$CHMeEt)$_4$, V(OC$_5$H$_{11}{}^{neo}$)$_4$, V(OCHMePr^n)$_4$, V(OCHMePr^i)$_4$, V(OCHEt$_2$)$_4$	4	brn.liq.,160/ , 112/, 142/, 100/, 110/, 104/, 108/0.05 (b.), α~1	ebul.	226
V(OC$_5$H$_{11}{}^t$)$_4$, V(OCMe$_2$Pr^n)$_4$,	4	grn.liq.,83/,110 /0,05(b.),α=1	ebul.	226
V(OCMe$_2$Pr^i)$_4$	4	liq. grn., .α=<1	ebul.	226
V(OCEt$_3$)$_4$, V(OCMeEtPr^n)$_4$	4	grn.liq.,128/ 0.05(b.), α=1	ebul.	226
V(OAd-1)$_4$ **V(OAd-2)$_4$** **V(OCH$_2$Ad-1)$_4$**	4	grn., μ_{eff}=1.75 bl.cr, μ_{eff}=1.57, poorly s. in eth., bz., 250 (dec.) brn. cr., s. in bz., α=1-2 (brn.-grn.), μ_{eff} =1.71	IR, ^{1}H, magn.prop. ESR, m-s, cryosc.	166
V(OPh)$_4$	3	α=1	m-s	11
V(OC$_2$H$_4$OEt)$_4$	5	-	-	1423
[V(η^2-3,5-Bu$^t{}_2$C$_6$H$_2$O$_2$-1,2)$_2$ Phen], oct. **[V(3,5-Bu$^t{}_2$C$_6$H$_2$O$_2$-1,2)$_2$Dip]**	6, 4	blk. cr., +CH$_2$Cl$_2$, C$_5$H$_{12}$→dec.	IR, ^{51}V, electr. sp., m-s, ESR, conduct.	612, 862
V(OSiEt$_3$)$_4$	4	liq.,150/0.1(b.)	-	1579
VCl$_2$(OR)$_2$ · ROH, R=Bu^n, Bu^t		grn. sld., s. in ROH, C$_7$H$_{16}$	ESR	335, 1338
[Et$_3$NH]$_2{}^+$[V(η^2-C$_6$H$_4$O$_2$-1,2)$_3$]$^{2-}$, oct. with 3 cycles		grn.-bl. cr., s. in ROH	IR, X-r	412
[R$_4$N]$_2$[V(OR')Cl$_5$], R=Me, Et, R'=Me, Et, Pr, Bu		grn. cr., s in ROH, μ_{eff} = 1.73-79 (77-295 K)	IR, electr.sp., magn. prop., ESP	142

$VO(OMe)_2 \cdot n[HAm]Cl$, n= 1, 2	5	-	IR, electr.sp., magn. prop., conduct.	582
$[VO(OEt)_2]_n$, $[VO(OPr^i)_2]_n$	5	brn. sld., amor., s. in ROH	IR, ESR	1613
$[VO(C_2H_4O_2\text{-}1.2)Dipy]$ $[VO(3.5\text{-}Bu^t_2\text{-}C_2H_2O_2\text{-}1.2)Dipy]$	6	stab. in s.	IR, electr. sp., m-s, ESR, conduct.	612
$VOCl(OMe) \cdot 2Py \cdot [R_3NH]Cl$, $VOBr(OMe) \cdot 3Py$, $VOI(OMe) \cdot 3Py$		bl. cr., s. in MeOH (br. s.)	-	582, 1449
$[VOCl(\eta^2,\mu\text{-}OCHMeCH_2OMe)]_2$, 2 trig. bipyrs. with a common edge, $(\mu\text{-}OR)_2$, Cl and O (alkox) – ax		bl. cr., s.in THF, tol.	IR, ^1H, ^{51}V, X-r	581
$K_2[VO(\eta^2\text{-}C_6H_4O_2\text{-}1,2)_2] \cdot EtOH \cdot H_2O$ anion- tetragon. pyr.		bl. cr.	IR, X-r	412
$(PhenH)_2[VO(C_6H_4O_2\text{-}1,2)(C_6H_4O(OH)\text{-}1,2)]_2$		α=2	IR, electr.sp., m-s, ESR, conduct.	612
$K_2VO[\eta^2\text{-}(OC(CF_3)_2)_2]$		bl.sld.,s .in MeOH, μ_{eff}=1,72	IR, magn. prop.	1750
$M_2[V_6O_7(OH)_n(RO_3)_{12\text{-}n/3}]$, n=0, 3, 6 **$Na_2[V_6O_7[EtC(CH_2O)_3]_4]$** **$Ba[V_6O_7(OH)_3[MeC(CH_2O)_3]_3] \cdot 3H_2O$,** **$M_2[V_6O_7(OH)_6[RC(CH_2O)_3]_2$**, anions- $[(VO)_6(\mu_6\text{-}O)(\mu\text{-}OH)_n(\eta^3,\mu_3\text{-}RO_3)_{12\text{-}n/3}]^{2-}$		bl. cr. ,μ_{eff} = 3.52, antiferr. bl. cr. brn. (bl.) cr. μ_{eff} =3.45	IR, electr.sp., ESR, magn. prop, voltametr., X-r	913 337, 1181
$(NH_4)_4[V_{10}O_{16}[EtC(CH_2O)_3]_4] \cdot 4H_2O$, anion - $[(VO)_8 V_2(\mu_6\text{-}O)_2(\mu_3\text{-}O)_2(\mu\text{-}O)_4(\eta^3,\mu RO_3)_4]$		blk. cr.	IR, magn.prop., voltametr., X-r	913
$[R_4N]_2[V_{10}O_{14}(OH)_2\{HOCH_2C(CH_2O)_3\}_4] \cdot 2H_2O$, **$[Et_4N][V_{10}O_{13}[EtC(CH_2O)_3]_5]$**, struct. analogs of $[V^V{}_{10}O_{28}]^{6-}$, RO_3 – on the surface		blk. cr., μ_{eff} =4.45		

$[V_{16}O_{20}\{\eta^3,\mu\text{-}(OCH_2)_3CCH_2OH\}_8(H_2O)_4]\cdot 3H_2O$, layers of oct.: $[V_2]$, $[V_6](\mu\text{-}O)_4[V_6]$, $[V_2]$ (each $[V_8]$ – block – the $[V_{10}O_{28}]$ struc. without 1 $[V_2]$ layer)	4	lihgt grn. (brn. ?) cr.	magn. prop, X-r	913
$[HAm][VOCl_2(OMe)]$; $[H_2Am][VOCl_2(OMe)]_2$				582
V(IV,V)				
$[V_2O_3(OEt)_3(Phen)]_2$, linear mol., 2 $[(V^{IV}O)(\mu\text{-}OR)_2N_2(\mu\text{-}O)]$ oct. sharing a common $(\mu\text{-}OR)_2$-edge in the center, each one sharing a common μ-O-vertex with a $[(V^VO)(\mu\text{-}O)(OR)_2)]$ tetrah.	5	or. cr.	X-r	972
$V_6O_7(OEt)_{12}$, oct. $[(MO)_6(\mu_6\text{-}O)]$, OR along the edges	hydrol.	dark grn. cr.	IR, X-r	903
$M_2[(V^V{}_{6-n}V^{IV}{}_nO_{13-n})(OH)_n\{RC(CH_2O)_3\}_2]$, n=0, 3, 6		grn. cr.	IR, magn. prop.,	337
$M_2[(V^{IV}{}_3V_3{}^VO_6)(\mu_6\text{-}O)(\mu\text{-}O)_3(\mu\text{-}OH)_3\{RC(CH_2O)_3\}_2]^-$ **$[R_4N]_2[(V^{IV}{}_4V_2{}^VO_6)(\mu_6\text{-}O)(\mu\text{-}O)_2(\mu\text{-}OH)_4[MeC(CH_2O)_3]_2]$** **$[R_4N][(V^{IV}{}_5V^VO)_6(\mu_6\text{-}O)(\mu\text{-}OH)_3[MeC(CH_2O)_3]_3]$** anions- oct. $[M_6(\mu_6\text{-}O)]$, μ-(O,OH)- along the edges, RO_3 – on the surface of anion		bl. cr. grn. cr. bl. cr., μ_{eff} =3.40	voltametr., X-r	913 1181
$M_2[V^{IV}{}_8V_2{}^VO_{16}[EtC(CH_2O)_3]_4]\cdot nH_2O$, M=Na, K, Bu_4N anion- $[(V^{IV}O)_8V^V{}_2(\mu_6\text{-}O)_2(\mu_3\text{-}O)_2(\mu\text{-}O)_4(\eta^3,\mu_3,\mu_3\text{-}RO_3)_4]^{2-}$ struct. analog of $[V_{10}O_{28}]$		cr. brn., bl., bl-grn	IR, magn. prop., voltametr., X-r	913
V(V)				
$[V(\eta^2\text{-}3,5\text{-}Bu^t{}_2C_6H_2O_2\text{-}1,2)_2Phen]^+$ $[SbCl_6]^-$, cation – oct. with 3 cycles	7	blk. cr., stab. sld., dec. in s.	^{51}V, voltamet., X-r	862

$VO(OMe)_3$= $[(VO)_2(\mu\text{-}OMe)_4(OMe)_2] \propto$ zigzag chains of dimers - pairs of $[VO(\mu\text{-}OR)_4(OR)]$ oct. with common $(\mu\text{-}OR)_2$ edge	3, 5, 6	yel. cr., s. in ROH, 60/0.1 (subl.), α=1.05	IR, ^{51}V m-s, cryosc. ,TGA, X-r	11, 118, 302, 607, 983, 1163, 1284, 1296, 1319, 1613, 1708, 1707
$VO(OEt)_3$	3, 5, 6	yel.liq., γ $\nu\rightarrow$dec., 0° (m), 82/5, 48/ 0,1 (b.), $d^{20}{}_4$ 1.167; $n_D{}^{20}$ 1.5103; ε^{25}=3.333; μ=1.18; α=1.3; $\Delta H_{form.}$= -285.5	IR, ^1H,^{51}V, electr. sp., m-s, cryosc., magn. prop. , dielectr., thermol.	11, 82, 296, 983, 1163, 1313, 1319, 1613, 1348, 1708
$VO(OPr^n)_3$	3, 5	yel. liq., -5-10 (m.), 97/1,5 (b.); $d^{25}{}_4$ 1.0752; $n_D{}^{20}$1.4953; ε^{25}=2.961, μ=1.15, α=1.1-1.3	IR,^1H,^{13}C , ^{51}V,electr. sp., m-s, magn., dielectr. prop, cryosc.	296, 374, 983, 1260, 1284, 1313, 1319, 1348, 1707
$VO(OPr^i)_3$	3, 4, 5, 6	colrl. liq., 70/0.1; 125/2(b.), $d^{25}{}_4$ 1.0324; $n_D{}^{25}$1.478; ε^{25}=3.299; μ=1.23, α=1	IR, Raman ^1H, ^{51}V, electr. sp., m-s, magn. prop., dielectr., cryosc.	11, 118, 296, 374, 983, 1163, 1260, 1284, 1319, 1348, 1613, 1707, 1756
$VO(OBu^n)_3$	3, 5, 6	yel (colrl.) liq., $d^{20}{}_4$ 1.034; $n_D{}^{20}$1.4903; ε^{25}=2.780; μ=1.12; 121/1 (b.)	IR, ^1H,^{51}V, electr. sp., m-s , magn., dielectr. prop	296, 374, 983, 1163, 1238, 1260, 1284, 1313, 1348, 1708
$VO(OBu^i)_3$	3, 5	yel (colrl.) liq., $d^{20}{}_4$ 1.030; $n_D{}^{20}$1.4823; 5-10 (m.); 114/2(b.); ε^{25}= 2.761; μ=1.10, α=1.1-1.2	IR, ^1H, ^{51}V, m-s dielectr. prop.; cryosc., thermol.	11, 296, 1348, 983, 1238, 1313, 1284, 1707
$VO(OBu^s)_3$	3, 5, 6	colrl. liq., 107/2(b.); $d^{20}{}_4$ 1.012; $n_D{}^{20}$1.4823; ε^{25}=2.969; μ=1.10, α =1	^{51}V, ^1H, m-s dielectr. prop., cryosc.	11, 296, 983, 1163, 1238, 1319

$VO(OBu^t)_3$	3, 6	colrl.cr., 49(57-?) (m.), 110/10 (b.); μ=1.16, α=1	IR ,Raman, ^1H, ^{13}C, ^{51}V, m-s, dielectr. prop.	11, 218, 296, 983, 1163, 1238, 1313, 1319, 1756
$VO(OC_5H_{11}{}^n)_3$	3	colrl liq.,., 153/2(b.), d^{20}_4 1.005; $n_D{}^{20}$1.4867	^1H, electr.sp., magn. prop.	374, 743, 983, 1238, 1260
$VO(OC_2H_4Pr^i)_3$	3	colrl. sld., 70 (m.); 142/2 (b.);$d^{20}_4$0.9991;$n_D{}^{20}$1.484	^1H, IR	983, 1238, 1313, 1707
$VO(OC_5H_{11}{}^{neo})_3$	3	α=1	^1H, m-s	11, 983
$VO(OC_5H_{11}{}^s)_3$	6	yel liq., 118/5(b.), α=1	^1H, ebul.	983, 1163
$VO(OC_5H_{11}{}^t)_3$	3, 6	colrl.liq., 118/ 2.5 (b.), d^{25}_4 0.9863; $n_D{}^{20}$ 1.4805; ε^{25}= 2.764; μ=1.1, α=1	dielectr., cryosc.	296, 1163, 1313
$[VO(OC_5H_9{}^c)_3]_2$, 2 trig. bipyr. with common (μ-OR)$_2$ edge	4	liq. colrl., -10(m.), $1<\alpha<2$	^{51}V, X-r	752
$VO(OC_6H_{13})_3$	6	139/2 (b.)	-	1163
$VO(OC_6H_{13}{}^t)_3$	6	yel. liq., 122/1,5 (b.), α=1	ebul.	1163
$VO(OC_6H_{11}{}^c)_3$	6	colrl.sld., 80(m.), α=1	ebul.	1163
$VO(OC_{10}H_{19})_3$ (menthoxid)	6	s. in Diox,, Dmfa	electr.sp.	172
$VO(OR)_3$, R= CPh_3, exo-norbornyl, endo-norbornyl, 1-adamantyl, 2-adamantyl	5	yel. sld., 195,130, 138(m.), 156 (subl.), 200(dec.), s.in hc.	IR, ^1H,^{13}C, ^{51}V	424
$VO(OPh)_3$	3, 6	dark sld., s. in ROH; α=1	m-s	11, 607
$VO(OC_6H_4Me\text{-}4)_3$	3	α=1	m-s	11
$VO(OCH_2CF_3)_{3-n}(OPr^i)_n$	4, 5	liq. yel.-or., α=1	IR, ^1H,^{13}C, ^{19}F	374
$VO(OCH_2CH_2F)_3$ **$VO(OCH_2CF_2CHF_2)_3$** **$VO[OC(CF_3)_3]_3$**	3 4 7	sld. yel. liq.,123/12(b) yel.sld., 62 (m.),60/vac(subl.)	IR, ^1H,^{51}V - IR, ^{19}F	1319 690 294

$[VO(\mu\text{-}OCH_2CH_2Cl)_3]_2$, 2 trig. bipyr.	3	sld., s. in C_5H_{12}	IR, ^1H, ^{51}V, X-	1319
$VO(CH_2CCl_3)_3$	3	-	IR, ^1H, ^{51}V	1319
$VO(OSiMe_3)_3$, $[VO(OSiPh_3)_3]\cdot 0.5C_6H_6$, tetrah.	5	colrl. sld., s. in CH_2Cl_2	IR, ^1H, X-r	558,776, 1318
$[VO(OSiBu^t{}_3)_2]_2O$	3	-	-	1723
$VO(RO_2)(RO_2H)$, $[(VO)(RO_2)(RO_2H)]_2$, $V(OH)(RO_2)_2$, $[V(OH)(C_2H_4O_2)_2]_2$	6	yel. sld., amor., each compound exist in 2 forms: RO_2H -term. or η^2-	IR, ^{13}C, ^{51}V, m-s	424
$VOCl(OMe)_2$		-	^{51}V	1284
$VOCl_2(OMe)$		yel. liq., 40/1 (b.)	^{51}V, m-s	11, 607, 1348, 1284
$VOCl(OEt)_2$ **$VOBr(OEt)_2$**		or. liq., 55/1; 45/0.15(b); $n_D{}^{20}$ 1.533; $d^{20}{}_4$ 1.300;75/2(b)	IR,^1H, ^{51}V , electr.sp., magn. prop., m-s	607, 635, 1163, 1313, 1348, 1613
$VOCl_2(OEt)$		yel. liq.; 52/1(b); $d^{20}{}_4$ 1.496; $n_D{}^{20}$ 1.588;	IR,^1H, ^{51}V, electr. sp.,magn. prop.	11, 635, 1163, 1313, 1348
$VOCl(OPr^n)_2$		-	^{51}V	1284
$VOHal(OPr^i)_2$, Hal=F, Cl		94/9 (b.), dec. in light	IR, Raman, ^{51}V, m-s	118, 1163, 1284, 1319, 1756
$VOBr(OPr^i)_2$		94/6 (b.)	-	1163
$VOCl_2(OPr^i)$; $VOF_2(OPr^i)$		78/7 (b), dec. in light	«	11, 1163, 1284, 1319, 1756
$VOHal(OBu^t)_2$, Hal= Cl, Br		-	-	1163, 1318
$VOCl_2(OR)$, R=Bu^n, Bu^i, Bu^t		dec. in light	^{51}V	1284, 1319, 1348
$VOCl(OCH_2CF_3)_2$, $VOCl(OCH_2CF_3)(OPr^i)$		yel.-or. liq., α=1	IR, ^1H, ^{19}F, cryos.	374
$VOCl(CH_2CF_2CHF_2)_2$		yel. liq., 123/12 (b.)	-	690
$VOCl(OPh)_2$		red cr., s. in EtOH		607

$[VOCl(\mu\text{-}OC_2H_4O)]_2$, 2 tetrah. connected via 2 (μ-RO_2)-gr.	colrl. (yel.?).cr., s. in RCl	IR, ^1H, ^{51}V, X-r	424, 1319
$VOCl[O(CH_2)_3OH]_2$	yel-brn. sld.	IR, ^1H, ^{51}V	1319
$VOCl[OCH_2CH(CH_2Me)O]$,	red oil	IR, ^1H, ^{51}V	1319
$VOCl_2[O(CHMe)_2OH)]$	«		
$(VOCl_2)_2[\mu\text{-}OCH_2CH(CH_2Me)O]$			
$[(VOCl)_2[VO(\mu_3\text{-}OH)_2]_2[\eta^2,\mu\text{-}CMe_2(CH_2O)_2]_4 \cdot 4CHCl_3$, struc. type of $Ti_4(OMe)_{16}$, 2 oct. $[V^2OCl(OH)O_3]$ and 2 $[V^1O(OH)_2O_4]$	amber cr.	^1H, ^{13}C, ^{51}V, X-r	425
$[(VOCl)(\mu\text{-}ORO)]_4$, R= $(CH_2)_3$, $CH_2CMe_2CH_2$, $CH_2CMeEtCH_2$, $CH_2CMePr^nCH_2$	or. cr., 87-148 (m.), ~ 150 (dec.)		
$[VOCl(\mu,\eta^2\text{-}O(CMe_2)_2O)]_2$ 2 trig. bipyrs. with a common $[O_2]$-edge from different RO_2	or. cr.	^1H, ^{13}C, X-r	424
$[BiVO(OC_2H_4OMe)Cl_3]_2$, 4 M at. form a rhombus	or. cr., s. in ROH	IR, ^1H, ^{13}C, DTA	1290
$[V_4O_4(OMe)_6\{\mu,\mu,\mu_3\text{-}(OCH_2)_3CMe\}_2]$	yel. cr	IR, ^1H, ^{13}C, ^{51}V, X-r	425
$[V_4O_4(OEt)_3\{(OCH_2)_3CR\}_3]$	red cr.		
$[V_6O_{11}(OH)_2\{(OCH_2)_3CR\}_2] \cdot 2Dmf \cdot Me_2O$	red cr.	IR, ^{17}O, ^{13}C, ESR, electr. sp., X-r	337
$[Bu_4N]^+[(VO)_6(\mu_6\text{-}O)(\mu\text{-}O)_5(\mu\text{-}OMe)_7]^-$	red-brn. cr.	IR, ^1H, ^{13}C, X-r	772
$M_2[V_6O_{13}\{(OCH_2)_3CR\}_2]$	red cr.	IR, ^1H, ^{17}O, ESR	1181

MCl_5 with alcohols in the presence of ammonia (method 5) and the alcohol interchange of $M(OPr^i)_5$ (method 6). Mehrotra proposed later the application of esters in the alcohol interchange reaction for $Nb(OEt)_5$ [223].

On the interaction of $[M(OR^n)_5]_2$ with s- or t-ROH it turns out usually to be impossible to substitute the fifth OR-group, which has the bridging function in the dimeric $[M(OR)_4(OR^n)]_2$, (R^n = Me, Et) molecules formed. The latter are liquids that can easily be distilled in vacuo without decomposition [205, 1126, 882]. The preparation of $Nb(OBu^t)_5$ represents then a considerable problem. The first attempt to substitute all 5 alkoxide groups in $Nb(OEt)_5$ on action of ^tBuOH yielded $Nb_2O(OBu^t)_8$ (this process was accompanied by the formation of Bu^t_2O), which on sublimation was transformed into $NbO(OBu^t)_3$ [205]. $Nb(OBu^t)_5$ was, however, obtained later under the same conditions and also on application of $AcOBu^t$ as an alkoxylating agent [1126, 1128] and as well on alcoholysis of $Nb(NEt_2)_4$ (accompanied by oxidation of the $Nb(OR)_4$ formed by action of alcohol and evolution of hydrogen gas) [196].

Recently, the anodic oxidation of metals (method 2) was also applied for the preparation of the niobium and tantalum derivatives of $M(OR)_5$ series (R = Me, Et, Pr^i, Bu^n) [1478, 1616, 1639]. It should be mentioned that a crystalline oxoisopropoxide $Ta_2O(OPr^i)_8{\cdot}{}^iPrOH$ (Fig. 4.1 *c*), was isolated from the ^iPrOH-based electrolyte. It is destroyed on heating in vacuo, yielding $Ta(OPr^i)_5$.

Oxoalcoxides of niobium of the $NbO(OR)_3$ series were obtained on the interaction of $NbOCl_3$ with solutions of NH_3 or NaOR in alcohols [791, 911] and also via alcohol interchange from $NbO(OEt)_3$; they are even formed on the oxidation of $Nb(OR)_4$ (the side products in the electrochemical preparation of $Nb(OR)_5$) by oxygen [911].

The derivatives in the lower oxidation states Nb(II), Nb(III), Ta(III) (known mainly for niobium) were obtained by the reduction of $M(OR)_5$ by sodium amalgam [404, 1187], and bimetallic methoxoniobates (IV) by reduction with hydrogen *in statu nascendi* (Mg + MeOH) or on cathodic reduction in solution (method 7). The alkoxide chlorides of Nb(III) and Nb(IV) crystallize on alcoholysis of the corresponding chlorides at low temperatures (method 4) [416, 1731].

12.16.3. Properties

The phenoxides of Nb(II) and alkoxides of Ta(III), as well as the corresponding derivatives of vanadium should be stabilized by the sterically hindered ligands. The alkoxide chlorides of niobium (III) and (IV) are diamagnetic clusters with double or single M–M bonds, respectively. All these compounds are colored. $Nb(OR)_4$ (R = Me, Et) are very sensitive red oils; their molecules are aggregated and diamagnetic [416, 1731]. In all the molecules of the structurally characterized derivatives of Nb (II–IV) the metal atoms have octahedral coordination (see Table 12.17).

$M(OR^n)_5$ starting with the ethoxides are light yellow (Nb) or colorless (Ta) liquids; $M(OMe)_5$, $M(OR^s)_5$, $M(OR^t)_5$, and $M(OC_5H_{11}^{neo})_5$ are colorless crystals. They can be easily distilled and sublimed in vacuo (which is used for their isolation and purification) and soluble in practically all the organic solvents. The results of the molecular weight determinations indicate that the derivatives of primary alcohols are dimeric in solution and that those of secondary and tertiary alcohols are monomeric. The ^1H NMR study of the solutions of $M(OR)_5$ has proved the existence of the monomer-dimer equilibrium, which is nearly completely shifted to monomer for the isopropoxides at 20°C. At the same time the methoxides form stable dimers, not dissociating up to 160°C [219]. The ^1H NMR data indicate the possibility of shifting the equilibrium of aggregation for $Nb(OMe)_5$ via the complex formation with donor molecules (of the solvent in particular) [1353, 237]. Numerous adducts of methoxides with O-, N-, S-donor ligands having 1:1 composition have been isolated in the solid state. There has recently been reported even the $Ta(OMe)_5 \cdot MeOH$ solvate, crystallizing from the solution of $Ta(OMe)_5$ in methanol at < 20°C [1639].

The structures of the isomorphous pairs of $M(OMe)_5$ or of $M(OPr^i)_5$ derivatives are built up of dimeric molecules, where the 2 metal octahedra share a common edge [1304, 1639, 1622] (Fig. 4.1 *a*). The crystalline bimetallic $NbTa(OMe)_{10}$ complex was found to be isostructural to the dimers described and to exist even in the gas phase and in solutions in hydrocarbons at low temperatures [788].

The data accumulated on properties of Nb and Ta alkoxides studied in detail permitted the connection to be traced between the molecular complexity and the boiling points for different members of the homologous series, which allowed some general conclusions to be made concerning the trends in the homologous series in general (see Chapter 3). Concerning the vapor pressures and the possibility of purification by distillation, see [205]. The evaporation enthalpies for methoxides, ethoxides, and n-propoxides of the 2 metals are close to each other and increase naturally from the lighter to the heavier homologs [928, 1569]. The M-OR bond energies are very close for the alkoxides of Nb and Ta (100 and 105 Kcal) and appear to be practically independent of R [1569].

The derivatives of the $MO(OR)_3$ have been described only for niobium. In contrast to $VO(OR)_3$, they are very unstable and disproportionate on transition into the gas phase into $Nb(OR)_5$ and $NbO_2(OR)$. They decompose also on prolonged storage undergoing ether elimination and condensation, which for the ethoxide leads to the crystalline $Nb_8O_{10}(OEt)_{20}$ [911]. This compound and the corresponding Ta-complex isomorphous to it have been also isolated on partial hydrolysis of $M(OEt)_5$ [219, 1617] (see Chapter 3). According to the NMR data, a dynamic equilibrium between the μ-O and μ-OR groups takes place in solutions of $[NbO(OEt)_3]_2$ in nonpolar solvents [791].

The terminal double bonds with the oxygen atoms have been observed according to the X-ray single-crystal data only in the tetrahedral molecule of $[NbO(OC_6H_3Ph_2\text{-}2,6)_3]$ [1802] and in the molecules of the heterometallic complexes like $[LiM^VO(OEt)_4(EtOH)]_2$ and $[Li_2(NbO)_2O(OCMe_2CH_2OMe)_6]$ [1622, 732]. Only the oxobridges have been observed in the other known structures of oxoniobium alkoxides, like a $[Nb_2(\mu\text{-}O)_2]$ cycle in the structure of the $[NbO(OC_6H_3Pr^i_2\text{-}2,6)_3]_2$ dimers [1703], or μ_3- and μ-O groups in the molecules of $[Nb_3O_2[O(CMe_2)_2O]_4[O(CMe_2)_2OH]$ and $[Nb_4O_4[O(CMe_2)_2O]_2(OPr^i)_8]$ [782], and in the structures of the abovementioned $M_8O_{10}(OEt)_{20}$ (Fig. 4.12 *b*). The same trend is observed in the few structures of the tantalum oxoalkoxides known so far (mainly the bimetallic complexes, see Table 12.17).

The absence of the monomeric derivatives of the $MO(OR)_3$ series for tantalum can be explained by the inability of its atoms to form the terminal double bonds with the oxygen atoms. The gas phase over all the $Ta(OR)_5$ contains quite stable binuclear molecules of $Ta_2O(OR)_8$, and it is the solvate of the same series $Ta_2O(OPr^i)_8 \cdot {}^iPrOH$ that crystallizes from the solutions of $Ta(OPr^i)_5$ in ${}^iPrOH$ after prolonged reflux [1639] (Fig. 4.1 *c*). In this latter molecule the 2 octahedra are sharing a μ-O–μ-OR edge. It should be mentioned that the mass-spectra of $Nb(OMe)_5$ do also contain the $M_2O(OMe)_7^+$-ions; however, their intensity does not exceed 0.6 to 5% of that of the $Nb(OR)_4^+$-ions, while for $Ta(OR)_5$ these values are comparable [1606]. The features described correspond to the known trend to decrease in multiplicity for the M=O bonds in the V, Nb, Ta (or Cr, Mo, W) series, which occur due to the increase in the energy of the d_π-orbitals of the metal atom M that gives rise to the higher stability of the oxobridges compared with that for a terminal bond. This results in formation of the highly condensed systems on hydrolysis of $Ta(OR)_5$ [219, 231, 815]. The other examples are provided by the structures of $Ta_7O_9(OPr^i)_{17}$. [1639] or $LiTa_9O_{13}(OEt)_{20}(EtOH)$ (Figs. 4.13 *a* and *b*) and $[Li_8Ta_8O_{14}(OEt)_{20}(EtOH)_8]$ [1519] close to those of isopolyanions, unknown for niobium $(Nb_8O_{10}(OEt)_{20}$ being the only exclusion).

The numerous alkoxide halides of niobium and tantalum containing the atoms of all the known halogenes from F to I and a broad range of radicals are considered in the Table 12.17.

A special role in the chemistry of Nb and Ta alkoxides is played be to the bimetallic complexes — precursors of the complex oxide materials with perovskite structures. Mehrotra has described a large variety of alkoxoniobates and-tantalates of alkaline $M^IM^V(OR)_6$ and alkaline earth metals $M^{II}M^V_2(OPr^i)_{12}$ [1136, 1509], obtained on direct interaction of the homometallic derivatives. Alkoxotantalates are solids or viscous noncrystallizing liquids soluble in alcohols and hydrocarbons. According to the mass-spectral data, the molecules of alkoxotantalates are present in the gas phase but undergo a considerable dissociation, which precludes their purification by distillation in contradiction to the data of Mehrotra [1562]. Of all the alkoxoniobates, these are the only Mg complexes that have been detected in the gas phase according to mass-spectra [898]. The investigation of solubility in the tricomponent $M^{II}(OR)_2$–$M^V(OR)_5$ –ROH (M^{II} = Mg, Ba; R = Me, Et, Pr^i, Bu^n) systems permitted the envisaging of formation of the complexes of 1:2 composition in solution, the $MgTa_2(OEt)_{12}\cdot 2EtOH$, and $M^{II}M^V_2(OPr^i)_{12}\cdot 2^iPrOH$, M^{II} = Sr, Ba disolvates being isolated as crystalline solids. In all the other cases, the complexation products turned out to be noncrystallizing [1562, 1622].

The results of the numerous structure studies lead to a conclusion that all the alkoxoniobates and -tantalates have similar composition and are isomorphous. The structures of $LiM^V(OR)_6$ (R = Me, Et) contain infinite chains of intermitting Li tetrahedra and Nb(Ta) octahedra sharing common edges. These chains are planar for the methoxides and helical for ethoxides [1519, 524, 1622]. The above-mentioned molecules of solvated magnesium ethoxotantalate and barium (strontium) isopropoxotantalate (niobate) consist of 3 octahedra sharing common edges, where the first of these molecules is linear because of the *trans* -arrangement of the solvating alcohol molecules and the second is bent as the solvating $^{i}PrOH$ molecules are in *cis*-position to each other. The molecules of $Be[Ta(OEt)_6]_2$ and $LaTa_2(OEt)_{13}$ have also the chain structure. The first one is linear and contains a tetrahedrally coordinated Be atom in the center. The second one is bent and asymmetric: the La-octahedron shares an edge with one Ta-octahedron and a face with the other (Fig. 4.3 *a-d*).The Al and Ta isopropoxides form complexes of 1:1 and 1:2 compositions and exist only in the liquid and gas phases [334].

It is rather interesting that in the systems where no crystalline complexes are formed by the alkoxides of Nb (Ta) and M^{II}, the refluxing or prolonged storage of solutions lead to precipitation of crystalline bimetallic oxoalkoxides — $[Mg(NbO)(OMe)_5(MeOH)_2]_2$ [898], $[SrTaO(OMe)_5(MeOH)_{2.5}]_4$, $[MgTaO(OBu^n)_5(^nBuOH)_4]_4$ (Fig. 4.12 *a*), and $[BaM^VO(OEt)_5(EtOH)_{1.5}]_4$ [1622, 1522], $[Pb_6Nb_4O_4(OEt)_{24}]$ [1253]. It is important that the metal ratios in the oxocomplexes described do correspond to the steichiometry of the desired oxide materials — $M^{II}MO_3$ — in contrast to those in $M^{II}M^V_2(OR)_{12}$.

Of great interest are the data on numerous $M[M^V(OPr^i)_6]_n$ — derivatives of the 3*d*-elements Cr^{III}, Fe^{II}, Co,Ni, Cu^{II} [12, 501, 618, 818,1109,1462,1561], prepared by interchange reactions of MCl_n with $KM^V(OPr^i)_6$. The other $M[Ta(OR)_6]_n$ ($R = Me, Et, Pr^n, Bu^n$) homologs were prepared from the isopropoxides by alcohol interchange reactions. The data on formation of bi- and trimetallic alkoxoniobates and tantalates under the conditions described in [12, 14, 501, 618, 818, 1109, 1462] was questioned. The products described could be obtained only in the presence of traces of water and were undoubtedly oxoalkoxides by nature. The mass-spectra of trimetallic "$BeAlM^V(OPr^i)_{10}$" (considered as the major proof of their individuality [14]) have discovered only the presence of the fragments of $[M(OR)_5]_2$ and $[AlM(OR)_8]$ [1622, 1561].

The major application domain for the alkoxides of Nb and Ta is the deposition of the oxide films from the gas phase by CVD technique [1339] (their application in the sol-gel technology is described in Section 9.8 and 10.2).

12.17. Chromium alkoxides

The studies of chromium (III) alkoxides were initiated in the 1960s by Hornuff [769] and by Bradley, who has even described isolation and characterization of Cr(IV) derivatives [30]. Quite a comprehensive investigation of the preparation and properties of chromium (II) alkoxides was carried out by Hor-

Table 12.17. Niobium, tantalum and protactinium alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
Nb(II)				
$[Nb(OC_6H_4Me\text{-}4)_2Dmpe_2]$-*trans* oct.	7	dark blocks, s. in tol. (purple), purple-bm. cr.	^1H, ^{13}C, ESR, X-r	404
Nb(III)				
$[Nb_2Cl_5(OEt)(EtOH)_4]$		red. cr., s.in ROH, stab., diamagn.	^1H, magn. prop.	416
$[Nb_2Cl_5(OPr^i)(Pr^iOH)_4]$ 2 oct. with common [(OR)Cl]-edge, Nb=Nb 2.61, 2 bonds Cl...HOR-ax		yel.-bm.cr., s. in ROH, stab., diamagn., +THF → $Nb(IV)+C_2H_4+...$	^1H, magn. prop., X-r	416
***trans*-$[Nb(OC_6H_3Pr^i_2\text{-},5)_2Dmpe_2]^+[Nb^V(OAr)_6]^-$** 2 oct., in cation- <MOC ~170, in anion 145-161		gm. cr.	X-r	404
Nb(IV)				
$[Nb(OMe)_4]_n$, **$\cdot PR_3$**, R=Me,Et,Bu, Ph etc.	dec. Nb^V, 7	red oil, α=1↔2	electr.sp., ESR	416, 1144

$[Nb(OEt)_4]_n$	5	red-br. oil, v. instabl., diamagn.	IR, electr.sp. magn. prop.	1731
$Nb(OAd\text{-}1)_4$ Ad=adamantyl ($C_{10}H_{15}$) **$Nb(OCH_2Ad\text{-}1)_4 \cdot 0.5Et_2NH$**	4	oliv-grn. cr., s. in eth., 140 (dec.), α=1, μ_{eff} = 1.40 bl. cr., α=1, s. in bz., diamagn.	IR, ^1H, magn. prop., ESR, m-s	166
$[NbCl_2(OMe)_2(MeOH)]_2 \cdot 2MeOH$, 2 oct. with common $(\mu\text{-}OR)_2$-edge,MeOH -ax., Nb-Nb 2.78		bl. cr., s. in $CHCl_3$, ROH, ins. in hc.	IR, ^1H, X-r	416, 689
$[NbCl_2(OMe)_2(MeCN)]_2$, 2 oct. with common $(\mu\text{-}OR)_2$-edge, 2 Cl-at. and 2 OR ax.		red-bm. cr., s. in $CHCl_3$, ROH, tol.	IR, ^1H, X-r	416
$[Nb(\mu\text{-}Cl)(OEt)_3Py]_2$		red cr., s.in $CHCl_3$, α=1.07, diamagn.	IR, electr.sp. magn. prop.	1731
$[Nb_2Cl_4(OEt)_2THF]_2O_2$= $[Nb_2(\mu\text{-}Cl)(\mu\text{-}OEt)Cl_3(OEt)THF_2]_2(\mu\text{-}O)_2$ 2 dimers of 2 oct. with common [(OR)Cl]-edge are bound by 2 (μ-O) in a cycle, <Nb-O-Nb 178		red cr.	^1H, X-r	416
$[Nb_2Cl_4(OPr^i)_2THF]_2O_2$		-	-	416
$[Nb_2Cl_5(OEt)_3Dipy_2]$		gm-bl. cr., μ_{eff} =1.39	IR, magn. prop.	488
$[NbCl_3(OR)Dipy]$↓, R=Me, Et,Pr^n,Bu^n		gm.cr., 115, 155, 205, 115 (m), s.inTHF, μ_{eff} =1.4-1.6	IR, magn. prop.	1711

$[Na(MeOH)_6]^+[Nb_2(OMe)_9]^-$ **$[Mg(MeOH)_6]^{2+}{}_2[Nb_2(OMe)_9]^-Cl_3$** **$[Mg(MeOH)_6]^{2+}[Nb_2(OMe)_9]^-I^- \cdot 2MeOH$** anion-2 oct. with a common face, $(\mu\text{-}OR)_3$, Nb=Nb 2.64, chains ROH...OR		bl.cr. wh. cr. v. instab. bl.-purpl cr., ins. in ROH	X-r	416
$[AmH]_2[NbCl_5(OR)]$, R=Me, Et,Pr^i		pink-vlt. cr.	IR	689, 1731
Nb(V)				
$Nb(OMe)_5$ 2 oct. with common $(\mu\text{-}OR)_2$-edge	5	corl. cr., α=2.11, 60 (m.), 153/0.1(b.), p-T (poly-therm); $\Delta H_{form.}$ = -337.9	IR, ^1H, ebul., m-s, X-r	205, 219, 788, 928, 1304, 1295, 1316, 1353, 1569
L, L=Py, N_2H_4, Dipy, γ-picolin, Hmpa, Diox, THF, $C_5H_{10}S$ etc.		sld., wh.	IR, ^1H	790
$Nb(OMe)_4(OBu^t)$	6	corl. cr., 163/0.8 (b.), α=2.05	-	1126
$Nb(OEt)_5$	2, 5	yel.liq.,160/0.1 (b.), α=2,02, p-T (polytherm), $\Delta H_{form.}$ = -378.6	IR ^1H, ^{13}C, ebul., m-s, TGA	23, 205, 219, 765, 928, 1295, 1316, 1436, 1569 1616
$Nb_8O_{10}(OEt)_{20}$ $=[Nb_8(\mu_3\text{-}O)_2(\mu\text{-}O)_8(\mu\text{-}OEt)_6(OEt)_{14}]$, centrosym. mol., 2 $[M(\mu\text{-}O)_4(OR)_2]$ oct. connect 2 $[M_3(\mu_3\text{-}O)(\mu\text{-}OR)(OR)_6]$ triades of oct.	hyd-rol.	colrl. cr., 169 (m.., dec.), s. in hc., ROH	IR, m-s, X-r	219, 911

$Nb(OEt)_4(OBu^t)$		colrl.liq.,138/0.1 (b.), α=2.0	ebul.	1126
$Nb(OPr^n)_5$	5, 6	yel-or. liq., 166/0.05, 182/0.8 (b), α=2.0; p-T (polytherm),ΔH_{form} -406.7	ebul.	205, 928, 1126 1128, 1569
$[Nb(OPr^i)_5]_2$ 2 oct. with common (μ-OR)$_2$-edge	2, 4, 5, 6	wh.sld., 79(m.), 60/0.1 (subl.), s. in ROH (polytherm), α=1.0	IR,^{1}H, m-s, X-r, cryosc.	205, 219, 1126, 1128, 1579, 1616, 1782
$Nb(OPr^i)_n(OEt)_{5-n}$, n=3, 4	6	wh. cr.	-	205
$Nb(OPr^i)_4(OBu^t)$	6	cr., 78/0.3 (subl.), α=1.15	ebul.	1126
$Nb(OBu^n)_5$	6	yel. liq., 195/0,l(b.), α=2.01	ebul.	205, 1126, 1128
$Nb(OBu^i)_5$	5, 6	sld.,150(m.),160/0.1(b.), α=2	^{1}H, ebul.	205, 219
$Nb(OBu^s)_5$	5, 6	yel. liq., 112/0.l(b.), α=1.14	ebul.	205, 1126
$Nb(OBu^t)_5$	4, 5, 6	wh.sld., 90/0.l (subl.), α=l	ebul.	205, 1126, 1579
$Nb(OC_5H_{11}{}^n)_5$	6	yel.liq., 228/0.15 (b.), α=2	ebul.	205, 1128
$Nb(OC_2H_4Pr^i)_5$ $Nb(OCH_2CHMeEt)_5$	5, 6	yel.liq.,199/,183/0.l(b.), α=1.8	ebul.	205
$Nb(OC_5H_{11}{}^{neo})_5$	5	sld.,120/10^{-2} (subl.),α=1.5	^{1}H,^{13}C,ebul.	205, 652

$[Nb(OC_5H_{11}{}^{neo})_4(OEt)]_2$, 2 oct. sharing a ($\mu$-OEt)$_2$ edge	6	wh. powd., s. in tol., 159 (dec.)	IR, ^1H, ^{13}C, ^{93}Nb, TGA, X-r	188
$Nb(OCHMePr^n)_5$, $Nb(OCHMePr^i)_5$	5, 6	yel.liq., 137/0.1 (b.), α=1.03	ebul.	205
$Nb(OCHEt_2)_5$	5, 6	yel.liq.,.138/0.1 (b.), α=1.16	ebul.	205
$Nb(OC_5H_{11}{}^t)_4(OEt)$	6	colrl. paste, 148/0.4(b.)	-	1126
$Nb(OAd\text{-}1)_5$ **$Nb(OAd\text{-}2)_5$**, Ad=adamantyl ($C_{10}H_{15}$)	4	colrl. cr., >350(dec.), s. in ArH, poorly -in eth., α=1	IR, ^1H, ESR, magn.prop.	166
$Nb(OPh)_5$ **L**, L=Py, Py-N-oxid, Ph_3AsO	4, 6	yel. cr., 209(m.), 320/0.2 (b.)	IR	595, 1128, 1053, 1435
$Nb(OC_6H_4Me\text{-}4)_5$	5	-	-	404
$[Nb(OC_6H_3Me_2\text{-}2,6)_5]$, trig. bipyr.	5	sld., 143-166 (m.)	X-r	404
$[Nb[OC_6H_3(C_6H_{11}{}^c)_2\text{-}2,6]_4H]$, square $[NbO_4]$	7	or. cr.	^1H, X-r	340
$Nb(OC_{10}H_7\text{-}\beta)_5$	4	or. cr, 185 (m..,dec.)	IR	601, 1053
$Nb(OCH_2CH{=}CHMe)_5$ **$Nb(OCHMeCH_2CH{=}CH_2)_5$** **$Nb(OCMeEtCH{=}CH_2)_5$** **$Nb(OC_3H_6CH{=}CH_2)_5$**	6	yel.liq., $n_D{}^{25}$ 1.5515, α=2 colrl.sld.,130/0.5(subl colrl. liq., α=1 yel. liq., 170/5 (b.dec.), $n_D{}^{25}$ 1.5245, α=2	IR, ^1H, ebul.	655

$Nb[OCH(CF_3)_2]_5$	5	paste, 85/0.1(b.), s. in bz., α=1	-	880
$Nb(OCH_2CF_2CHF_2)_5$	4	colrl. oil, $140/10^{-3}$ (b.)	-	690
$Nb(OSiMe_3)_5$, $Nb(OSiEt_3)_5$ **$[Nb(OCH_2SiMe_3)_5]_2$** 2 oct. with common $(\mu\text{-}OR)_2$-edge	4, 6 6	colrl. oil, 210/0.1 (dec.) colrl. sld., 111(m.), $120/10^{-4}$ (subl.), s. in hc., α=2	- IR, ^1H, $^{13}C\ \{^1H\}$	235, 1579 652
$Nb(OC_2H_4OMe)_5$	6	colrl. liq.	m-s	1652
$[Nb_4(OC_2H_4O)_5(OPr^i)_{10}]$, zigzag chains of 4 oct. with a common edge	6	colrl. cr., s. in org. solv., ins. in in ^iPrOH	IR, ^1H, X-r	781
$[Nb_3O_2[O(CMe_2)_2O]_4[O(CMe_2)_2OH]$ non-linear chain of 3 oct. with a common edge **$[Nb_4O_4[O(CMe_2)_2O]_2(OPr^i)_8]$=** $[Nb_4(\mu_3\text{-}O)_2(\mu\text{-}O)_2(\eta^2,\mu\text{-}RO_2)_2(OPr^i)_8]$, struct type of $Ti_4(OMe)_{16}$	6 . 6	colrl. cr., s in tol., Dme, THF, eth., ins. in ROH, C_nH_{2n+2} colrl. cr., s. in petrol. eth.., , poorley- in ^iPrOH	IR, ^1H, X-r IR, ^1H, ^{13}C , X-r	781 781.
$[Nb(OEt)_2[MeC(CH_2O)_2(CH_2O\text{-}\mu)]_2]_2$, 2 oct. with common $(\mu\text{-}O)_2$-edge	6	wh. powd.	IR, ^1H, ^{13}C, ^{93}Nb, TGA, X-r	188
$Nb(OC_6H_4OH\text{-}1,2)_5$, $Nb(C_6H_4O_2\text{-}1,2)_5$	4	red cr.	-	601
$NbHal_n(OEt)_{5-n}$, Hal=F, Cl, n=1-4		colrl. cr.	IR, ^1H	282, 646
$NbCl(OMe)_4$ **$NbCl(OEt)_4$**		colrl. cr., α=2; 124 (m), α=1.91, 220/vac (subl.)	m-s	938, 1316, 1435
$[NbCl_2(OR)_3]_2$, R=Me, Et, Pr^n, Bu^n		α=2; 162 (m, R=Me)	m-s	791, 787, 1316, 1435, 1711

$NbC1_3(OMe)_2$	wh. cr.,100(m.)	IR, ^1H, m-s	787
$[NbC1_3(OEt)_2L]$, L=Py,Ph_3PO, Ph_3AsO, **$NbC1_3(OPr^i)_2$**	cr., 70(m.) cr., 113 (m)		132, 247, 938, 1435
$[NbCl_3(OPr^i)_2Hmpa]$, oct., 1 at. Cl and OR- ax, OR-equ *-trans* Hmpa	cr., 92(m.), s. m CH_2C1_2	X-r	787
$NbC1_4(OMe)$ **$NbC1_4(OEt)(MeCN)$**	cr., 70 (m.); α=2 yel. cr., s. in bz., eth., 180°→$NbOCl_3$+RCl	IR, ^1H, m-s	637, 938, 1435
$NbBr_4(OR)(MeCN)$, R=Me, Et, Pr^n, Pr^i, Bu^n, $C_5H_{11}{}^{neo}$	rot-or. cr., 110-125 (m.., dec.)	IR	1435
$NbF_4(OPh)$, ·MeCN	yel. cr.,72, 88 (m.), α=4, 1	IR, ^{19}F	1435
$NbCl_n(OPh)_{5-n}$, n=1-4, **·L,** L= Py, MeCN, α-picolin, Dmfa, Dmso	cr., or.- brn., α=2; m.: 240, 234, 196, 188 (n=1-4); +H_2O→ colrl; α=1	IR, cryosc.	601, 1053, 1053, 1053, 1435
$NbBr_n(OPh)_{5-n}$, n=1-4	brn. cr., 237-120 (m.,dec.), α=2	IR, ebul.	1435
$[NbCl_3(OC_6H_3Me_2\text{-}2,6)_2THF]$-*cis*, oct. **$[NbCl_4(OC_6H_3Me_2\text{-}2,6)THF]·C_6H_{14}$-*trans***	red cr.,178(m.) s. in hc.,THF red cr., 143(m.)	^1H, m-s, X-r	876, 1789

$NbCl_2(OC_6H_3Pr^i_2\text{-}2,6)_3$, $[NbCl_3(OAr)_2]_2$, 2 *cis*-oct. with common $(\mu\text{-}Cl)_2$-edge, **$[NbCl_n(OAr)_{5-n}L]$,** L=Py, PMe_2Ph,THF, oct., trans-mer (n=2), cis-mer (n=3), trans (n=4)	red cr., s. in hex., bz.	^1H, X-r	388
$[NbCl_3(OC_6H_3Ph_2\text{-}2,6)_2THF]\cdot C_6H_{14}$, oct.	-	X-r	1789
$[NbCl_3(OC_6HPh_4\text{-}2,3,5,6)_2].2C_6H_6$, tetragon. pyr.	-	X-r	1025
$[NbCl_n(OC_{10}H_7\text{-}\beta)_{5-n}$, n=1-4	n=2, red cr., 215 (m., dec.), s. in Dmfa	IR, TGA	601, 1053
$NbCl_3(OC_{10}H_9)_2$ (antranoxid)	grn. cr.	-	601
$NbCl_2(OSiBu^t_3)_3$	-	-	1723
$[NbCl_3(OC_2H_4OMe)_2]$	-	IR, ^1H	850
$[NbCl(2,2'\text{-}CH_2[C_6H_2Bu^t_2\text{-}4,6]_2O_2)_2]$, trig. bipyr.	red cr., 275/0.01 (subl.), s. in eth., hc.	IR,^1H,^{13}C, m-s, X-r	746
$MNb(OR)_6$, M=Li, Na, K, R=Me, Et, Pr^i, Bu^t	colrl. cr., s. in ROH, hc., electrolyts	ebul., conduct.	223
$[LiNb(\mu\text{-}OMe)_4(OMe)_2]_\infty$, zigzag chain of alternating $[Nb(\mu\text{-}OR)_4(OR)_2]$-*cis* oct. and $[Li(\mu\text{-}OR)_4]$ tetrah.	colrl. cr., s. in ROH	m-s, X-r	1519
$[LiNb(\mu\text{-}OEt)_4(OEt)_2]_\infty$, helix of alternating $[Nb(\mu\text{-}OR)_4(OR)_2]$-*cis* oct. and $[Li(\mu\text{-}OR)_4]$ tetrah.	colrl. cr., s. in ROH (36.2%), THF, bz.(11.7), s.in system *	IR, m-s, X-r	524,1622
$[LiNb(OC_5H_{11}{}^{neo})_6]$	181-210(m.),125/10^{-4} (subl.), s. in hc., α=2	IR, ^1H, $^{13}C\{^1H\}$	652

$\cdot 2\ {}^{neo}C_5H_{11}OH$	182-191(m.), $125/10^{-4}$ (subl. -ROH), s. in hc.		
$[LiNb(OCH_2SiMe_3)_6]_2$= $[Li_2Nb_2(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_6]$, Nb-oct., Li-tetrah. **$\cdot 2Me_3SiCH_2OH$**	cr.,181 (m.), $120/10^{-4}$ (subl., -2ROH) 130(m.),$155/10^{-4}$ (subl.)	IR,^1H,^{13}C $\{^1H\}$, X-r	652
$MgNb_2(OR)_{12}$, **2ROH**, R=Et, Pr^i	visc.liq., s. in bz. cr., 25°→ -2ROH	IR	223, 1509
***cis*-$[Ba(^iPrOH)_2][Nb(OPr^i)_6]_2$=** $[Ba(^iPrOH)_2Nb_2(\mu\text{-}OPr^i)_4(OPr^i)_8]$ angular, central $[BaO_6]$ oct. shares with 2 $[NbO_6]$ oct. the $(\mu\text{-}OR)_2$ edges	colrl. cr., ins. in ROH, s. in bz., THF, 20°→ROH, s. in system *	IR, m-s, X-r	182, 1622, 1782
$[Cd_2Nb(\mu\text{-}OPr^i)_4(OPr^i)_3(\mu\text{-}I)I]_2$, 2 $[NbCd_2]$ trian., Nb-oct. shares $(\mu\text{-}OR)_2$ - edge and OR-vertex with 2 tetrah.: $[Cd(\mu\text{-}OR)_3\ I]$ and $[Cd(\mu\text{-}OR)_2\ I_2\ ]$, $[Cd_2(\mu\text{-}I)_2]$- group in the center	-	X-r	1691
$[LaNb_2(OPr^i)_{13}]$= $(RO)_4Nb(\mu\text{-}OR)_2La(\mu\text{-}OR)_3Nb(OR)_3$	colrl. cr.. s. in ROH (5-30%), hc., 150 (m.), s. in system *	X-r	1782, 1621
$[Ce_2Nb_2(\mu_3\text{-}O)_2[\eta^2,\mu\text{-}O(CMe_2)_2O]_4(OPr^i)_6]$, $Ti_4(OMe)_{16}$ struct . type **$[Ce_2Nb_2O[O(CMe_2)_2O]_6[O(CMe_2)_2OH]_2(OPr^i)_6]$**	yel. cr., s. in hex.	IR,^1H	782
$Sn^{IV}I_2[Nb(OPr^i)_6]_2$	yel. cr., s in tol.-hex.	IR,^1H,^{13}C,^{119}Sn	1690
$[Et_4N][NbHal_4(OR)_2]$, R=Me, Et; Hal=Cl, Br **$M[NbCl_5(OEt)]$; $M[NbCl_n(OPh)_{6-n}]$**, n=1, 2	colrl. (Cl), yel. (Br) cr. yel. cr.	IR, ^1H	247, 850, 938,1435

$NbO(OMe)_3$	5, 7	sld., 185 (dec.)	IR, m-s	911
$NbO(OEt)_3$, $NbO(OPr^i)_3$, $NbO(OBu^n)_3$	5, 7	colrl. visc. liq. (sld.wh), α=2	IR, ^1H, m-s	791, 911
$NbO(OBu^t)_3$	subl. 1	sld. wh.	-	205
$Nb_2O(OBu^t)_8$ (1)	6	sld.wh., 110/0.01 (subl.)	-	205
$[NbO(OC_6H_3R_2\text{-}2,6)_3]$, R=Me, Bu^t	5	yel. sld., α=l, s. in RC1, bz.	IR, ^1H, ^{13}C, m-s	893
$[NbO(OC_6H_3Pr^i{}_2\text{-}2,6)_3]_2$ 2 trig. bipyr. sharing a $(\mu\text{-}O)_2$ edge	hyd-rol.	-	X-r	1703
$[NbO(OC_6H_3Ph_2\text{-}2,6)_3]$, tetrah.	-	yel. cr.	X-r	1802
$NbO(OCH_2CF_3)_3{\cdot}MeCN$	5	sld..,35(m.), 98/0,4(b.) s. inRC1,ROH,MeCN, α=2	IR, m-s	791
$NbO(OC_2H_4OMe)_3$	6	liq.	IR	1652
$Nb_3O_2[O(CMe_2)_2O]_5[O(CMe_2)_2OH]$= $Nb_3(\mu\text{-}O)_2[\mu,\eta^2\text{-}RO_2]_2[\eta^2\text{-}RO_2]_3[\eta^2\text{-}RO_2H]$ non-linear chain of 3 oct.	- -	-	X-r	782
$[Nb_4O_4[O(CMe_2)_2O]_2(OPr^i)_8]$ struct. type of $Ti_4(OMe)_{16}$		-	X-r	782
$NbOCl_2(OMe){\cdot}L$, L=MeOH, 2 Hmpa		wh. sld., s. in tol., α=l	IR, ^1H	791
$[NbOCl_2(OEt)Dipy]$, oct.		-	IR, X-r	870a
$NbOCl_2(OCH_2CCl_3){\cdot}2Dmso$		cr,110 (m.), s. in tol., α=l	IR, ^1H, cryosc.	791
$[Li(NbO)(OEt)_4(EtOH)]_2$, $[Li_2(NbO)_2(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_2(ROH)_2]$, $Ti_4(OMe)_{16}$ struct. type, Nb^2- oct., Li^1- tetrah.		cr. colrl., 20° → ROH	IR , X-r	1622, 1621

$[Li_6Nb_4O_6(OPh)_{14}THF_6]THF$		-	X-r	1256
$[Li_2(NbO)_2O(OCMe_2CH_2OMe)_6,]$, $[Li_2(NbO)_2(\mu_4\text{-}O)(\eta^2,\mu\text{-}OR)_4(\eta^2\text{-}OR)]$, Nb -oct., CN Li –5		cr., vol.	X-r	732
$[Mg(NbO)(OMe)_5(MeOH)_2]_2$ $Ti_4(OMe)_{16}$ struct. type, Mg^1 and Nb^2- oct.		cr., s. in ROH	X-r	898
$[Ba_4Nb_4(\mu_4\text{-}O)_4(\mu\text{-}OEt)_{20}(EtOH)_6]$, $[Ba_4O_4]$-cube, CN Ba 8 and 9, Nb- oct.		s. in ROH (3%), in bz. (27%)	X-r	1621
$[Pb_6Nb_4O_4(OEt)_{24}]$, 8 faces of $[Pb_6]$-oct. are capped by 4 μ_3-OR and 4 $[ONb(OR)_5]$-oct., $[PbO_6]$ - trig. prism		colrl. cr., s. in C_5H_{12}, in s. → $Nb(OR)_5$+...	^1H, ^{13}C, ^{207}Pb, X-r	1253
Ta(III)				
$[Ta(OR)_3]$, R=CBu^t_3, $SiBu^t_3$	7	-	-	1187
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_3L]_2(N_2)$, L=THF, Py, 2 trig. bipyr. $[TaO_4N]$	5	yel. ,or. cr., s. in eth., stab.	^1H, ^{13}C, X-r	1438
$[TaCl(OBu^t)_2]_2$	5	yel. powd., s. in $CHCl_3$	IR, ^1H	1172
Ta(V)				
$Ta(OMe)_5$ isomorph. with its Nb-analog	2, 5	colrl. cr., 48(m.), 140/0.02 (b), s. in ROH, α=1.98, p-T (polytherms), $\Delta H_{form.}$=338.8	IR, ^1H, m-s, ebul., X-r	237, 237, 219, 1295, 928, 1569
·MeOH		21(m.., dec.)		1639

·L, L=Py, N_2H_4, Dipy, γ-picolin, Hmpa, Diox, THF, $C_5H_{10}S$ etc.			IR, ^1H	788, 790
$Ta(OMe)_4(OBu^t)$	6	colrl. visc. liq., 154/0.8 (b.)	-	1126
$Ta(OEt)_5$	2, 4, 5	colrl. liq., 20 (m.),150/0.02 (b.); α=1.98, p-T polytherm, $\Delta H_{form.}$ = -391.6	IR, ^1H, m-s, ebul., TGA	23,219, 237, 928,1436, 1639, 1579, 1569
$Ta_8O_{10}(OEt)_{20}$, isomorph. with its Nb-analog	hyd-rol.	wh. sld.., s. in hc. ROH, 235 (m., dec.), t→$Ta(OEt)_5$↑	IR, m-s, ebul.	1617
$Ta(OEt)_4(OBu^t)$	6	clolrl. visc. liq., 145/0.2 (b.)	-	1126,
$Ta(OPr^n)_5$	5, 6	liq., 184/0.15; 50/0.02 (b.): p-T polytherm; α=1.95, $\Delta H_{form.}$ =-391.6	IR, ^1H, m-s, ebul.	237, 1126, 928, 1569
$Ta(OPr^n)_4(OEt)$	6	yel. visc. liq., 178/0.3(b.), α=2	-	1126, 882
$Ta(OPr^i)_5$ isomorph. with its Nb-analog **·En/2**	2, 5, 6	wh. sld., α=1.00; 122 (m., from tol.),135(fromROH), 122/0.1(b.), s. in ROH (polytherm)	IR, ^1H, m-s, ebul., X-r	92,205, 219, 1639
$[Ta(OPr^i)_4(OMe)]_2$, 2 oct. sharing a common $(\mu\text{-}OMe)_2$-edge	6	colrl. cr., 70(m), $81/10^{-1}$(b), α=1.84	cryosc., X-r	205, 847
$Ta(OPr^i)_4(OEt)$	6	sld., 130/0.2 (subl.), α=2	ebul.,cry sc	205,882,1126
$Ta(OPr^i)_4(OBu^t)$	6	wh. cr., 90/0.6 (subl.)	-	1126

$[Ta_2O(OPr^i)_8(Pr^iOH)]$ 2 oct. sharing a common [(OR)O]-edge	2	wh. cr., s. hex., ROH, 70°→ ROH↑; >200°→ $Ta(OR)_5$↑	IR, m-s, X-r	1639, 1784
$Ta_7O_9(OPr^i)17$, 2 $[Ta_4]$-tetrah, $=[Ta_7(\mu_3\text{-}O)_3(\mu\text{-}O)_6(\mu\text{-}OR)(OR)_{13}]$,	2	wh. cr., 150 (dec.)	IR, m-s, X-r	1639, 1784
$Ta(OBu^n)_5$	2, 5, 6	liq. yel., 217/0.2(b.), α=2.02	IR, m-s, ebul.	237, 1126, 1579, 1639
$Ta(OBu^n)_4(OEt)$	6	visc. liq., 199/0.1 (b.), α=2	ebul.	882, 1126
$Ta(OBu^i)_5$	5, 6	sld.,157(m.),185/0.1(b), α=2	^1H, ebul.	237, 205, 219
$Ta(OBu^i)_4(OEt)$	6	paste, 180/0.5 (b.), α=2	ebul.	882
$Ta(OBu^s)_5$	5, 6	cr., 90/0.3 (subl.); α=1.06	ebul.	237, 205, 882, 1126
$Ta(OBu^s)_4(OEt)$	6	visc. liq., 138/0.6 (b.), α=2	ebul.	1126, 882
$Ta(OBu^t)_5$	5, 6	sld. wh., 110 (m.), 130/0.5 (b.), 82/ 0.05 (subl.); α=1.01	ebul.	237, 205, 882
$TaO(OR)_3$, $R=Bu^t$, $C_6H_2Bu^t$	5	wt., grn. slds., v.s. in hc., α=1 (bz.), 2 (hex)	IR, ^1H, m-s	1317
$Ta(OBu^t)_4(OMe)$	6	sld., 110(m.), 96/0.05 (subl.); α=1	cryosc.	205
$[Ta(OBu^t)_4(OEt)]_2$	6	cr., 96 (m.), 84/ 0.1 (subl.), α=1	cryosc.	205, 802

$Ta(OBu^t)_4(OPr^i)$	6	sld.,94 (m),86/0.02(subl.), $\alpha=1$	cryosc.	205
$Ta(OC_5H_{11}{}^n)_5$	6	yel.liq.,233/0.1(b.), $\alpha=2$	ebul.	205, 237
$Ta(OC_5H_{11}{}^n)_4(OEt)$	6	or. liq., 231/0.5 (b.)	-	237
$Ta(OC_2H_4Pr^i)_5$, $Ta(OCH_2CHMeEt)_5$	6, 5	visc.liq., 210/, 204/0.1(b.), $\alpha=2$	ebul.	237
$Ta(OC_5H_{11}{}^{neo})_5$	5	sld., 90(m.),130/0 (b.), $\alpha=1.35$	ebul.	237
$Ta(OCHMePr^n)_5$,$Ta(OCHMePr^i)_5$, $Ta(OCHEt_2)_5$, $Ta(OC_5H_{11}{}^t)_5$	5	visc. liq., 148/, 137/, 153/, 142/0.1(b), $\alpha=1$	ebul.	205, 237
$Ta(OC_5H_{11}{}^t)_4(OEt)$	6	sld.,58 (m.),170 /0.1 (b.), $\alpha=1$	cryosc.	1126
$Ta(OC_5H_{11}{}^t)_4(OPr^i)$	6	sld., 90(m.), 139/ 0.1 (b.), $\alpha=1$	cryosc.	205
$Ta(OPh)_5 \cdot Py$	4, 5	cr., 224 (m.), $\alpha=2$	cryosc.	595, 1010, 1053, 1053, 1312, 1435
$Ta(OPh)_4(OEt)$	6	yel.cr., 208 (m.,dec.)	-	882
$[Ta(OC_6H_4Me\text{-}4)_5]_2$. 2 oct. with common ($\mu$-OR)$_2$ edge	5	yel. cr., s. eth., hex., 186(m.)	^1H, ^{13}C, X-r	1010
$[Ta(OC_6H_3Me_2\text{-}2,6)_5$	5	wh. cr.	IR, ^1H, ^{13}C, m-s	323
$[Ta(OC_6H_3Pr^i{}_2\text{-}2,6)_2(OMe)_3]_2$, 2oct. sharing a common (μ-OMe)$_2$-edge	7	wh. cr.	X-r	1718

$Ta(OC_{10}H_7\text{-}\beta)_5$	4	yel.cr., 180(m..), α=2.00	-	601
$Ta[O(CH_2)_nCH=CH_2]_5$ **$Ta(OCMeEtCH=CH_2)_5$**	6	colrl. liq., α=1-2	IR, ^1H, ebul.	655
$Ta[OCH(CF_3)_2]_5$	5	paste, 90/ 0.8 (b.), α=1	-	880
$Ta(OCH_2CF_2CHF_2)_5$	4	gl., 170/10^{-3} (b.)	-	690
$Ta(OR)_5$, R=$SiMe_3$, $SiMe_2Et$, $SiMeEt_2$, $SiEt_3$, $SiMe_2Pr^n$, $SiMe_2Pr^i$	6	sld., 80-180 (m.), 84-210/0.01(b.), α=1	-	235, 1579
$Ta(OC_2H_4OMe)_5$	6	liq., α=1	IR, m-s	1639
$Ta(OC_6H_4OH\text{-}1,2)_5$	4	yel. cr., ins. in bz.	-	601
$TaHal_3(OMe)_2$, Hal=Cl, Br **$[TaCl_2(OEt)_3]_2$-*trans*,** 2 oct. with common $(\mu\text{-}OR)_2$ edge; **$\cdot$Py** **$[TaHal_3(OEt)_2L]$**,L=Py,PPh_3,$OPPh_3$		wh. sld. cr., s. in tol., ins. in C_5H_{12}, α=2	IR, ^1H, X-r	247, 132, 646, 1317
$TaF_4(OPh)$, $\cdot$MeCN		cr., 81, 92 (m.), α=4.1	IR, ^{19}F	1435
$TaCl_n(OPh)_{5-n}$, n=1-4 **$\cdot$L,** L= Py, MeCN, α-picolin, Dmfa, Dmso		cr., yel.-bm., α=2; n=1-4: 253, 218, 174, 157 (m.)	IR, cryosc.	601, 1053, 1053, 1435
$TaBr_n(OPh)_{5-n}$, n=2, 4		cr., yel.,brn.,247, 167 (m.)	IR	1435
$TaI(OPh)_4$, $TaI_4(OPh)\cdot MeCN$		cr., yel., blk.-vlt., s.in bz.	IR,m-s,cryosc.	1435
$[TaCl_n(OC_6H_3Me_2\text{-}2,6)_{5-n}THF]$, n= 3, 4		yel. cr., m.:170, 163	-	1530, 1789

$[TaCl_3(OC_6H_3Pr^i_2\text{-}2,6)_2]_2$, isomorph. to Nb-analog **$[TaCl_3(OAr)_2L]$**, isomorph. to Nb-analogs L= Py, PMe_2Ph, Et_2O **$TaCl_2(OC_6H_3Pr^i_2\text{-}2,6)_3 \cdot L$**	yel. cr., s. in petr. eth., hex. grn. cr., s. in hex., bz.	IR, ^1H, ^{13}C, m-s, X-r	256, 323, 389, 388
$[TaCl_2(OC_6H_3Bu^t_2\text{-}2,6)_3]$-*trans* tetragon. pyr., OAr-ax.	yel.cr., s. in hex., 120 (m.)	IR, ^1H, ^{13}C, m-s, X-r	389
$[TaCl_3(OC_6H_3Bu^t_2\text{-}2,6)_2]$, tetragon. pyr.	or.cr.,170 (subl.) s. in tol.,		323
$[TaCl_2(OC_6H_3Ph_2\text{-}2,6)_3]$ **$TaCl_n(OC_6H_2Bu^t_3\text{-}2,4,6)_{5-n}]$**, n=2, 3	- or.cr., α=2(hex.), 1 (bz.)	-	340, 1317
$TaCl_n(OC_{10}H_7\text{-}\beta)_{5-n}$, n=1-4	or. cr., s. in Dmfa	IR	601, 1053
$TaCl_3(OC_{10}H_9)_2$ (antranoxid)	grn. -bl. cr., s. in CS_2	-	601
$TaCl_n(OSiBu^t_3)_{5-n}$, n=2, 3 **$TaCl_4[OSi(C_6H_4Me\text{-}2)_3(Et_2O)]$**, oct.	-	m-s, X-r	177, 990
$[TaCl_3(OC_2H_4OMe)_2]$= $[TaCl_3(\eta^2\text{-}OR)(\eta^1\text{-}OR)]$, oct. with one chelate cycle	-	IR, ^1H, X-r	499, 850
$[TaCl_3(C_6H_4O_2\text{-}1.2)]$	or. cr., s. in bz.	IR, ^1H, ^{13}C	661
$TaOCl_2(OMe) \cdot 2Dmso$	wh. cr., 131(m.), α=1	IR, ^1H	791
$[Ta_2OCl_3(OC_6H_3Pr^i_2\text{-}2,6)_5]$ 2 oct. with common $[\mu\text{-}OCl_2]$-face	yel. cr.	IR, ^1H, ^{13}C, X-r	389
$MTa(OR)_6$, M=Li, Na, K, Rb, Cs; R=Me, Et, Pr^i, Bu^t	colrl. cr., s. in ROH, hc., electrolytes, α~1	ebul., conduct.	667

$[LiTa(OR)_6]_\infty$ R=Me, Et - isomorph. with the Nb-analogs	cr. (R=Me, Et, Bu^n), s. in ROH 79, 35, 77%, visc. liq. (R= Pr^i), s. in systems*	IR, m-s, X-r	1562,
$[Li(TaO)(OEt)_4(EtOH)]_2$, isomorph. with the Nb-analog	clrl. cr.	X-r	1562
$[Li_8(EtOH)_8Ta_8O_{14}(OEt)_{20}]\cdot 4EtOH$ 2 $[Ta_4]$ - tetrah., connected by 2 μ-O, 4 Li-tetrah., 1 - trig. bipyr.	cr., s. in hex., tol., ins. in ROH	X-r	1519
$[LiTa_9O_{13}(\mu\text{-}OEt)_6(OEt)_{20}(EtOH)_2]$	cr.,s.in hex., tol., ins. in ROH	X-r	1519
$Be[Ta(\mu\text{-}OEt)_2(OEt)_4]_2$, linear., Be-tetrah. shares $(\mu\text{-}OR)_2$edges with 2 Ta oct.	cr., s. in ROH, THF	IR, m-s, X-r	1561
$Mg(EtOH)_2[Ta(OEt)_6]_2$-, linear, *trans*-$[MgO_4(ROH)_2]$-oct. shares $(\mu\text{-}OR)_2$ edges with 2 $[TaO_6]$ oct.	cr. (R=Me, Pr^i), 40, 32 (m.), s. in ROH 18, 8.5%, visc. liq. (R= Me, Bu^n), s.in systems*	IR, m-s, X-r	1562
$[MgTaO(OBu^n)_5(^nBuOH)]_4$, $[Mg_4(\mu_3\text{-}O)_4]$-cube, $[TaO(\mu\text{-}OR)_2(OR)_3]$ and $[MgO_3(\mu\text{-}OR)_2(ROH)]$- oct.	clrl. cr., ins. in ROH at 20°, on heating s. with dec.	X-r	1522
$[SrTaO(OMe)_5(MeOH)_{2.5}]_4$, $[Sr_4(\mu_3\text{-}O)_4]$ - cube, $[TaO(\mu\text{-}OR)_2(OR)_3]$-oct., $[SrO_3(\mu\text{-}OR)_2(\mu\text{-}ROH)\,(ROH)_2]$- 8-vertex polyhedron	"	X-r	1522

$[BaTaO(OMe)_5(MeOH)_{2.5}]_4$ **$[BaTaO(OEt)_5(EtOH)_{1.5}]_4$**, isomorph. with the Nb-analog		“	X-r	1522
$[BaTa_2(OPr^i)_{12}]$ = ***cis*-$[M^{II}(^iPrOH)_2Ta_2(OPr^i)_{12}]$**, M^{II}=Ba, Sr, isomorph. with the Nb-analogs		cr. (R=Pr^i), 51(m.), visc. liq. (R= Me,Et), s. in systems*	IR, m-s, X-r powder	1562
$[CdI\{Ta(OPr^i)_6\}(^iPrOH)_2]$ 2 oct. sharing a common $(\mu\text{-}OR)_2$ edge		-	X-r	1691
$[LaTa_2(OPr^i)_{13}]$, isomorph. with the Nb-analog		s. in systems*	IR, m-s, X-r	334
$MTa(OPh)_6$, M=Na, K		-	IR	1053
$KTa(OAr)_6$,Ar=$C_6H_3Me_2$-3,5;$C_6H_2Me_3$-2,4,6		-	IR, ^1H, ^{27}Al	343
$[IZnTa_2O_2(OPr^i)_7]_2$ 2 $[ZnTa_2]$- trian. of 2 Ta-oct. and Zn-tetrah.		clrl. cr., s. in org. s., expect hc.	IR, ^1H, $^{13}C\{^1H\}$, X-r	180
$[Et_4N][TaHal_4(OR)_2]$,R=Me,Et;Hal=Cl, Br		colrl. (Cl), yel. (Br) cr.	IR, ^1H	247, 850
$[Et_4N][TaCl_n(OC_2H_4OMe)_{6-n}]$, n=4, 5		-	IR, ^1H	850
$[MoO_2Ta_2O_2(OMe)_8]_2$, **$Mo_4Ta_4O_{16}(OPr^i)_{12}$** [847]; **$AlTa(OAr)_8$** [343] *The solubility isotherm is studied for the $M(OR)_n$ - $M^V(OR)_5$ - ROH system at 20°C				
Pa				
$Pa(OEt)_5$	5	yel.sld., 300 (dec.), s. in bz., α=5.7	IR	1045
$Pa(OEt)_3Hal_3$		colrl. sld.	IR, X-r powd.	247
$[Et_4N][Pa(OEt)_2Hal_4]$, Hal= Cl, Br		wh. sld. (Cl), yel. (Br)	«	247

vaths in the late 1970s [770]. The preparation, separation, and characterization of Cr(VI) alkoxides (esters of chromic acids) was first described in a paper by Zeiss [1807] and then quite recently developed further by Osborn *et al.* [1527].

12.17.1.Synthesis

The main route to the derivatives of Cr(II–IV) is provided by alcoholysis of corresponding alkyl or sylilamides (method 4). The exchange reactions of chlorides with alkali metals alkoxides (method 5) have been applied to the preparation of Cr(III) phenoxides and some dioxoalkoxocomplexes of Cr(VI). An interesting modification of method 5 is the interaction of silver chromate with alkylhalids: the feasibility of this reaction indicates that chromium (VI) alkoxides are more likely the esters of the chromium acid and not the usual metal complexes, where one can identify the positively charged central atom and negatively charged alkoxide ligands. The acidic character of chromium anhydride is demonstrated also by its easy interaction with alcohols leading to formation of chromium acid esters (method 3). An important role in the preparation of chromium (III) alkoxides is also played by redox reactions: this oxidation state is the most stable for chromium and can be achieved by both thermally or photochemically activated oxidation of chromium by alcohols and as well by the reduction of chromium (VI) by primary or secondary alcohols. It should be mentioned here that the alkoxocomplexes of chromium (V) are considered to be the intermediates in the reduction of hexavalent derivatives in the presence of diols, but the corresponding individual products have not been isolated and characterized [1162].

12.17.2. Properties

The most important feature of the chromium compounds, as well as of the other derivatives of early transition 3*d*-elements, appears to be a very pronounced difference between the derivatives of different oxidation states (Table 12.18). The alkoxides of chromium (II and III) are in the majority the insoluble and non-volatile polymers. The most important exclusion from this rule appears to be the volatile chelate $Cr(OCMe_2CH_2OMe)_3$ complex, and in the future, possibly, the number of the representatives of this family will increase. The derivatives of chromium (IV and VI) are monomers highly soluble in organic solvents. The lack of volatility for Cr(VI) compounds in contrast to those of Cr(IV) is caused apparently by the high electronegativity of the central atom, leading to thermal destruction and not to evaporation.

The redox reactions have been quite well studied for the chromium derivatives. Thus it is known that nearly all Cr(II) derivatives are pyrophoric and ignite in the presence of the traces of oxygen [770]. In the presence of alcohols they are spontaneously converted into Cr(III) alkoxides (apparently with the release of hydrogen gas). A very easy while not spontaneous oxidation has been observed for the Cr(III) derivatives of tertiary alcohols: they cannot be isolated as individual products even on alcoholysis of chromium (III) dialkylamides. The quantitative transformation into $Cr(OR)_4$ requires, however, the application of oxidants such as O_2, Br_2, $Pb(OAc)_4$, $CrO_2(OBu^t)_2$, $(Bu^tO)_2$, CrO_3, and CuCl [30]. The reaction of thus obtained monomeric $Cr(OR)_4$ with primary or secondary alcohols gives again insoluble polymeric $Cr(OR)_3$ and corresponding aldehydes or ketones, resulting from the oxidation of the alcohols, $Cr(OR)_3$ are formed also on interaction of $CrO_2(OR^t)_2$ with primary or secondary alcohols.

The transitions between different oxoforms for hexavalent derivatives are scarcely studied. The derivatives of all the three known series (i.e., $CrO_2(OR^t)_2$, $Cr_2O_5(OR^t)_2$, and $Cr_3O_8(OR^t)_2$) are formed simultaneously on CrO_3 interaction with alcohols in hydrocarbon media and can be separated by thin-layer chromatography on silica gel [131].

In the polymeric structures of the first members of the homologous series of trivalent chromium derivatives, the metal atoms possess octahedral coordination [1366], while the derivatives of branched radicals are often monomeric $[Cr(OR)_2L_2]$ molecules with square planar coordination [1571] or dimeric $[Cr(OR)_2]_2$ with triangular cordination of the metal atoms [795, 1185]. The monomeric $[Cr(OR)_3L_2]$ are trigonal bipyramids [1571], while the derivatives of chromium (IV) and (VI) are tetrahedral [167, 1573, 1527].

12.17.3. Application

The major practical application has been developed so far for $Cr(OR)_4$. They are used in combination with metalalkyls as the catalysts of stereoregular polymerization by Ziegler [696]. They can also serve as versatile precursors of othervise hardly accessible chromium derivatives — for example,

$$Cr(OBu^t)_4 + B_2H_6 \xrightarrow{THF} Cr[BH_4]_2{\bullet}2THF \ [1219]$$

$$Cr(OBu^t)_4 + 4LiR \longrightarrow CrR_4 \ [1180]$$

Table 12.18. Chromium alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
Cr(II)				
$Cr(OR)_2$↓, R= Me (vlt.), Et, Pr^n (or.), Pr^i (red), Bu^n, Bu^s, Bu^t, $C_5H_{11}{}^n$, $CHMePr^n$, $CHEt_2$, adamantyl-1, CEt_3, CPh_3, Ph (·THF) (bl.),, $C_6H_3Me_2$-2,6 (red), $C_6H_2Bu^t_3$-2,4,6, β-$C_{10}H_7$ (brn.-grn.), C_6H_4OMe-2	5, 4	μ_{eff}=5.16 (Me, Pr^i)	IR, electr. sp., magn. prop.	6, 350, 518, 770
$[Cr(OCBu^t_3)_2THF_2]$ **$[Cr(OCBu^t_3)(OCHBu^t_2)]_2$**, 2 trian. sharing a (μ-$OCHBu^t_2$) edge	7 5	bl.-grn. cr., 196 (m.) vlt. cr., s. in hc.	- X-r	795, 1185
$[Cr(OC_6H_2Bu^t_2$-2,6-Me-4$)_2THF_2]$	5	bl. cr., s. in hc.	IR	518
$[Cr(OC_6H_2Bu^t_3$-2,4,6$)_2L_2]$, L= THF, Py, square	5	grn. cr., s. in C_5H_{12}	IR, X-r	518, 1148
$\{Cr[OSi(OBu^t)_3]_2(Et_2NH)_2\}$, square	4	purple cr., s. in C_5H_{12}	IR, X-r	1571
$[(LiTHF)_3Cr(OPh)_5]_2$, 2 cubes $[Li_3Cr(\mu_3\text{-}OR)_4]$, with the $[Cr_2(\mu\text{-}OR)_2]$ cycle in the centre **$(LiTmeda)_2Cr(\mu\text{-}OPh)_4$**		deep bl. cr., s. in THF, b. C_7H_{16} pink cr., s. in THF, hc.	IR, X-r	518
$[LiTHF_2]_2Cr_2(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_6]$, linear chain, 2 $[CrO_4]$ squares sharing $(\mu\text{-}OR)_2$		purple cr., s. in THF, b. C_7H_{16}, μ_{eff}=3.24	IR, X-r	518

(LiTmeda)$_2$Cr(μ-OC$_6$H$_3$Me$_2$-2,6)$_4$,		purple cr., s.in eth., μ_{eff}=4.64		
[NaTmeda]$_2$Cr(μ-OC$_6$H$_3$Me$_2$-2,6)$_4$·PhMe, linear chain, central [CrO$_4$]-square and 2 [NaO$_2$N$_2$] tetrah .		purple cr., s. in THF, tol.	IR, X-r	
***trans*-[(NaL)$_4$Cr$_2$(μ$_3$-OR)$_8$],** R= Pr^i, Ph, C$_6$H$_3$Me$_2$-2,6, β-C$_{10}$H$_7$; L= THF, Py, oct. [Na$_4$Cr$_2$]-*trans*, on 8 faces μ$_3$-OR, [NaO$_5$] and [CrO$_4$] -tetragon. pyr.		yel. or grn. cr., s. in tol., Py, μ_{eff}=2.84--3.46	IR, X-r	
[Li(THF)$_2$CrCl(OCBu^t$_3$)$_2$], tetrah. Li and Cr-trian. sharing a [Cl(OR)] edge		grn. cr., s. in ethers	X-r	795
[Na$_9$Cr$_3$Cl(OC$_6$H$_4$OMe-2)$_{14}$], [Cr$_3$(μ$_3$-Cl)] trian. - centre		purpl.cr.,s.in THF, μ_{eff}=3.2	IR, X-r	518
[Cr$_2$M$_2$(μ-OBu^t)$_6$(OBu^t)$_2$], M=Ge, Sn [1683, 1681,1684]; **CrAl$_2$O$_2$(OPr^i)$_4$** [1244]				
Cr(III)				
Cr(OR)$_3$↓, R= Me, Et (Al(OH)$_3$ – bayerit struct. type, [CrO$_6$] – oct.), Pr^n, Pr^i, Bu^n, Bu^t, Ph	2, 5, 6, 7	greyish –grn. or –bl. slds., ins. in org. solv.μ_{eff}=3.56 (Me)	IR, electr. sp., magn. prop., X-r powd.	6, 30, 229, 248, 769, 104, 1062, 1108, 1366, 1410
Cr(OCHBu^t$_2$)$_3$·THF	5	purple cr.,130 (m.), s.in hc., α=1 (s.), 2 (m-s), μ_{eff}=3.2	IR, electr.sp., magn. prop., m-s	167
Cr(OAd-1)$_3$↓ ,Ad=adamantyl (C$_{10}$H$_{15}$); +NO →**Cr(OAd-1)$_3$·NO**	4	greish grn. sld. red-brn. cr., s. in eth.	IR,^{1}H, ESR, m-s, magn.prop.	166

$Cr(OPh)_3$, ·$6NH_3$	5	light grn., vlt .sld.	IR	1502, 1431
$Cr(OC_{10}H_7)_3$	5	brn .sld.	IR	1062
$Cr(OC_6H_4Ph\text{-}4)_3(Et_3N)$	5	grn. sld.	IR	1062
$Cr(OR)_3$, R=C_2H_4Cl, CH_2CCl_3, CH_2CF_3	5	-	IR, ^1H, ^{19}F, magn. prop.	316
$\{Cr[OSi(OBu^t)_3]_3(NHEt_2)_2\}$, trig. bipyr.	4	purple cr., s. in C_5H_{12}	IR, X-r	1571
$Cr(OC_2H_4OEt)_3$	2	bl. polymer	IR	268
$Cr(\eta^2\text{-}OCMe_2CH_2OMe)_3$, oct. with 3 cycles	4	grn. cr, 60/1, 0°/10^{-4} (subl.)	IR, m-s, X-r	739
$Cr(OC_2H_4OH)_3\downarrow$	4-7	grn.-bl. sld.,350(dec.)	IR, DTA	1502
$Cr(OCH_2CH(OH)CH_2OH)_3\downarrow$	4-7	" 350(m.,dec.)	IR	1502
$CrHal_2(OMe)L$, Hal = F, Cl; L= MeOH, MeCN, Diox, **$[CrF_2[H_2N(CH_2)_3NH_2](\mu\text{-}OMe)]_2$**		grn. slds., 56 -100(m.), μ_{eff}=3.75-3.80	IR, electr. sp., magn. prop.	502, 1678
$LiCr(OBu^t)_4\downarrow$		ins. in THF, μ_{eff}=3.59, $+O_2 \rightarrow Cr(OBu^t)_4$	IR, electr. sp. , magn. prop.	30, 1573
$[Li(THF)Cr(OCHBu^t_2)_4]$ Li-trian. and Cr-tetrah. sharing a $(\mu\text{-}OR)_2$ edge		bl.-grn. cr.,124 (m.), α=1 (bz.)	IR, ESR, electr. sp., X-r	167
$LiCr(OAd\text{-}1)_3Cl\downarrow$ **$Li_3Cr_4(OAd\text{-}1)_{12}Cl_3$**		pink cr., purple cr., s.in THF-eth., 350(dec.), μ_{eff}=3.20	IR, ^1H, ESR, magn. prop., m-s, cryosc.	166
$[NaTmeda]_4Cr_4O_3(OPh)_{10}]$, 2 trian. -$[NaCr_2(\mu_3\text{-}O)]$ cycle, CN Na and Cr=5		bl. cr., s. in tol., ins. in hex., μ_{eff}=3.49	IR, X-r	518

$K_3[Cr(\eta^2-C_6H_4O_2-1,2)_3]\cdot 1.5H_2O$, anion - oct. of 3 cycles		dark grn.. cr.	X-r	1336
$KCr[O_4C_6H_8(OH)_2]$ ↓ (derivative of mannit)		-	-	1596
Cr(IV)				
$Cr(OBu^t)_4$, tetrah. (gas electronogr.)	4, 7, 5-7	bl. cr., 37(m.), $70/10^{-3}$ (b.); ΔH_{form}= -305 ; α=1; μ_{eff}=2.82	IR, ^1H, ESR, m-s, magn. prop.	30, 218, 696,960, 1573
$Cr(OR)_4$, R= CMe_2Et **(1)**, $CMeEt_2$ **(2)**, CEt_3 **(3)**, $SiEt_3$ **(4)**	4, 7	bl. liq., α=1;110/2.5 (subl.) **(1)**; 135/2.5 **(2)**; μ_{eff}=2.79 **(2, 3)**; +ROH (p,s)→$Cr(OR)_3$	IR, electr. sp., ESR, m-s, magn. prop., cryosc.	30
$Cr(OCHBu_2^t)_4$ tetrah.	5+7	grn. cr., 206 (m.), s. in hex., α=1, 2 (m-s), μ_{eff}= 3.2	IR, electr. sp., ESR, magn.prop.,m-s, X-r	167
$Cr(OCHMeBu^t)_4$	6	light bl. sld, 64 (m.), μ_{eff}=3.1	IR, electr. sp.	513
$Cr(OAd-1)_4$	4, 5-7	bl. cr., air-stab., s. ohnly in tol., α=1, μ_{eff} =2.68.	IR, ^1H, ESR, magn. prop., m-s, cryosc.	166
Cr(V)				

$Li[CrO_2(\eta^2\text{-}[OC(CF_3)_2]_2)]THF$ **$M[CrO(\eta^2\text{-}[OC(CF_3)_2]_2)_2]$,** M=Li (·THF), K, [PyH], [Et$_4$N], anion- tetragon. pyr. $\downarrow H_2O$ **$[Li(H_2O)]_2^+[CrO(\mu\text{-}O)(\eta^2\text{-}RO_2)]_2^-$** **·2Py,** anion - 2 tetragon. pyr. sharing a (μ-O)$_2$ edge		purple cr., 152 (m.) **m.**: 165, 237, 144, 188; μ_{eff} :1.84-;2.38;s. in MeOH, 110°/vac→ **LiCr^{III}O(RO$_2$)** grn. cr., s. in Py, Ccl$_4$, μ_{eff}=2,20	IR, ^{1}H, ^{19}F, ESR, electr. sp., magn. prop., X-r	409, 1214, 1750
Cr(VI)				
$CrO_2(OR)_2$, R= Bu^t, $C_5H_{11}{}^t$, CMeEtBu^t	3	red liq.	optic sp.	1807
$[CrO_2(OR)_2]$, R= CPh$_3$, SiMe$_3$, SiPh$_3$, Si(C$_6$F$_6$)$_3$, tetrah.	3, 5	red cr.	IR, ^{1}H, X-r	1527
$[CrO_2(OCH_2CF_3)_2]$, **$CrO_2[OCH(CF_3)_2]_2$** **$CrO_2[OC(CF_3)_3]_2$**	5 F	brn .sld. or.-red. liq.	IR, ^{1}H, ^{19}F	315, 316, 294
$[CrO_2(OR)_2]$, R=C$_2$H$_4$Cl, CH$_2$CCl$_3$	5	brn. sld., 150, 122(m.)	IR	315
$[CrO_2(OSiBu^t{}_3)_2]$	3	-	-	1723
$[CrO_2Cl(OCPh_3)]$, tetrah.		red cr.	IR, ^{1}H, X-r	1527
$Cr_2O_5(OR)_2$, $Cr_3O_8(OR)_2$, R=Bu^t, SiMe$_3$	3	red liq.	IR, ^{1}H	131, 1527

12.18. Molybdenum and tungsten alkoxides

The compounds of these two elements belong apparently to the most studied and most fully characterized alkoxoderivatives of metals. The particular features of their synthesis and physicochemical properties are discussed in detail in a large number of review publications authored by Chisholm [370] who made tremendous contributions to the development of the chemistry of these substances. The synthetic routes to the bimetallic alkoxide derivatives of molybdenum and tungsten (VI) along with the discussion of their physicochemical properties and application prospects are also reviewed in [1638, 908].

12.18.1. Synthesis

The preparation of the derivatives of the lower oxidation states (II–IV) is based almost exclusively on the alcoholysis reactions (method 4). The corresponding alkyl- or silylamides serve as initial reagents for the obtaining of $M_2(OR)_6$ and $M_2(OR)_8$. The derivatives of divalent molybdenum were obtained from the mixed-ligand alkyl alkylamide derivatives (type $Mo_2Bu^i_2(NMe_2)_4$), which in this case undergo a reductive elimination of a saturated hydrocarbon). For the alkoxide derivatives of molybdenum and tungsten (V) quite a small number of representatives is known, being prepared mainly by means of different redox reactions (method 7, see below). The nonoxo derivatives of tungsten (VI) can be prepared by alcoholysis of corresponding alkylamides; oxocomplexes of both tungsten and molybdenum (VI) have been prepared by exchange reactions of the chlorides with alkali alkoxides (method 5) or with alcohols in presence of ammonia or amines. Various alkoxoderivatives of Mo and W(VI) can also be prepared by anodic oxidation of metals (method 2). The approach to the derivatives of unusual or rare alcohols is provided by the alcohol interchange reaction (method 6) using the most stable and easily prepared alkoxides as precursors.

12.18.2. Molecular structures

See also Chapter 4. The molybdenum (II) alkoxides isolated as alcohol or amine solvates of $[Mo(OR)_2L_2]$ composition are the typical examples of binuclear clusters with a quadruple metal-metal bond not supported by any bridging ligands. Square planar coordinated (not taking into account the M-M bond) metal atoms are situated exactly in front of each other, which leads to the molecules with eclipsed conformation.

The derivatives of molybdenum and tungsten (III) are known in predominantly two different forms — dimers with triple metal-metal bond on one hand (more typical for the molybdenum compounds and stabilized for both metals by highly ramified radicals) and butterfly tetramers (see Section 4.4.2). The polymers are observed for the derivatives of both metals with R = Me, Et. The dimeric molecules demonstrate the gauche conformation (CN = 3) in the absence of additional neutral ligands, which becomes eclipsed when such ligands are added. The formation of a butterfly cluster structure is typical for the molybdenum (III) derivatives of primary alcohols with bulky radicals and for the majority of tungsten (III) alkoxides in the absence of additional donor ligands. It is worth noting that in the crystal structure of $W(OPr^i)_3$ both dimeric and tetrameric molecules are present in 1:1 ratio.

The molecular complexity of molybdenum (IV) alkoxides is determined by the size and ramification of the alkyl group — the polymeric (R = Me), dimeric (CN = 5, two bridging OR-groups, $R = Pr^i$) with a double metal-metal bond, and even monomers ($R = Bu^t$). The first representatives of $W(OR)_4$ homologous series are tetramers with the $[Ti_4(OMe)_{16}]$-type structure. The derivatives of ramified or bulky alcohols are known only as mixed-ligand complexes (such as dimeric solvates of alkoxide halids with alcohols, various alkoxide hidrides and monomeric complexes with phenantroline, see Table 12.19).

The homoleptic derivatives of Mo and W(VI) are rather scarcely studied. The only structurally characterized complex, $W(OMe)_5$, possesses the molecular structure analogous to those of alkoxide halids, i.e. a dimer built up of two edge-sharing octahedra. The structure of monooxo homometallic derivatives is unknown and their individuality appears questionable. The only dioxocomplex of molybdenum(V) isolated as pyridin solvate demonstrates the $[Ti(OMe)_{16}]$-type structure (Table 12.19).

The alkoxide only derivatives of hexavalent elements are monomeric octahedral complexes, as has been shown in the case of $M(OMe)_6$, M = Mo, W and $W(OPh)_6$. [691, 1453, 1538].

The first representatives of the homological series of monooxocomplexes are centrosymmetric dimers (pairs of edge-sharing octahedra), the oxogroups being situated in the equatorial plane in *trans*-position to the bridging alkoxide groups [900]. The derivatives of ramified radicals ($C_4F_9^t$) are monomers with tetragonal pyramidal coordination of the central metal atom (the apical position is always occupied by the double-bonded oxygen atom) [845]. The dioxocomplexes studied so far are either derivatives of functional alcohols, such as

2-methoxyethanol [900], or the complexes of alifatic alkoxides with N- or P-donor ligands. They are monomers with *cis*-arrangement of oxogroups and *trans*- of alkoxide groups.

12.18.3. Physical properties

The connection between the molecular complexity and the molecular structure on one hand and the physicochemical characteristics on the other hand can clearly be traced for the derivatives of these elements. The alkoxides of molybdenum (II) and tungsten (III) are nonvolatile and thermally unstable as the metal atoms in these compounds are present in anomalous oxidation states and the thermal decomposition appears to precede their evaporation. For the derivatives of molybdenum (III) a sharp difference is observed between the poorly soluble and practically nonvolatile polymeric methoxide and ethoxide and compounds containing the ramified radicals, which can be distilled without decomposition and are unlimitedly soluble in both polar and nonpolar organic solvents. The observed difference in thermal stability of molybdenum (IV) and tungsten (IV) alkoxides (see Table 12.19) is due apparently not only to the difference in their molecular complexity but also to their different stability to intramolecular redox processes: the mass-spectra of the tungsten derivatives [364] indicate the occurrence of disproportionation to different oxidation states analogous to that observed for the rhenium (V) alkoxides (see Section 12.21). The connection between the molecular complexity and the solubility and volatility of the compounds is most apparent for the derivatives of hexavalent metals: $W(OR)_6$ are volatile monomeric species perfectly soluble in any organic solvents; the individual $MO(OR)_4$, M = Mo, W, are dimeric and possess rather high solubility, but in the presence of microadmixtures of alkaline alkoxides they polymerize and become less soluble. The dioxospecies $MO_2(OR)_2$ spontaneously change their characteristics in time (undergo aging): the freshly prepared samples consist predominantly of dimeric molecules, possess moderate (for molybdenum) or even good (for tungsten) solubility in polar organic solvents, and are volatile under a vacuum. On storage they polymerize building polymeric oxo-bridged structures, analogous to those of the corresponding oxide chlorides and lose both solubility and volatility.

12.18.4. Chemical properties

The chemical transformations of the title alkoxides can be subdivided into 2 large groups, where the first should include the processes not conncected with a change in the metal atoms oxidation state such as ligand substitution (chemical modification), complex formation with donor ligands, and the processes of thermolytical and hydrolytical decomposition. The second group would include in this case the redox reactions, which in their turn can be subdivided into those connected with the oxidative addition to the metal-metal multiple bonds for the low-oxidation state derivatives and those of reduction of metal (VI) centers. The processes leading to formation of heterometallic derivatives will be discussed separately below.

12.18.4.1. Nonredox transformations

Ether elimination. The most important and the most unusual property of molybdenum and tungsten (VI) alkoxides is their trend to ether elimination. It was first discovered by Bradley for niobium *tert*-buthoxide [205] (see Chapter 5). The driving force of this process is the ability of molybdenum and tungsten atoms in higher oxidation states to form the M–OR bonds with increased multiplicity and also the very high stability of M=O double bonds. The decomposition speed appears therefore to be much higher for molybdenum than for tungsten derivatives (as this property is more pronounced for molybdenum). According to the mechanism described, the decomposition speed increases with the increase in size and ramification of the hydrocarbon radical $Me < Et << Pr^i < Bu^t$. This very reaction is one of the major obstacles precluding the possibility of purification of M(VI) alkoxides by distillation or sublimation. The other obstacle is the trend of oxoalkoxides to disproportionation into alkoxo and dioxospecies [968, 950]:

$$MO(OR)_4 \longrightarrow M(OR)_6 + MO_2(OR)_2$$

The ether elimination is also observed as the first step in thermal decomposition of these alkoxides. The same reaction appears also to be responsible for the observed difference in the hydrolytic behavior of molybdenum and tungsten alkoxides: the hydrolysis of the W alkoxides leads as for the majority of other metal alkoxides to the formation of hydroxospecies, forming sols and gels on polycondensation, while in the case of Mo alkoxides the added water, being a stronger acid than alcohols, acts as a catalyst for the ether elimination reaction and causes the formation of individual isopolyanions (independently of the nature of the alkyl radical or quantity of water added) [1774]:

$$MoO_n(OR)_{6-2n} + H_2O \longrightarrow H_2[Mo^V{}_2Mo^{VI}{}_4O_{19}]^{2-}$$

As is shown in the reaction equation above, the hydrolysis of the molybdenum species is accompanied by their partial reduction that can be noticed due to the appearing dark blue coloration of the samples, which is characteristic of Mo(V,VI) compounds (for details see Chapter 9).

Chemical modification. Partial stabilization in relation to the ether elimination and an increase in volatility (due to formation of monomeric species) can be achieved via the chemical modification of the title alkoxides (interaction with the "acidic" reagents such as functional alcohols or **β-diketonates)** [124, 1638]:

$$\mathbf{MoO(OEt)_4 + 2HOC_2H_4OMe \longrightarrow MoO_2(OC_2H_4OMe)_2 + 2EtOH + Et_2O}$$

$$\mathbf{WO(OR)_4 + Hacac \longrightarrow WO(OR)_3(acac) + ROH}$$

The substitution reactions on action of phosphorus trihalids or acylhalids on molybdenum (II) alkoxides have also been investigated in detail:

$$\mathbf{2Mo_2(OR)_6 + 4AcOX \longrightarrow Mo_4(OR)_8X_4 + 4AcOR}$$

It is interesting to note that the partially substituted derivatives obtained in spite of having the same composition demonstrate quite different molecular structures: the fluorosubstituted compound is a tetrahedral cluster, the chloroderivative a square planar, one and the bromosubstituted a butterfly type cluster [370] (Figs. 4.7 *b* and 4.5 *b*, Sections 4.4.2, 4.4.5).

Complex formation with neutral ligands. The low-valent derivatives of molybdenum and tungsten demonstrate a pronounced trend to formation of complexes with Lewis bases. The complex formation enhances stabilization of alkoxides toward thermal and chemical decomposition and simplifies their isolation. Thus the derivatives of Mo(II) are known exclusively as the complexes with corresponding alcohols, amines, or phosphines. For $\mathbf{M_2(OR)_6}$ compounds the stability of complexes with neutral ligands is much higher for the complexes of tungsten than for those of molybdenum, while the phosphine complexes are much more thermally stable than amine ones. For the alkoxides of trivalent metals the complex formation can lead to changes in molecular structures and the order of metal-metal bonds: for example, on addition of a neutral ligand the equilibrium between dimeric **(M≡M)** and tetrameric **($\mathbf{M_4}$** tetrahedron or a "butterfly") shifts usually to the dimeric forms:

$$M_4(OR)_{12} \leftrightarrow 2M_2(OR)_6$$
$$M_2(OR)_6 + 2L \longrightarrow L(RO)_3M{\equiv}M(OR)_3L$$

The addition of a **π-acceptor** ligand type NO can increase the stability of dimers, decreasing at the same time the multiplicity of the metal-metal bond:

$$M_2(OR)_6 + 2NO \longrightarrow ON(RO)_2M(\mu\text{-}OR)_2M(OR)_2NO$$

In case of Mo(VI) compounds, the introduction of N- or P-donor ligands appears to be the only way to isolate the derivatives of ramified alcohols:

$$[MoO_2(OR)_2]_n + 2nL \longrightarrow nMoO_2(OR)_2L_2$$

The breakdown of metal-metal bonds without changes in the oxidation state. The processes of this kind have been first discovered by Schrock *et al.* in the course of investigation of the mechanisms of the catalytical action of low-valent tungsten alkoxocomplexes in the reaction of olefine metathesis [349, 1017]:

$$W_2(OBu^t)_6 + RC{\equiv}CR \longrightarrow 2(Bu^tO)_3W{\equiv}CR$$
$$W_2(OBu^t)_6 + RC{\equiv}N \longrightarrow (Bu^tO)_3W{\equiv}CR + (Bu^tO)_3W{\equiv}N$$

The $C{\equiv}N$ bond in nitriles is cleaved in the same way by molybdenum(III) derivatives, but, and this is worth noting, the metal-nitrogen bond in the structure of $(Bu^tO)_3Mo{\equiv}N$ in the solid state is triple $(M{\equiv}N)$ and terminal, while in that of $(Bu^tO)_3W{\equiv}N$ it becomes asymmetrically bridging.

12.18.4.2. Redox transformations

Oxidation of the metal-metal bond. The most frequently studied redox processes are those of oxidative addition to the multiple metal-metal bonds in the molecules of low-valent derivatives. They lead very often to the formation of heteroleptic derivatives that keep, however, a metal-metal bond in their structure. That happens, for example, on the interaction of $M_2(OR)_6$ with alcohols (for M = W only) [17, 314, 368], halogenes [367, 870], or alkyl or acylperoxides [370]:

$$2W_2(OPr^i)_6 + 2^iPrOH \longrightarrow [(OPr^i)_3W(\mu\text{-}H)(\mu\text{-}OPr^i)_2W{\bullet}(OPr^i)(\mu\text{-}OPr^i)]_2$$
$$Mo_2(OR)_6 + 2X_2 \longrightarrow Mo_2(OR)_6X_4$$
$$X = Cl, Br, I, RO, R'COO$$

On reaction with molecular oxygen, the oxidation proceeds usually deeper and is accompanied by the cleavage of metal-metal bond [357, 364]:

$$Mo_2(OPr^i)_6 + O_2 \longrightarrow MoO_2(OPr^i)_2 + 2Pr^iO\bullet$$
$$Mo_2(OPr^i)_8 + O_2 \longrightarrow 2MoO(OPr^i)_4$$
$$W_2(OR)_6 + 3/2O_2 \longrightarrow W_2O_3(OR)_6$$

Even molybdenum and tungsten (VI) alkoxides can act as oxidants: the coproportionation leads to formation of M(IV) derivatives—for example [357],

$$Mo_2(OPr^i)_6 + WO(OPr^i)_4 \longrightarrow Mo_2WO(OPr^i)_{10}$$

Reduction of the compounds of molybdenum and tungsten (VI). The first reaction of this group that was studied was the reduction of tungsten phenoxide by the alkaline metals (Li, Na, K) in inert solvents that led to bimetallic complexes of W(V) [600]:

$$W(OPh)_6 + Na \longrightarrow NaW(OPh)_6$$

A bimetallic complex of molybdenum (V) was obtained on cathodic reduction of molybdenum (VI) oxomethoxide in the course of its electrochemical synthesis [902]:

$$MoO(OMe)_4 + LiCl + MeOH \longrightarrow [Li(MeOH)Mo_2O_2(OMe)_7]_\infty$$

As has been shown recently, a partial reduction of some molybdenum derivatives can occur spontaneously on storage via oxidation of the organic radical. Thus, molybdenum (VI) oxoisopropoxide transforms completely in 2 months according to the equation:

$$6MoO(OPr^i)_4 \longrightarrow Mo_6O_{10}(OPr^i)_{12} + 4Pr^i_2O + 2^iPrOH + 2Me_2CO$$

It has been supposed that the reason for the high reducive activity ofjust the isopropoxogroup lies in the possibility of **β-hydrogen** atom transfer.

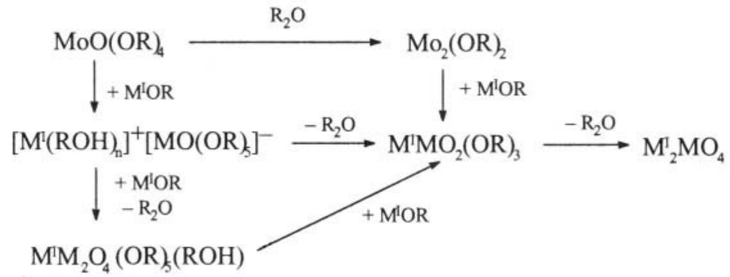
12.18.4.3. Complex formation of molybdenum and tungsten alkoxides with the alkoxides of other metals; formation of bimetallic alkoxides

The reactions of complex formation with the alkoxides of other metals have been studied for the derivatives of di-, tri-, penta-, and hexavalent metals. The investigation of molybdenum and tungsten (VI) alkoxides with the derivatives of other metals is complicated by the etherelimination reaction leading in some cases to precipitation of inorganic molybdates directly from solutions in organic solvents. However, the bimetallic drivatives of the title metals with the representatives of practically all the other groups of the Periodic Table have been described in the literature. It should be noted that practically in all the cases when the analogous derivatives of both molybdenum and tugsten could be isolated and characterized they turned to be very close in their molecular structure or even isostructural. As the metal atoms in the compounds of **$M(OR)_6$** series have saturated coordination, all the bimetallic compounds described are in fact oxocomplexes.

Alkoxomolybdates and tungstates of alkaline metals (lithium and sodium) belong to 3 main series:

- **$M^IM^{VI}O(OR)_5 \cdot nROH$** (R = Me, Et) are very unstable representatives of the monoooxoseries that have been discovered by conductometric titration in alcohols [1638]. The only solid product of this series that has been isolated and characterized was **$[NaWO(OEt)_5(EtOH)_2]_2$**, which structure belongs to the **$[Ti_4(OMe)_{16}]$** type. The oxogroups at tungsten atoms are terminal. The comparison of bond lengths and angles in this structure led the authors to the conclusion that it can be best described as ionic **$[Na(EtOH)_2]_2{}^+[WO(OEt)_4]_2{}^-$**.
- Dioxocomplexes of **$M^IM^{VI}{}_2O_4(OR)_5 \cdot ROH$, R = Et, Pr^i [1638]** composition are stable in both solid phase and in solution at room temperature. They are formed slowly on the reaction of alkali alkoxides with excess of **$MO(OR)_4$** and demonstrate very high solubility in alcohols and slightly lower in hydrocarbons. The unusual mixed-ligand complex **$LiMo_2O_4(OPr^i)_4(OC_2H_4OMe)$**, formed on reaction of **$LiMo_2O_4(OPr^i)_5 \cdot {}^iPrOH$**, with 0.5 to 2 equivalents of **HOC_2H_4OMe** in hexane belongs also to this series [902].
- Dioxocomplexes of **$M^IM^{VI}O_2(OR)_3$** R = Me, Et, **C_2H_4OMe** composition [1638] are formed on the direct interaction of **$MO_2(OR)_2$** with **M^IOR** in alcohols (according to the data of conductometric titration) and with the exception of 2-methoxyethoxides are very unstable. The stability against the ether-elimination reaction is apparently due to the stability of the molecular structures if the corresponding complexes as 2-methoxyethoxide complexes of sodium appear to be much more stable than those of lithium, due presumably to the small size of the atoms of the latter [902].

The mutual transformations of alkali alkoxomolybdates and tungstates can be generalized in the form of the following scheme:



The complex formation of tungsten alkoxides with the alkoxides of other metals than the alkali, bismuth, and rhenium (see Section 12.21) has not been investigated in detail, and therefore the major attention below will be paid to the description of the bimetallic alkoxides of molybdenum.

The investigation of the interaction of molybdenum alkoxides with those of alkaline earth metals is hindered by ether elimination leading to crystallization of inorganic molybdates of $M^{II}MoO_4$ composition. The most stable are magnesium methoxomolybdates (V and VI), with $Mg_2Mo^{V}{}_2O_2(OMe)_{10}(MeOH)_4$ and $Mg_2Mo^{VI}{}_2O_4(OMe)_8(MeOH)_4$ [52] composition, formed on alcoholysis of $MoCl_5$ in the presence of magnesium methoxide and demonstrating the molecular structures of $Ti_4(OMe)_{16}$ type. The molybdenum (VI) derivative can be obtained both on oxidation of the Mo(V) complex by oxygen and on the interaction of $MoO(OMe)_4$ with magnesium methoxide in a MeOH–THF mixture with subsequent precipitation by hexane [908]. The formation of the dioxo-complex in this latter case can be due also to ether elimination. The bimetallic 2-methoxyethoxides of $M^{II}Mo_2O_5(OR)_4{\cdot}nROH$ ($n = 0, 1$; M^{II} = Ca, Sr, Ba) composition turned out to be more stable. The structure of the barium compound turned out to belong to the well-known type of triangular aggregates $M_3(\mu_3\text{-}X)(\mu\text{-}X)_3X_n$, X = O, OR [910] (see Section 4.3).

The interaction of molybdenum and bismuth ethoxides is also accompanied by ether elimination and the crystallization of a crystalline cubic phase of approximate composition $Bi_2O_3{\cdot}3MoO_3$. The mixed solutions of bismuth and tungsten ethoxides and those of molybdenum and bismuth 2-methoxyethoxides turned out to be more stable. The occurrence of the interaction between the components was revealed by their tremendously increased solubility in the presence of each other (see Fig. 8.1 *h*).

The formation of the bimetallic complex of molybdenum and aluminium $MoO_2Al_2(OPr^i)_8$ was revealed by mass-spectrometric study of viscous pastes, obtained by addition of $MoO(OPr^i)_4$ to the liquid samples of aluminum isopropoxide [898]. The only structurally characterized complex of molybdenum and a trivalent metal is $La_2Mo_4O_8(OPr^i)_{14}$, formed according to the following reaction [909]:

$$2La(OPr^i)_3 + 4MoO(OPr^i)_4 \longrightarrow La_2Mo_4O_8(OPr^i)_{14} + 4Pr^i_2O$$

No formation of bimetallic complexes is observed on $MoO(OPr^i)_4$ dissolution in the alcohol solutions of zirconium isopropoxide, due presumably to the high stability of the structure of the latter. A very unusual complex of $Zr_3Mo_8O_{24}(OPr^i)_{12}(^iPrOH)_4$ composition precipitates slowly from solutions of isopropoxides in hexane subjected in advance to evacuation to dryness and redissolution repeated three times. The structure of the complex obtained is very close to that of the zirconium methoxide hydrolysis product, $Zr_{13}O_8(OMe)_{36}$ (Fig. 5.1 *c*) [901]. The formation of a complex very rich in oxoligands is presumably due to the trend of $Zr(OPr^i)_4{\cdot}^iPrOH$ to form oxocomplexes on desolvation (see Section 12.12).

The bimetallic complexes are not formed on direct interaction of either molybdenum or tantalum alkoxides. The introduction of steichiometric amounts of water into the solution of corresponding methoxides in methanol with subsequent evacuation and recrystallization from toluene leads to the formation with high yield of the bimetallic polyoxocomplex $[MoO_2Ta_2O_2(OMe)_8]_2$ [847].

Oxidation of $Mo_4Ta_2O_8(OPr^i)_{14}$ with molecular oxygen leads to the formation of $Mo_3Ta_2O_8(OPr^i)_{10}$, $Mo_4Ta_4O_{16}(OPr^i)_{12}$, and, in the presence of Li 2-methoxyethoxide, to $LiMo_4Ta_3O_{14}(OPr^i)_9(OC_2H_4OMe)_3$ [847].

12.19. Uranium and transuranium elements alkoxides

The alkoxides of actinides are rarely studied except the derivatives of uranium and thorium, as interest in the alkoxides of these 2 elements has increased by the hope to use them in the isotope-separation processes. The study of uranium alkoxides was initiated by groups led by Gilman and Bradley in the 1950s. The major part of this work is still carried out at the Nuclear Research Center at Los Alamos in the United States by the group of Sattelberger *et al.* [1671]. The detailed data on alkoxides of uranium is provided in a number of

Table 12.19. Molybdenum and tungsten alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
Mo(II)				
[Mo(OPr^i)$_2$Dipy$_2$] oct.	4	purple cr., v. s. in bz., paramagn.	Raman, electr. sp., X-r	365
[Mo(OR)$_2$L$_2$]$_2$, R= Pr^i, C$_5$H$_{11}$^{neo}, C$_5$H$_9$^{c}; L=Py, Me$_2$NH, MeNH$_2$, PMe$_3$, ^{i}PrOH, ^{c}C$_5$H$_9$OH, ethane-like mol., M$\equiv$M 2.11-2.20	4	purple cr. (exc.-C$_6$F$_5$-grn.), s.inhc;[Mo(OPr^i)$_2$(^{i}PrOH)$_2$]$_2$ $\rightarrow$Mo$_2$(OR)$_4$ (slowly)	IR, ^{1}H, electr. sp., X-r	357
[Mo(OC$_6$F$_5$)$_2$L$_2$]$_2$, L=Me$_2$NH, PMe$_3$ ethane-like mol., Mo$\equiv$Mo 2.15, 2.22	4 -7	red-brn. sld., s. in CH$_2$Cl$_2$	X-r	1, 421
Mo$_4$Cl$_6$(OMe)$_2$ [(Ph$_2$PCH$_2$-)$_2$], square [Mo$_4$], 2 bonds Mo=Mo 2.22, 2 bonds Mo-Mo 2.81		brn. cr.,s. in MeOH	X-r	418
[Mo$_6$Cl$_8$(OC$_6$F$_5$)$_4$Hmpa$_2$]		yel. cr., 300/10^{-4} (dec.)	TGA, m-s	4
Na$_2$[Mo$_6$Hal$_8$(OR)$_6$], R=Me, Et, Hal=Cl, Br		yel. cr., s. in ROH	IR, ^{1}H, ^{13}C,	363,
Na$_2$[Mo$_6$(μ_3-X)$_8$(OMe)$_6$]·10MeOH, X=OMe, Cl, oct. [Mo$_6$], Mo=Mo 2.54-2.61		brn. cr., diamagn.	X-r	1195
[Na(2,2,2-crypt)]$_2$[Mo$_6$(μ_3-Cl)$_8$(OR)$_6$], R=Me (6MeOH),Ph, Mo=Mo 2.61		or.-red cr., s. in MeOH	electron. sp., EHMO-calcul.	1292
[Na(2,2,2-crypt)]$_2$[Mo$_6$$\mu_3$-Cl)$_8Cl_4(OR)_2$], R=Me, CH$_2C_{14}H_9$		“		
MoAl$_2$O$_2$(OR)$_4$, R= Pr^i, Bu^n [Ouhadi **19**, 203; **95**, 1973]				
Mo^{II,III}$_4$H$_3$(OBu^t)$_7$(HNMe$_2$), butterfly, =[Mo$_4$(μ-H)$_3$(μ-OR)$_3$(OR)$_4$L], Mo=Mo 2.38-2.50	7	dark brn. cr., s. in tol., hex.	IR, ^{1}H, X-r	365

[K(18-crown-6)]$^+$[Mo$_4$H(OC$_5$H$_{11}$^{neo})$_{10}$]$^-$ anion [Mo$_4$(μ_4-H)(μ_3-OR)$_2$(μ-OR)$_4$(OR)$_4$]$^-$ - butterfly		-	IR, ^{1}H, ^{13}C, X-r	271
Mo(III)				
Mo(OMe)$_3$↓	4	brn. sld.	IR	350
Mo(OEt)$_3$	4	blk. sld., 110/10^{-3} (subl.), s.in C$_5$H$_{12}$, α=4	IR, m-s	350
[Mo(OPr^i)$_3$]$_2$, **·L,** L=Py, (Me$_2$PCH$_2$-)$_2$	4	yel. cr., 70-90/10^{-3} (subl.), s.in hc., ΔH$_{form}$= - 397	IR, ^{1}H, ^{13}C	309, 350, 859
[Mo$_4$(OMe)$_2$(OPr^i)$_{10}$]= [Mo$_4$(μ-OMe)$_2$(μ-OPr^i)$_2$(OPr^i)$_8$] [Mo$_4$]-square, 2 bonds Mo≡Mo 2.24	6	yel. cr., s. in hex.	IR, ^{1}H, ^{13}C, X-r	361
[Mo(OBu^t)$_3$]$_2$	4	red cr.,110/10^{-3} (subl.), >190°(H$_2$O,O$_2$-traces) →MoO$_2$, s. in hc., THF	IR, ^{1}H, ^{13}C {^{1}H}, m-s, X-r	124, 638, 350
[Mo(OC$_5$H$_{11}$^{t})$_3$]$_2$	5	red-brn. cr., s. in Dme	^{1}H, ^{13}C{^{1}H}	638
[Mo(OCH$_2$R)$_3$]$_4$, butterfly R=Pr^i, C$_5$H$_9$^{c}, C$_6$H$_{11}$^{c}, C$_4$H$_7$^{c}(·ROH)	6	dark-grn. cr., s. in hex.	^{1}H, ^{13}C, X-r	354
[Mo(OC$_5$H$_{11}$^{neo})$_3$L]$_2$,L=Me$_2$NH, Py ↓60°/vac.	4	red sld., 60 (dec.)	IR, ^{1}H, ^{13}C	350,365, 638
[Mo(OC$_5$H$_{11}$^{neo})$_3$]$_2$ ethane-like mol., M≡M 2.22 ↓C$_5$H$_{12}$	4	yel. cr., 110/10^{-3} (subl.), s. in hc., THF	IR, ^{1}H, ^{13}C , X-r	
[Mo(OC$_5$H$_{11}$^{neo})$_3$]$_\infty$		or. cr.	IR	
[Mo(OC$_5$H$_{11}$^{neo})$_3$(μ,η^1,η^2-NCNMe$_2$)]$_2$ ethane-like mol., Mo=Mo 2.45		deep purple cr., s. in hex.		365
[Mo$_4$O(OC$_5$H$_{11}$^{neo})$_{10}$Py]=		-		372

$[Mo_4(\mu_3\text{-}O)(\mu\text{-}OR)_4(OR)_6Py]$, asymmetric butterfly, 5 bonds Mo=Mo				
$Mo(OCMe_2Ph)_3$	4	yel.-or. sld., 90 (dec.), s. in hc., THF	IR, ^1H	350
$[Mo(OC_{10}H_{19})_3]_2$ (D-, L-menthoxides)	4, 6	-	optic sp.	1257
$[Mo(OPr^i)(OC_6H_3Me_2\text{-}2,6)_2]_2$, ethane-like mol. Mo≡Mo 2.24 **$Mo(OC_6H_3Me_2\text{-}2,6)_3$**	6	or. cr., s. in ArH, hex. low s. in bz.	IR, ^1H, X-r	403
$[Mo(OC_6H_4Ph\text{-}2)_3(Me_2NH)]_2$, ethane-like mol., M≡M 2.25, $[MoO_3N]$-tetragon. pyr.	4	red cr., s. in hc.	^1H	116
$[Mo[OCMe_2(CF_3)]_3]_2$ **$[Mo[OCMe(CF_3)_2]_3]_2$** ethane-like mol., Mo≡Mo 2.23	5 5	or. cr., s. in $(Me_2Si)_2O$ or. cr.	^1H, ^{13}C,X-r	638
$[Mo(OC_6F_5)_3]_2$	4		-	1
$[Mo(OSiMe_3)_3]_2$ ↑50°/vac. **$[Mo(OSiMe_3)_3(Me_2NH)]_2$**, ethane-like mol. Mo≡Mo 2.23, $[MoO_3N]$-tetrag	4	red cr., $100/10^{-3}$ (subl.) purple cr., s. in hc., THF	IR, ^1H, ^{13}C, m-s, X-r	350
$Mo(OSiEt_3)_3$	4	red cr.,$150/10^{-3}$ (subl.), s.in hc.	IR, ^1H, ^{13}C	350
$[Mo(OCH_2SiMe_3)_3]_2$	5	-	^1H,$^{13}C\{^1H\}$	638
$Mo_2[(O(CMe_2)_2O]_3$	4	yel. cr., $170/10^{-3}$ (subl.), low s. in bz., CH_2Cl_2	IR, ^1H, m-s	350
$[Mo_4F_2(OPr^i)_{10}]$ $=[Mo_4(\mu\text{-}F)_2(\mu\text{-}OR)_2(OR)_8]$, $[Mo_4]$- square planar, Mo≡Mo 2.23 (2 bonds) **$Mo_2F_2(OPr^i)_4(PMe)_3$**		dark red cr., s. in hc. red-brn. sld. , s. in hex.	IR, ^1H, ^{13}C, electr.sp., X-r	346

$[Mo_4(\mu\text{-}F)_4(OBu^t)_8]$ (in struct. with 2 mol. **$[Mo_4F_3(OBu^t)_8(NMe_2)]$** chinese lantern, Mo≡Mo 2.26 (2 bonds)		blk. cr., s. in hc.	IR, ^1H, ^{13}C, X-r	365,
$[Mo_4Hal_3(OPr^i)_9]$, Hal=Cl, Br, I $[Mo_4(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_3Br_3]$, butterfly, Mo=Mo 2.51 (5 bonds)		blk. cr., s. in hex.	IR, ^1H, ^{13}C, electr. sp., X-r (Br)	346, 346
$[Mo_4Hal_4(\mu\text{-}OPr^i)_8]$, Hal=Cl, Br, I $[Mo_4]$, square planar (Cl), butterfly (Br), Mo=Mo 2.38 and 2.48		or. cr. (Cl, Br), blk. (I), diamagn. (Cl)	IR, ^1H, ^{13}C, electr. sp., X-r	346, 346
$Mo_4Cl_7O(OMe)_3[(Ph_2PCH_2\text{-})_2]$, square $[Mo_4]$, $[Mo_4Cl_4(\mu_4\text{-}O)(\mu\text{-}Cl)_3(\mu\text{-}OR)_3$ $(\eta^1\eta^1\text{-}L)_2$, , 2 bonds Mo=Mo 2.45, 2 bonds Mo-Mo 2.68, 2.71		brn. cr., s. in MeOH	X-r	418
$Mo_4O_2Hal_2(OPr^i)_6$, Hal=Br, I		red-brn. sld., s. in tol.	IR, ^1H, ^{13}C, electr. sp.	346
$[(KPy)Mo(\mu\text{-}OC_5H_{11}{}^{neo})_4]_2$ butterfly, in centre Mo≡Mo 2.26		cr.	IR, ^1H, $^{13}C\{^1H\}$ electr. sp.	271
$[K(18\text{-}crown\text{-}6)]^+[Mo_2(OR)_7]^-$, R= Pr^i, Bu^t , $C_5H_{11}{}^{neo}$ (anion – 2 ψ-trig. bipyr. sharing a common (OR)-vertex, Mo≡Mo 2.22)		yel.-or. cr.		
$[K(18\text{-}crown\text{-}6)_2]^+$ $[Mo_4O(OC_5H_{11}{}^{neo})_{11}]^-$, butterfly anion $[Mo_4(\mu_3\text{-}O)(\mu\text{-}OR)_4(OR)_7]$ -		grn. cr., s. in bz.-THF	X-r	271
$[K(18\text{-}crown\text{-}6)]^+[Mo_4H(OC_5H_{11}{}^{neo})_{12}]^-$, anion – butterfly, $[Mo_4(\mu_4\text{-}H)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_6]$-			X-r	271
Mo(III, IV)				
$[Mo_6(\mu_6\text{-}O)(\mu_2\text{-}OEt)_{12}(OEt)_6]^-4.8$ H_2O, trig. a ntiprism $[M_6]$, Mo=Mo 2.61	hyd-rol.	brn. cr.	X-r	763

Mo(IV)				
$Mo(OMe)_4$	4	purple sld.	IR	371
$Mo(OEt)_4$	4, 5	grn. sld.(brn. liq.?),70/10^{-4} (b.), μ_{eff} = 0.31 (2.70?)	IR, ^1H, ^{13}C, electrs p., magn. prop.	371, 751
$[Mo(OPr^i)_4]_2$, 2 trig. bipyr. sharing a $(\mu\text{-}OR)_2$ edge, Mo=Mo 2.52	4	bl. cr., 70/10^{-3} (b.), s. in hc., ΔH_{form}= - 548.4	IR, ^1H, ^{13}C X-r	309,350, 367, 371
$[Mo_3O(OR)_{10}]$, $R={}^iPr, C_5H_{11}{}^{neo}$, $=[Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_6]$, trian. $[M_3]$ (Mo=Mo 2.53) , 3 oct.	7	grn. cr., s. in CH_2Cl_2, hex.	IR, ^1H, cryosc., X-r	357
$[Mo(OBu^t)_4]_2$↓	4	bl. sld., 70/10^{-3} (subl.), s. in hc., diamagn.	IR, ^1H, ^{13}C	371
$Mo(OC_5H_{11}{}^{neo})_4$	4	bl.-grn.sld., s. in hc.	IR, ^1H, $^{13}C\{^1H\}$, electr.sp.	371, 271
$[Mo(OAd\text{-}1)_4(Me_2NH)]$, Ad=adamantyl $(C_{10}H_{15})$, trig. bipyr., N-ax., **PMe_3** **$Mo(OAd\text{-}2)_4 \cdot NHMe_2$** **$Mo(OCH_2Ad\text{-}1)_4$**↓	4	grn. cr., 160 (dec.), ins. in in eth., α=1, μ_{eff}=2.62 bl. cr.,v.s. in in eth. pale bl. cr., μ_{eff}=2.72 bl. cr., μ_{eff} =1.58	IR, ^1H, ESR, magn. prop., m-s, cryosc.	166
$[Mo(OC_6H_4Ph\text{-}2)_4(Me_2NH)_2]$, oct.	4	rot cr., s. in hc.	^1H, X-r	116
$Mo(OSiR_3)_4(HNMe_2)_2$, R=Me, Et oct.	4	**Me**: yel.cr.,100/10^{-4} (b.), **Et**: or.-brn.sld., 76 (dec.), s. in hc.	IR, X-r	371
$[Mo_2Br_2(OC_5H_{11}{}^{neo})_6Py]$, 2 oct. sharing a $[(OR)_2Br]$ face, Mo=Mo 2.53		grn. cr., s. in C_5H_{12}, tol.	^1H, X-r	365
$KMo_2(OPr^i)_7Br_2$↓		bright bl. cr.	IR, ^1H, $^{13}C\{^1H\}$, electr.sp.	271

[$Mo_2WO(OPr^i)_{10}$]= [$Mo_2W(\mu_3$-O)(μ_3-OR)(μ-OR)$_3$(OR)$_6$], trian. [M_3], M=M		grn. cr., s. in hex.	^{1}H, electr. sp., cycl. voltam., X-r	356
Mo (V)				
MoCl(OMe)$_4$ **$MoCl_3(OMe)_2 \cdot 3MeOH$**		blk cr., 150 (dec.), grn. cr., -6 (m.), s. in bz., ROH	-	596
[$MoHal_2(OR)_3]_2$,R=Me,Pr^i, Ph; Hal=Cl,Br,I, 2 oct. sharing common (μ-OR)$_2$ edge		or. (I-brn.) cr., s. in hc., ROH	IR, ^{1}H, m-s, X-r	367, 596, 870
$MoCl_3(OC_6H_3Me_2$-2,6)$_2 \cdot$THF		purple cr., s. in THF, α=1	^{1}H, m-s	1789
[AmH][$MoCl_4(OR)_2$], R=Me, Et		grn. cr., 156 (m., dec.), ins. in MeOH, μ_{eff}=1.71	IR,ESR, electr. sp., magn. prop.	596, 1088, 1356
MoO(OMe)$_3$	5	red cr.,115 (dec.), s. in MeOH	-	596
[$MoO_2(OPr^i)Py]_4$, $Ti_4(OMe)_{16}$ - struct. type =[(MoO)$_4$(μ_3-O)$_4$(μ-O)$_2$(μ-OR)$_4$Py]	7	red cr., s. in Py	IR, ^{1}H, X-r	357, 364
[(MoO)(μ_3-O)(OSiMe$_3$) (Me$_2$NH)]$_4$ cube [$Mo_4(\mu_3$-O)$_4$]	3	red cr., s. in tol.	^{1}H, electr. sp., m-s, X-r	917
[$MoOCl_2(OMe)Py_2$]		red-brn. cr., s.in MeOH	-	596
[(MoO)$_2$Cl$_2$O(OEt)$_2$L]$_2$, L=EtOH, PMe$_3$ =[(MoO)$_4$(μ_3-O)$_2$(μ-OR)$_4$Cl$_4$L$_2$], $Ti_4(OMe)_{16}$ - struct. type, Mo-Mo 2.66		or.-red cr., s. in CH_2Cl_2	IR, X-r	1014
[(MoO)$_4$Cl$_3$O$_2$(OH)$_3$(OEt)$_2$(EtOH)$_2$]$_2$= [(MoO)$_8$Cl$_6$(μ_3-O)$_4$(μ-OH)$_4$(OH)$_2$(μ-OR)$_4$ (ROH)$_4$], 2 fused planar rings of 4 trian. [$Mo_2(\mu_3$-O)] sharing common (μ-OH) vertex, Mo-Mo 2.65		red-brn. cr., s. in Dmfa, Dmso, ins. in tol., eth. etc.	X-r	156, 1014

$[(MoO)Cl_2(\mu\text{-}OR)_2]_2(\mu\text{-}ROH)]$, R= Et, Pr^n, 2 oct. sharing common $[(OR)_2(ROH)]$ face	or.-brn. cr., s. in ROH, CH_2Cl_2	IR, ^1H, X-r	794, 1014
$[(MoO)Cl_2(OEt)]_2[\mu,\eta^1,\eta^1\text{-}C_2H_4(OH)_2]$ 2 oct. sharing common $[(OR)_2(ROH)]$, Mo-Mo 2.68	or. sld., s. in eth.	IR, ^1H, X-r	794
$[(MoO)_3Cl_4O(OEt)_3]_2$= $(MoO)_6Cl_6(\mu_3\text{-}O)_2(\mu\text{-}OR)_6(\mu\text{-}Cl)_2$, cyclic mol., 2 trian.$[M_3(\mu_3\text{-}O)]$, Mo-Mo2 at. Mo CN 6, 1 at 5	bl. cr., s. in ROH	^1H, X-r	1014
$[Me_2NH_2]_2[(MoO)_2O_2(OC_6F_5)_4]$, anion- 2 tetragon. pyr. sharing a $(\mu\text{-}O)_2$ edge, Mo=Mo 2.55	red-brn. cr., s. in bz., CH_2Cl_2	X-r	1
$[Li(MoO)_2(OMe)_7(MeOH)]$, zigzag chain tetragon. pyr.$[Li(\mu\text{-}OR)_4(ROH)]$ and pairs of oct. $[(MoO)_2(\mu\text{-}OR)_7]$ sharing a $(\mu\text{-}OR)_3$ face	red cr., s. in ROH	IR, X-r	902
$Li(MoO)_2(OEt)_7$ zigzag chain tetrah. $[Li(\mu\text{-}OR)_4]$ and pair oct. $[(MoO)_2(\mu\text{-}OR)_7]$ sharing a $(\mu\text{-}OR)_3$ face	red cr., s. in ROH	IR, X-r	847
$Mg_2(MoO)_2(OMe)_{10}(MeOH)_4$, $[Mg_2(MoO)_2(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_4(ROH)_4]$, $Ti_4(OMe)_{16}$ -struct. type	red cr., s. in ROH	IR, X-r	52
$M_2Mo_4O_8(OPr^i)_{14}$, M= Nb, Ta, zigzag chains oct. $[M(OR)_6]$ and pairs of oct. $[(MoO)_2(\mu\text{-}O)_2(\mu OR)_2]$ sharing a $(\mu\text{-}O)_2$ edge, Mo-Mo 2.58	or. cr., s. in tol.	IR,TGA, X-r	847
$[Et_4N][Mo(OR)_2Hal_4]$, R=Me, Et, Hal=Cl, Br	brn.-or. (Cl), yel.-grn. (Br) cr.	electr.sp., magn. prop.	1356

Mo(V, VI)

$Mo_6O_{10}(OPr^i)_{12}$, zigzag chain, $[(Mo^{VI}O)(OR)_3(\mu\text{-}OR)_2(Mo^VO)(\mu\text{-}O)_2(Mo^VO)$	7	yel. (red ?) cr., α=1, s. in tol.	IR, ^{13}C, ^{17}O, ^{95}Mo, m-s,	357, 905

(μ-OR)]$_2$, 2 bonds Mo^V-Mo^V 2.58			X-r	
$Mo_4(Mo,W)_2O_{10}(OPr^i)_{12}$ struc. analog of $Mo_6O_{10}(OPr^i)_{12}$	7	yel.-brn.cr., α=1, s. tol.	IR, ^{1}H, ^{13}C, X-r	847
$(MoO_2)_3(OSiMe_2Bu^t)_4Py_3\downarrow$	3	tan sld.	IR	917
$Mo_4Cl_4O_6(OPr^i)_6$, $Ti_4(OMe)_{16}$ - struct. type, $(Mo^{V,VI}O)_4Cl(\mu_3\text{-}O)_2(\mu\text{-}OR)_4(OR)_2$,		red cr., s. in ROH	IR, X-r	127
$[Na(H_2O)_3]^+{}_7[Na(H_2O)_3(Mo^{VI}O)_6(Mo^VO_2)_{18}H_{15}O_{97}[(OCH_2)_3CCH_2OH]_7]^{7-}$, Mo^V-Mo^V 2.60		red-brn. cr., diamagn.	IR, X-r	914
$[Bu_4N]_4[Mo^{V,VI}{}_8O_{24}(OMe)_2]\cdot MeOH\cdot H_2O$, anion-$[(Mo^{VI}O_3)_2(Mo^{VI}O_2)_2(Mo^VO)_4(\mu_3\text{-}O)_2(\mu\text{-}O)_8(\mu OR)_2]^{4-}$		red cr., s. in MeOH, diamagn.	IR, electr. sp., X-r	1018
$[Mg(MeOH)_6]^{2+}[Mg_2Mo_8O_{22}(OMe)_6(MeOH)_4]^{2-}\cdot 6MeOH$, anion-$[Mg_2(Mo^{V,VI}O)_8(\mu_4\text{-}O)_2(\mu_3\text{-}O)_6(\mu\text{-}O)_6(\mu\text{-}OR)_6(ROH)_4]$		or. cr., s. in MeOH	IR, X-r	53
$Mo_3Ta_2O_8(OPr^i)_{10}$ $=[(RO)Ta(OR)_3(\mu\text{-}OR)_2(MoO)(\mu\text{-}O)_2(MoO)(\mu\text{-}OR)_2Ta(OR)_3(\mu\text{-}O)(MoO_2)(\mu\text{-}O)]$, cycle		yel.-brn.cr., α=1, s. in tol.	IR, ^{1}H, ^{13}C, ^{17}O, X-r	847
Mo(VI)				
$Mo(OMe)_6$, oct.	2, 5	or. cr., s. in hc., ROH, 67 (m.,dec.)	IR, Raman, ^{1}H, X-r	812, 1453, 1560
$[Mo(\eta^2\text{-}OC_2H_4O)_3]$ **$[Mo[\eta^2\text{-}O(CMe_2)_2O]_3]\cdot 2CH_2Cl_2$**, oct.	4	yel. cr., s. in CH_2Cl_2	^{1}H, ^{13}C, X-r	284
$MoF(OMe)_5$ **$MoF_2(OMe)_4$**		yel.liq.,50°$\rightarrow R_2O$+MeF yel. sld.	IR, Raman, ^{1}H, ^{19}F	1714
$MoO(OMe)_4$, 2 oct. sharing common $(\mu\text{-}OR)_2$ edge	2, 6	yel. cr., 140 (dec.), s. in hc., ROH, α=1 (m-s)	IR, m-s, X-r	900, 950, 1637
$MoO(OEt)_4$	2, 5	yel. liq., 140 (dec.), s. in hc.,	IR, m-s	950, 1637

		ROH, α=1		
$MoO(OPr^i)_4$	5, 6	yel. oil, 18 (m.), $60/10^{-4}$ (b.), s. in hc., ROH, α=1 (m-s), 2 (in hc.)	IR, ^1H, ^{17}O, m-s, cryosc.	357, 356, 950, 1637
$MoO(OBu^t)_4$	7	yel. liq., $85/10^{-4}$ (b.), α=1	IR, ^1H, ^{17}O	357
$MoO(OC_5H_{11}{}^{neo})_4$	7	yel. sld., $75/10^{-4}$ (subl.), s. in hc., $\alpha\geq2$	IR, ^1H, cryosc.	357
$MoO(OC_4F_9{}^t)_4$, tetragon. pyr.	5	yel. cr., 60 (subl.), s. in hc.	IR, X-r	845
$[(MoO)(\eta^2\text{-}O_2)(\mu,\eta^2\text{-}OCH_2CHMeO)(MeOH)]_2\cdot2MeOH$, 2 pentag. bipyr. sharinga $(\mu\text{-}O)_2$ edge (from diff. RO_2)	6	yel. cr., s. in MeOH	IR, X-r	1479
$(MoO)_2(\mu\text{-}O)[\eta^2\text{-}O(CMe_2)_2O]_2[\eta^2\text{-}O(CMe_2)_2OH]_2$, 2 oct. sharing a $(\mu\text{-}O)$ vertex	3	colrl. cr.	X-r	929, 1077
$MoO(1,2\text{-}O_2C_6H_2Bu^t{}_2\text{-}3,5)_2$	6	purple cr., α=2 (bz, $CHCl_3$), 1 (Dmso, Dmfa) -grn., diamagn.	IR,electr.sp., magn. prop., ESR	1751
$MoOCl(OC_4F_9{}^t)_3$, tetragon. pyr.		or. cr., 60 (subl.), s. in hc.	IR, X-r	845
$[Bu_4N]_2[MoO(OH)(1,2\text{-}O_2C_6H_2Bu^t{}_2\text{-}3,5)_2]_2$		purple cr., diamagn.	"	1751
$[Bu_4N]_2[Mo_4O_{10}(OMe)_2(1,2\text{-}O_2C_6H_4)]$, anion- $[(MoO_2)_2(MoO)_2(\mu_3\text{-}OMe)_2(\mu\text{-}O)_4(\eta^2\text{-}O_2R)]$, $Ti_4(OMe)_{16}$ - struct. type		colrl. cr., s. in MeOH	X-r	879, 1018
$[MoO_2(OMe)_2]_n$	3, 6	wh. powd., $120/10^{-3}$(subl., dec.), s. in ROH (fresh), THF, ins. in hc., α=2(m-s); UV, $H_2O\rightarrow$bl.	IR, ^1H, ^{13}C, m-s, X-r powd.	917, 950, 1637
$(MoO_2)_2O(OMe)_2$, **$\cdot$2MeOH**	3	wh. powd.,225 (dec.) colrl. cr., 100 (dec.)	IR, TGA, X-r powd.	470, 1087
$[(MoO_2)_4(OMe)_4O_2(ONHCMe_2)]$	3	colrl. cr., s. in ROH	IR, X-r	1320

$=[(MoO_2)_4(\mu_3\text{-}OR)_2(\mu\text{-}OR)_2(\mu\text{-}O)_2L]$, struct. type of $Ti_4(OMe)_{16}$				
$[MoO_2(OEt)_2]_n$	3, 5	wh. powd., $100/10^{-3}$ (subl.), s. in MeCN, THF, $\alpha=2$ (m-s); UV, $H_2O \rightarrow$ bl.	IR, ^1H, ^{13}C, m-s, X-r powd.	917, 950, 1200, 1637
$MoO_2(OPr^n)_2$	3	colrl. cr., $90/10^{-3}$ (subl.)	IR, ^1H, ^{13}C, m-s	917
$MoO_2(OPr^i)_2$ $[MoO_2(OPr^i)_2Py_2]_4$ $[MoO_2(OPr^i)_2Dipy]\cdot 0.5PhMe$, oct.	6, 7	wh. sld., unstab.(→bl.), s. in tol. yei. liq., stab. wh. cr., s. in CH_2Cl_2	IR, ^1H, ^{17}O, m-s, X-r	357
$MoO_2(OBu^t)_2$, $\cdot 2Py$, $\cdot Dipy$	7	yel. liq., $55/10^{-4}$ (b.), $\alpha=1$ wh. sld., s. in tol.,eth.	IR, ^1H, ^{17}O, m-s, cryosc.	357, 356
$[MoO_2(OC_5H_{11}{}^{neo})_2Py_2]$ $MoO_2(OC_5H_{11}{}^t)_2Dipy$	7	yel. liq., 50/vac.(dec.) wh. sld., s. in tol., eth.	IR, ^1H, ^{17}O,	357 357
$MoO_2(OPh)_2Py_2$	3	golden yel. cr.	IR, ^1H, ^{13}C	917
$MoO_2(OCMe_2CH{=}CH_2)_2\cdot 2MeCN$	5	wh. sld., s. in MeCN	IR	134
$MoO_2(OSiMe_2Bu^t)_2Py_2$ $MoO_2(OSiBu^t{}_3)_2$ $[MoO_2(OSiPh_3)_2]$, tetrah., $\cdot PPh_3$, trig. bipyr.	3 3 5	colrl. cr. stab. to hydrol. and thermol. wh. cr., s. in CH_2Cl_2	IR, ^1H, ^{13}C IR, ^1H, ^{31}P, X-r	917 1723 776
$MoO_2(\eta^2\text{-}OC_2H_4OR)_2$, R= Me (oct.), Et.	6	yel.cr.,100(m., dec.), s. in ROH (polytherm) 7% (20°)	IR, m-s, X-r	900, 1638, 1652
$[MoO_2(\eta^2\text{-}OC_2H_4OH)_2]$-*cis*, oct.	3	colrl. cr., s. in ROH, THF, H_2O	IR, X-r	1437
$[MoO_2(\eta^2\text{-}OC_2H_3MeOH)_2]$ $[MoO_2(\eta^2\text{-}O(CH_2)_3O)]$	3	colrl. cr., 149(m.) 220 (dec., bl.)	IR, ^1H, X-r powder	1437
$[MoO_2[\eta^2\text{-}O(CHMe)_2(OH)]_2]$ $\cdot 2R(OH)_2$-*cis*, oct.	3	colrl. cr.	X-r	154, 929

$[MoO_2(OMe)(\eta^2\text{-}O(CMe_2)_2OH)]_2$ ·2MeOH, 2 oct. sharing $(\mu\text{-}OMe)_2$	3	colrl. cr., s. in MeOH	X-r	929
$[(MoO_2)_4[\eta^2,\mu_3,\mu\text{-}MeC(CH_2O)_3]_2(OEt)_2]$	3	colrl. cr., s. in EtOH	IR, X-r	1752
$Li(MoO_2)(MoO)O(OC_2H_4OMe)(OPr^i)_4$ = $[Li(MoO_2)(MoO)(\mu\text{-}O)(\eta^2,\mu_3\text{-}OC_2H_4OMe)(\mu_3\text{-}OR)(\mu\text{-}OR)_2(OR)]_2$, 2 trian. $[LiMo_2]$ sharing 2 $(\mu\text{-}O)$		colrl. cr., s. in hc.	IR, X-r	902
$[NaMo_2O_4(OR)_5(ROH)]$, R= Et, Pr^i, $=[Na(ROH)(MoO_2)(MoO)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_2(\mu\text{-}O)]_2$, 2 trian. $[NaMo_2(\mu_3\text{-}OR)_2]$ sharing 2 bonds $(\mu\text{-}O)_2$, oct. Mo,CN Na 4		light yel. cr., 80-100 (dec.), s. in hc., ROH	IR, m-s, X-r	1638
$[Na_2(MoO_2)_2(\eta^2,\mu_3\text{-}OR)_2(\eta^2,\mu\text{-}OR)_4]_\infty$, $R=C_2H_4OMe$, $Ti_4(OMe)_{16}$ - struct. type		colrl.cr.,170(m.,dec.),s. in ROH	IR, X-r	900, 1638
$[Bu_4N]^+[(MoO_2)_3[\eta^2,\mu_3\text{-}MeC(CH_2O_3)_3]_2(OR)]^-$, R=H, Me, C_2H_4Cl, anion- trian. $[M_3]$		colrl. cr., s. in ROH	X-r	685, 1039
$[Bu^n{}_4N]^+{}_2[(MoO_2)_4O_2(OMe)_4X]^{2-}$, X=OMe, Cl; anion-$[(MoO_2)_4(\mu_3\text{-}OR)_2(\mu\text{-}OR)_2(\mu\text{-}O)_2X]$, $Ti_4(OMe)_{16}$ - struct. type		colrl. cr., s. in ROH	X-r	879, 1018
$[Bu_4N]_2[(Mo_8O_{20}(OMe)_4[\eta^3,\mu_3,\mu\text{-}MeC(CH_2O)_3]_2]$, anion- $[(MoO_2)_6(MoO)_2(\mu\text{-}O)_6(\mu_3\text{-}OMe)_2[\eta^3,\mu_3,\mu\text{-}RO_3]_2(OMe)_2]$, 2 gr. $Ti_4(OMe)_{16}$ - struct. type		colrl. cr., 150 (dec.), s. in ROH	X-r	1039
$Na_4[Mo_8O_{24}(OMe)_4]$· 8MeOH, anion- $Ti_4(OMe)_{16}$ - struct. type, $[(MoO_2)_6(MoO)_2(\mu_4\text{-}O)_2(\mu_3\text{-}O)_4(\mu\text{-}O)_4(\mu\text{-}OR)_2(OR)_2]$,		colrl. cr., s. in ROH	IR, X-r	1087
$[Mg(MoO_2)(OMe)_4(MeOH)_2]_2$, $Ti_4(OMe)_{16}$ - struct. type, $[Mg_2(MoO_2)_2(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_4(ROH)_4]$		colrl. cr, s. in ROH	IR, X-r	52
$[M^{II}Mo_2O_5(OC_2H_4OMe)_4(MeOC_2H_4OH)]$,		colrl. cr., s. in ROH, not	IR, X-r	910

$=[M(MoO_2)_2(\mu\text{-}O)(\mu_3,\eta^2\text{-}OR)_2(\mu,\eta^2\text{-}OR)_2\ (\eta^2\text{-}ROH)]$, M= Sr, Ba, trian. $[MMo_2(\mu_3,\eta^2\text{-}OR)_2]$, 2 oct. Mo sharing a common $[(\mu_3\text{-}OR)_2(\mu\text{-}O)]$ face, CN Ba=10	stabl. ($\rightarrow BaMoO_4\downarrow$)		
$M_2[Mo_2O_5(C_6H_4O_2\text{-}1,2)_2]$, $M=NH_4(\cdot 2H_2O)$, $[Ba(H_2O)_5]/2$, anion $-[(MoO_2)_2(\mu\text{-}O)(\mu_3,\eta^2\text{-}OR)_2]$ - 2 oct. sharing a $(\mu\text{-}O)_3$ face (from 2 different RO_2)	colrl. cr.	X-r	1586, 1727
$[La_2Mo_4O_8(OPr^i)_{14}]$ $=[La_2(MoO)_4(\mu_4\text{-}O)_4(\mu\text{-}OR)_8(OR)_6]$, oct. $[La_2Mo_4]$-*trans*, CN La= 9, Mo 6.	yel. cr., s. in hex.	IR, X-r	909
$Zr_3Mo_8O_{24}(OPr^i)_{12}(^iPrOH)_4$ $=$ $[Zr_3(MoO_2)_4(MoO)_4(\mu_3\text{-}O)_8(\mu\text{-}O)_4\ (\mu\text{-}HOR)_4\ (OR)_{12}]$, $[ZrO_8]$ connected to 2 oct. Zr in the center, 4 trig. bipyr. $[MoO_2]$ and 4 oct.$[MoO]$	colrl. cr., s. in hex., $+ROH\rightarrow Zr(OR)_4\cdot ROH\downarrow$	IR, X-r	901
$[MoO_2Ta_2O_2(OMe)_8]_2$ $=$ 2 trian. $[MoTa_2]$ as in $Ti_4(OMe)_{16}$ struct. type connected by linear μ-O	colrl. cr., s. in org. s. with dec.	IR, X-r	847
$Mo_4Ta_4O_{16}(OPr^i)_{12}$, in the vertexes of a distorted cube - $[MoO(\mu\text{-}O)_3]$ tetrah. sharing vertexes with $[Ta(OR)_3(\mu\text{-}O)_3]$ oct.	colrl. cr., s. in org. s.	IR, ^1H, X-r	847
$LiMo_4Ta_3O_{14}(OPr^i)_9(OC_2H_4OMe)_3$ a cube of alternating $[MoO(\mu\text{-}O)_3]$ and $[Ta(\mu\text{-}O)_3(OR)_3]$ units in the corners, where one of the 4 Ta-units is replaced by a $[Li(OC_2H_4OMe)_3]$ one	colrl. cr., s. in tol.	IR, ^1H, X-r	847
$[Bu_4N]_2^+[(MoO_2)_3(RO_3)_2(OR')]^-$, $R=MeC(CH_2)_3$, R'=H, Me, C_2H_4Cl	colrl. cr., s. in MeOH	IR, X-r	685, 1039
$[Bu_4N]^+_2[(MoO_2)_2(MoO)_2(\mu_3\text{-}OMe)_2(\mu\text{-}O)_4(\eta^2\text{-}C_6H_4O_2\text{-}1,2)_2]^{2-}$	colrl. cr., s. in MeOH	IR, X-r	879, 1018
$[Bu_4N]_2[Mo_8O_{20}(OMe)_2[MeC(CH_2O)_3]_2(OMe)_2]]$,	colrl. cr., s. in MeOH	IR, X-r	1039

anion - $[(MoO_2)_6(MoO)_2(\mu\text{-}O)_6(\mu_3\text{-}OMe)_2[\eta^3,\mu_3,\mu\text{-}RO_3]_2\ (OMe)_2]^{2-}$				
W(III)				
$W_2(OEt)_6(\mu\text{-}MeHNCH_2\text{-})_2]$, 2 tetrah. sharing a ($\mu$-N~N) gr., W≡W 2.296	4	or. cr., s. in hc.	^1H, ^{31}P, X-r	341
$[W(OPr^i)_3]_2$, ethane-like mol., W≡W 2.31 ↑Me_3N		yel. sld., s. in hex.	^1H, m-s, cryosc., X-r	16, 341, 347, 366
$[W(OPr^i)_3]_n$, n=2 and 4 (1:1) in the same struct. ↓hex.+tol. (0°)	4, 6	blk. cr., s. in hex.		
$[W(OPr^i)_3]_4$ = $[M_4(\mu\text{-}OR)_4(OR)_8]$, rhombus $[M_4]$ ↑-L		blk. cr., s. in hex.		
$[W(OPr^i)_3L]_2$, L= Me_2NH, PMe_3, Py, 2,6-$Me_2C_6H_3$-N=C, ethane-likemol., W=W 2.3-2.5	4	brn., yel. , blk. cr., s. in hc.		
$W(OR)_3Py(2,6\text{-}Me_2C_6H_3NC)$, R=$Pr^i$, Bu^t 2 trig. bipyr. sharing a $[(\mu\text{-}OR)_2(\mu\text{-}N)]$ face				368
$W_4O(OPr^i)_{10}\cdot 0.5\ Et_2O$	hydrol.	cr., s. in eth.	IR, ^1H, ^{13}C	362, 368
$[W_4O_2(OPr^i)_8]_2$ $=[W_4(\mu\text{-}O)_2(\mu\text{-}OR)_2(OR)_6]_2$, 2 tetrah. $[W_4]$, W-W 2.5 and 2.9, central gr.$[W_2(\mu\text{-}OR)_2]$	7	or. cr., s. in hex.	^1H, X-r	368
$[W_6H_5(OPr^i)_{13}]$, $[W_6(\mu\text{-}H)_4(\mu\text{-}OR)_8H(OR)_5]$,oct.$[M_6(\mu\text{-}X)_{12}X_6]$	7	blk. cr., s. in hc.	IR, NMR, X-r	368
$[W(OBu^t)_3]_2$,	4, 7	red cr., 100/10^{-4} (subl.), >190° (H_2O, O_2-traces) → WO_2	IR, ^1H, ^{13}C	16, 124, 207, 414
2 L, L=Py, 4-Me-Py, W≡W 2.39		s. in hc.,	X-r	270, 347

$\cdot RN{=}C$, $R = Bu^t$, $C_6H_3Me_2$-2,6, ethane-like mol., W=W 2.52		blk. and grn. cr.		
$[W(OCH_2R)_3]_4$, $R = Pr^i$, $C_5H_9{}^c$, $C_6H_{11}{}^c$, $C_4H_7{}^c$ (ROH), butterfly	4	grn. cr., s. in hc.	^1H, ^{13}C	16, 354
$[W(OC_5H_{11}{}^{neo})_3]_n$	4	blk. sld.	-	16
$[W(OC_5H_{11}{}^{neo})_3L]_2$, L=Py, PMe_3 ethane-like mol., W≡W 2.362, $[WO_3P]$ - square	4	yel.-or. cr., s. in hc.	IR, ^{31}P, NMR, X-r	341
$[W(OC_6H_{11}{}^c)_3]_2$, ethane-like mol., W≡W 2.34	6	yel. cr., s. in hc., THF	IR, ^1H, electr sp., X-r	355
$[W(OC_{10}H_{19})_3]_2$ (D-, L-menthoxides) ethane-like mol., W≡W 2.34	4, 6	yel. cr., s. in hc.	IR, NMR, X-r	1257
$[W(OCMe_2CF_3)_3]_2$, **$\cdot 2L$**, L=MeCN, Py, 4-Me-Py, $(ArN)_2C/2$, W-W 2.39-2.50		red cr. blk., brn. cr., s. in bz., eth.	^1H, ^{19}F $\{^1H\}$, X-r	270, 587
$[W(OC_6F_5)_3(NHMe_2)]_2$ ethane-likemol., W≡W 2.22	4	purple cr., s. in bz.	IR, X-r	1
$[W(OSiMe_2Bu^t)_3]_2$, ethane-like mol. (W≡W bond)	4	yel. cr., s. in bz.	IR, ^1H, m-s, X-r	348
$[W_2[\mu,\eta^2\text{-}O(CMe_2)_2O]_3]$, about W≡W (2.27) three 6-membered rings	6	light yel. cr., s. in hc., THF	IR, X-r, ^1H, electr. sp.,	355
$[WHal_2(OR)(ROH)_2]_2$, R=Me, Et, Pr^n, Hal=Cl, Br		yel.-grn. cr., s. in ROH, $CHCl_3$, diamagn., α=1	IR, ^1H, ESR, electr. sp.	474, 390
$W_4OCl(OPr^i)_9 \cdot 0.5\ Et_2O$= $[W_4(\mu\text{-}O)(\mu\text{-}OR)_2(OR)_7Cl]$, tetrah. $[W_4]$, W=W 2.45 (3 bonds), W-W 2.9 (3 bonds), $[WO_4]$- square		cr., s. in hex.	IR, ^1H, $^{13}C\{^1H\}$, X-r	362
$K_2[W_2(OC_5H_{11}{}^{neo})_8]$		cr.	IR, ^1H, ^{13}C	271

$[(KPy)_2W_2(\mu\text{-}OC_5H_{11}{}^{neo})_8]$ butterfly, W≡W 2.33 in the centre **$[K(18\text{-}crown\text{-}6)][W_2(OR)_7]$**, R= OPr^i, Bu^t		cr. yel. cr.	$\{^1H\}$,electr. sp., X-r	
$[Na(18\text{-}crown\text{-}6)]^+[Mo_4E(OC_5H_{11}{}^{neo})_{10}]^-$, E=P, As, butterfly anion $[Mo_4(\mu_3\text{-}E)(\mu\text{-}OR)_4(OR)_6]^-$			IR, ^1H, ^{13}C, electr. sp., X-r	271
W(IV)				
$W(OMe)_4$	4→7	grn. cr.	IR	364, 341
$[W(OEt)_4]_4$= $[W_4(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_{10}]$, $Ti_4(OMe)_{16}$ - struct. type	4→7	brn. cr.	IR, NMR, m-s, X-r	364, 341
$W(OR)_4(Phen)$, R= Me, Et, Pr^n, Bu^n	5	dark sld., stab. to air, 27(dec.).; μ_{eff}=1.7-1.6	IR, electr. sp., magn. prop.	1581
$[W_2H(OPr^i)_7(\eta^2\text{-}OCPh_2)]$, 2 oct. sharing a common $(OR)_3$ face, W-W 2.65, cycle [WOC]	5, 7	brn. cr.	IR, ^1H, ^{13}C, X-r	111
$[W_2H(OPr^i)_7]_2$ = $[(OR)_3W(\mu\text{-}OR)_2(\mu\text{-}H)W(OR)(\mu\text{-}OR)]_2$ zigzag $[W_4]$ chain, 2 bonds W=W 2.45	4 (7)	brn-blk. cr., s. in hex.	^1H, X-r	17, 111, 366, 341
$[W_3O(OPr^i)_{10}]$= $[W_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_6]$ trian. $[M_3]$ (=M 2.54) of 3 oct.	7	dark bl. cr.	^1H,electr.sp., cyclic voltam., X-r	356
$[W_4O_2(OPr^i)_{12}]$= $[W_4(\mu\text{-}O)_2(\mu\text{-}OR)_3(OR)_9]$, trian. $[W_3]$, W=W 2.40 (1 bond) and $[W(OR)_6]$ sharing a $(\mu\text{-}OR)_3$ face	7	blk. cr., s. in tol.	^1H, m-s, X-r	160
$[W_3(\mu\text{-}O)_2(OBu^t)_8]$, trian. $[W_3]$, M-M 2.93 (1 bond), 2.45 (2 bonds), CN W 3, 4, 5	7	grn. cr.,s.in hc.; >10°→ $W_2(OR)_6$+$WO_2(OR)_2$	IR, ^1H, X-r	348

$[W(OC_5H_{11}^{neo})_4]_2$↓, $\cdot$Py **$[W_3(\mu_3\text{-}O)(OC_5H_{11}^{neo})_{10}]$** **$[W(OC_5H_{11}^{neo})_4]_4$**	7	purple sld., s. in tol.+ Py	IR, ^1H, ^{13}C, electr.sp.	271, 360, 358
$[W_4(OC_5H_9^c)_{16}]$ **$[W_2H(OC_5H_9^c)_7(Me_2NH)]$,** 2 oct. sharing a common $[H(OR)_2]$ face, **$\cdot PMe_3$**	7 4	brn. cr. grn.cr.,+ROH→ **$W_2(OR)_6$,** yel.-red cr.	IR, ^1H, ^{13}C, X-r	111, 314
$[W(OC_6H_3R_2\text{-}2,6)_4]_4$, R= Me, Pr^i, square; **C_6H_{12}**, trig. bipyr.	5	red and bl. cr., s. in tol., eth.; red-or. cr.	^1H, ^{13}C, X-r	1017
$W(OC_6F_5)_4(Et_2O)(MeCH_2C\equiv)_2$	5	red cr., s. in eth.	IR, ^1H, ^{13}C, ^{19}F	939
$[W_2O(OSiMe_2Bu^t)_6Py_2]$ 2 oct. sharing a common $[O(OR)_2]$ face **$[W_2(\mu\text{-}O)(\mu\text{-}OBu^t)(OSiMe_2Bu^t)_5Py_2]$,** tetragon. pyr. and oct. with a common edge, W=W 2.48	7	grn. cr., s. in Py	IR, ^1H, ^{13}C, X-r	348
$[WCl_2(OR)_2(ROH)]_2$, R= Me↓, Et, Pr^n, Pr^i 2 oct. sharing a common $(\mu\text{-}OR)_2$ edge, W=W 2.48-2.50		grn. cr., s. in bz., $CHCl_3$, diamagn.	IR, ^1H, electr. sp., X-r	43, 417, 415, 1342, 1450
$[WCl_2(\mu\text{-}OEt)(OR)(ROH)]_2$, R= Pr^i, $C_5H_{11}^s$ 2 oct. sharing a common $(\mu\text{-}OEt)_2$ edge, W=W 2.48-2.50		grn. cr.	IR, ^1H, electr. sp., cyclic voltam., X-r	417, 716
$[W_2IH(OC_5H_{11}^{neo})_6(MeNH_2)]$, 2 oct. with a common $[(OR)IH]$ face		grn. cr., s. in hc.	^1H, X-r	366
$[WCl_2(OC_6H_3Ph_2\text{-}2,6)_2(PMe_nPh_{3\text{-}n})_2]$-*trans, trans, trans*, oct.		grn. cr.	IR, ^1H, ^{13}C, X-r	897
$[WCl_2(OCH_2CF_3)_2(PMe_2Ph)_2]$- ***cis, trans, cis*-** oct.		grn. cr., s. in tol.	IR, X-r	1370

$[Me_4N]_2[WCl_5(OMe)]$			magn. prop.	1450
$M_2[WCl_2(OC_6F_5)_4]$, $M=[Na(Et_2O)_x]$, Bu_4N, Ph_4As		yel.-grn. powd., s. in CH_2Cl_2; +THF, MeCN → dec.	^1H, ^{19}F, ESP	939
$K(18\text{-Crown-6})_n[W_2(\mu\text{-}H)(\mu\text{-}O)(OR)_6]$, $R=Pr^i$, Bu^t, $n=1\text{-}5$		reddish cr., s. in Py	IR, ^1H, ^{13}C, electr.sp.	271
$MW_2H(OR)_8\downarrow$, $M=Na,K$, $R=Pr^i, C_5H_{11}^{neo}$, **·2 THF**		yel., grn. sld., s. in ROH, THF	^1H, ^{23}Na, X-r	366, 358
$[NaW_2(\mu\text{-}H)(\mu\text{-}OPr^i)_4(OPr^i)_4Dig]$, trian. $[M_3]$, 2 oct. $[WO_5H]$ (W=W 2.43) and trig. bipyr. $[Na(OR)_2O_3]$		brn.cr., s. in hex.- Dig		
W(V)				
$[W(OMe)_5]_2$ 2 oct. sharing a common $(\mu\text{-}OR)_2$ edge, W-W 2.79	5	bl. cr., s. in hc.,ROH	X-r	262
$W(OEt)_5$	5	brn. liq., 120/0.1 (b.), s. in ROH, diamagn.	IR, ^1H	1342
$[W_2(OC_5H_9^c)_8(\eta^2\text{-}OC_5H_8^c)]$, oct. and 7-vertex polyhedron sharing a $(\mu\text{-}OR)_3$, cycle [WOC]	7	dark grn. cr.	^1H, ^{13}C, X-r	111
$W(OPh)_5$ **$W(OC_6H_4Me\text{-}4)_5$**	7	yel. cr., $\mu_{eff}=1.26$ $\mu_{eff}=1.41$	magn. prop.	600
$[W_2Cl_3(\mu\text{-}OMe)_2(OMe)_5]$, 2 oct. sharing a common $(\mu\text{-}OR)_2$ edge, W-W 2.73		red-brn. cr., s. in MeOH, diamagn.	IR, ^1H, X-r	1343
$[WCl(OPr^i)_4]_2$, 2 oct. sharing a common $(\mu\text{-}OR)_2$ edge		pale grn. cr., s. in hc., ROH	IR, ^1H, X-r	100
$[WCl_2(OR)_3]_2$, R= Me, Et, 2 oct. sharing a common $(\mu\text{-}OR)_2$ edge, W-W 2.71		red cr., s. in hc., ROH	IR, ^1H, elect sp., X-r	415, 1407

$[WCl(OR)_4]_2$, R=Me, Et, Pr **$[WCl_3(OR)_2]_2$**		red-brn. cr., diamagn.	IR, ^1H, electr. sp.	604, 926, 1342, 1356
$[WCl(OC_6H_3Me_2\text{-}2,6)_4]$, tetragon. pyr.		red-brn. cr., >300 (m.)	^1H, m-s, X-r	1789
$[WCl_3(OC_6H_3Ph_2\text{-}2,6)_2L]$*-trans*, L=THF, PMe_2Ph, oct.		red cr., paramagn.	^1H, X-r	897
$WBr_3(OAr)_2 \cdot ArOH$, Ar=Ph, C_6H_4Me-2, -4, $C_{10}H_7$-α, -β		blk. cr., s. in eth., bz., $CHCl_3$, stab.	-	604
$\{WCl_2(OEt)[\eta^2\text{-}O(CMe_2)_2O]\}_2$ 2 oct. sharing a common $(\mu\text{-}OR)_2$ edge and $[\mu,\eta\text{-}ORO]$		red. cr., s. in CH_2Cl_2	electr.sp., X-r, cyclic voltamet.	415
$NaW(OEt)_6$		yel. cr., paramagn.	^1H, magn. prop.	1342, 926
$[(LiTHF_2)W(OPh)_6]$, tetrah. Li and oct. W sharing a common $(\mu\text{-}OR)_2$ edge		or. cr., s. in tol.	IR, ^1H, ESR, X-r	453
$M[W(OPh)_6]$, M= K, $[Et_4N$, anion - oct.]		yel. cr., m.: 255, 190; s. in THF and MeOH	IR, ^1H, ESR, X-r	453
$[(NaTHF_3)_2W(\mu\text{-}OPh)_6]^+[OPh]^-$, cation - linear chain $[M_3]$ of 3 oct.		yel. cr., 260 (dec.), s. in THF	IR, ^1H, ESR, X-r	453
$[AmH][WCl_n(OR)_{6-n}]\downarrow$, R=Me, Et, Pr^n, Bu, n=4, 5 **$NaWCl(OEt)_5$**		yel. (n=5), grn. (n=4) cr., μ_{eff}= 1.33-1.55	IR, electr. sp., magn. prop.	604, 926, 1356
W(VI)				
$W(OMe)_6$, oct.	2,4, 5, 7	colrl. cr., 43 (m.), $50/10^{-3}$ (subl.), s. in hc., ROH	IR, Raman, ^1H, ^{13}C, cryosc., m-s, X-r , gas. electronogr.	207, 393, 691, 812, 968, 1453 1476, 1560
$W(OEt)_6$	4, 5	colrl. liq.,20 (m.),45- $70/10^{-2}$(b.), s.in hc.,ROH	IR, Raman, ^1H, ^{13}C,m-s, cryosc.	207, 968

$W(OPr^n)_6$	4	colrl. liq., $72/10^{-3}$ (b.), s. in hc., ROH	IR, Raman, ^1H, ^{13}C, cryosc.	207
$W(OPr^i)_6$	4	yel. sld., $40/10^{-3}$ (b.), s. in hc., ROH	IR, Raman, ^1H, ^{13}C, cryosc.	207
$W(OC_3H_5)_6$	4	colrl. liq., $60/10^{-3}$ (b.), s. in hc.	IR, Raman, ^1H, ^{13}C, cryosc.	207
$W(OBu^n)_6$	5, 6	colrl. liq., s. in hc., ROH	IR, m-s	968
$W(OAr)_6$, Ar= Ph(**1**), C_6H_4Me-4 (**2**), -2 (**3**), oct. $C_6H_3Me_2$-2,4, C_6H_4Bu-4, C_6H_4Ph-4, $C_{10}H_7$-α, -β	4, 5, 6	red (blk.) cr., s. in hc., THF, MeCN, CCl_4, ins. in H_2O;**1**:98(m.),μ=2.13,**2**:134 (m.),μ=2.07;**3**:121(m., dec.)	IR, ^1H, X-r	61, 393, 600, 595, 1176, 1476, 1538
$[W(\eta^2\text{-}OC_2H_4O)_3]$, oct.	3	wh. cr.	X-r	1412
$[W[\eta^2\text{-}O(CMe_2)_2O]_3]$, oct. **$W[(\eta^2\text{-}O(CMe_2)_2O]_2(OPh)_2$-*cis***, oct.	6 4	pale yel. cr. yel. cr.	IR, ^1H, $^{13}C\{^1H\}$ m-s, X-r	1007 369
$W[(C_6H_4)_2O_2]_3\downarrow$	4	red cr., 270/0.5 (subl.)	-	600
$W[(OC_{10}H_6)_2]_3$ (1,1'binaphtoxides-2), 2 isomers	4	dark red cr., s. in tol.	^1H, circular dichroism sp.	478
$WF(OMe)_5$ **$WF_2(OMe)_4$-*cis, -trans*** **$WF_3(OMe)_3$-*cis, -trans*** **$WF_4(OMe)_2$-*cis***, **$WF_5(OMe)$**		colrl.liq., -10 (m.),60/vac (b.) sld., $\Delta H_{form.}$ - 363 liq. - 405 sld. - 418	^1H, ^{19}F ^1H, ^{19}F, thermochem.	812, 705 274, 1216, 1714
***trans*-$WF_n(OEt)_{6-n}$**, n=2, 3, 4, 5-instab. ***cis*-$WF_n(OPh)_{6-n}$**, n=2, 3, 4, 5		-	^1H, ^{19}F	281, 1216
$[WCl_2(OMe)_4]$-*cis*, oct. **$[WCl_n(OMe)_{6-n}]$**, n=3,4,5		cr., colrl. (n=**2**), yel.(**3**), 79 (m.), 60-80/10^{-4}, s. in ROH	^1H, X-r	704, 705

$WCl_2(OEt)_4$		yel.-grn. cr., 29 (m.), subl./vac., s. in ROH, hex., $\alpha=1$	IR, m-s	968
$[WI_2(OBu^t)_4]$-*trans*, oct.		wh. cr., s. in hex.	^1H, X-r	414
$[WF_n(OPh)_{6-n}]$, **$[WCl_2(OPh)_4]$-*trans***, oct.		blk.cr., 136(m.), s. in bz.	^1H, ^{19}F, X-r	705
$[WCl_2(OAr)_4]$,$[WCl_3(OAr)_3]$, $[WCl_4(OAr)_2]$, Ar=3-, 4-Me, 4-Bu^t, 4- PhC_6H_4, 2-, C_6H_4Cl-4, $C_6H_3Me_2$ -3,5, $C_6H_2Me_3$-2,4,6		blk. cr., 180-200 (m., dec.), s. in tol.-hex.		600, 595, 1327
$[WCl_n(OC_6H_3Me_2\text{-}2,6)_{6-n}]$, n=1, 2, 3, 4, 5, oct. <W-O-C 180°		cr., brn.(n=**2**), blk.(**3**); blk. 162 (m.)(**4**); purple, 244 (m.) (n=**5**), s. in tol., CH_2Cl_2	^1H, ^{13}C, m-s, X-r	877, 876, 1327, 1789
***mer*-$[WCl_3(OC_6H_3Pr^i_2\text{-}2,6)_3]$**		blk. cr.		1327, 1789
***cis*- $[WCl_4(OC_6H_3Pr^i_2\text{-}2,6)_2]$**, oct.				
***cis*-$[WCl_4(OC_6H_3Ph_2\text{-}2,6)_2]\cdot 0.5C_7H_8$**, oct.		blk. cr.		1327, 897
***trans*-$[WCl_4(OC_6H_3Ph_2\text{-}2,6)_2]$**, oct.				
***trans*- $\{WHal_4[OCMe(CF_3)_2]_2\}$**, Hal=F, Cl , oct.		wh. cr.	^{19}F, X-r	1305
$WCl_n(OCH_2CF_3)_{6-n}$, n=0-5				
$[WCl_2(OC_6F_5)_4]$, $[WCl_2(OC_6H_3F_2\text{-}2,6)_4]$		grn., blk. cr., s.in CH_2Cl_2	^{13}C, ^{19}F	939
$WCl_2[O(CMe_2)_2O]_2$, oct.		yel. cr., s. in $R(OH)_2$	IR, ^1H, ^{13}C, X-r	284, 1007
$[WCl_4(O_2C_6H_3R\text{-}1,2)]$, R=H, Me, Bu^t oct.		dark grn. cr., s. in tol.-hex.	^1H, electr. sp., X-r	1192
$WCl_{6-2n}[(OC_{10}H_5R)_2]_n$, R=Me, Ph, n=1, 2 (1,1'-binaphtoxides-2)		purple powd., s. in tol., CH_2Cl_2	^1H,^{13}C,sp.circular dichroism	478
$[WO(OMe)_4$, 2 oct. sharing $(OR)_2$ edge	5	cr., 126 (m.-rapidly, dec.), s. in tol., THF, ROH	IR, ^1H, m-s, X-r	393, 600, 968

		(polytherm), 6% (20°), α=1		
$WO(OEt)_4$	5	colrl. cr.,≈130(dec.), s. in hc., ROH, MeCN	IR, ^1H, m-s	356, 393, 600, 968
$WO(OBu^t)_4$, **·THF**	5, 6	pale yel. cr., 62 (m.),40/10^{-3} (b.), s. in hc., eth., THF	IR, ^1H, m-s, X-r	207, 393, 414, 420, 968
$W_2O_3(OR)_6$, R=Pr^i,Bu^t, $C_5H_{11}{}^{neo}$	7	-	^1H, cryosc.	370
$WO(OC_5H_9{}^c)_4$	6		^1H	111
$WO(OC_6H_{11}{}^c)_4$, 2 oct. sharing a common $(OR)_2$ edge	5	colrl. cr., s. in hc., THF	IR, ^1H, X-r	393
$[WO(OC_6H_3Me_2\text{-}2,6)_4]$	7	red cr.	-	1017
$[WO(OSiMe_2Bu^t)_4Py]$-*trans*, oct. **$[(WO)O(OSiMe_2Bu^t)_2Py]_2$** 2 oct. sharing a common $(\mu\text{-}O)_2$ edge	7	colrl. cr. colrl. cr.	IR, ^1H, ^{13}C, X-r	348
$[WO\{\eta^2\text{-}O[C(CF_3)_2]_2O\}_2THF]$, oct., [O, THF]-*cis* **$[W_2O_3(RO_2)_2(OROH)_2]$**	5	colrl. cr., s. in THF	^{19}F, m-s, X-r ^1H	515 1007
$WOF(OEt)_3$, $WOF_2(OEt)_2$		cr. and oil	^{19}F	281
$WOCl_2(OR)_2$, R=Me,Et, Pr^n, Pr^i, Bu^n, Bu^i,Bu^t **$WOCl_3(OR)$,** R=Me,Et, CMe=CHCOOR		cr.,150(dec.),s.in MeCN, THF blk. cr.	IR, m-s	436, 600, 968
$[WOCl_3(OC_6H_3R_2\text{-}2,6)]_2$, R=Me,$Pr^i$,$Bu^t$ (Bu^t-4) 2 oct. sharing a common $(\mu\text{-}Cl)_2$ edge **$[WOCl_3(OC_6H_4Bu^t\text{-}4\ )$**		purple cr. purple amor.sld, s. in hc.	IR,^1H, ^{13}C $\{^1H\}$, X-r	643
$[WOCl(O_2C_6H_4\text{-}1,2)(OC_6H_4OH)(Et_2O)$, oct. **$[WOCl_3(OC_6H_4OH\text{-}1,2)(Et_2O)]$**		yel. cr., s. in eth.	IR,^1H, ^{13}C, X-r	1294

$[(Na^1(EtOH)_2]_2(W^2O)_2(OEt)_{10}$ struct. type of $Ti_4(OMe)_{16}$		colrl.cr.,20 (dec.),s. in system $NaOR-WO(OR)_4-ROH$, s. in ROH 31% (20°)	IR, X-r	1638
$[WO_2(OR)_2]_n$, R= Me, Et, C_2H_4OMe	2, 5, 6	colrl. gl., s. in hc., MeCN, -ROH (fresh), 70° → $WO(OEt)_4$+...; UV, t → bl.	IR, m-s	968, 1638, 1652
$[WO_2(\eta^2\text{-}OC_2H_4OH)_2]$	3	colrl. cr., $+H_2O \rightarrow$ bl.	IR	1437
$MWO_2(OEt)_3$, M=Li, Na		gl., powd.	IR	1638
$[Na_2(WO_2)_2(OC_2H_4OMe)_6]_\infty$, $Ti_4(OMe)_{16}$ - struct. type, $[Na_2(WO_2)_2(\eta^2,\mu_3\text{-}OR)_2(\eta^2,\mu\text{-}OR)_4]$		cr.,87(m.),s.inROH, $t \rightarrow WO_2(OR)_2\uparrow$+...	IR, m-s, X-r	1638, 907
$[Me_3PhN]^+{}_2[(WO_2)_2(\mu\text{-}O)_2(\mu\text{-}OMe)_2(OMe)_2]^{2-}$ anion - 2 oct. sharing a common $[O(OR)_2]$ face		colrl. cr., s. in ROH	IR, NMR, X-r	392
$\{[Li(WO_2)(\eta^2,\mu_3\text{-}OR)(\eta^2,\mu\text{-}OR)_2]^{\cdot}[Li(\eta^2ROH)_2]\}_2{}^{2+}$ $[W_6O_{19}]^{2-}$, R=C_2H_4OMe, cation-$Ti_4(OMe)_{16}$ - struct. type		colrl. cr., s. in ROH, tol.	IR, X-r	902

$Re_{4-x}M_xO_{6-y}(OMe)_{12+y}$, M= Mo, W; $0.05<x<2.5$, $0<y<2$ [904, 1151] reviews, the most complete of which are [1574], Clark [386], and also VanderSluys and Sattelberger [1671].

12.19.1. Synthesis

Nearly all the methods described in Chapter 2 have been applied for the preparation of uranium derivatives. The reaction of metallic uranium with alcohols in the presence of halogenes (method 1) doesn't lead, as it turned out, to homoleptic alkoxides, but is a facile route to alkoxide halides [79, 1669]:

$$U + I_2 + 2{}^iPrOH \xrightarrow{{}^iPrOH} UI_2(OPr^i)_2({}^iPrOH) \xrightarrow{{}^iPrOH} U_2I_4(OPr^i)_4({}^iPrOH)_2$$

The interaction of U and Pu with a mixture of alcohol and CCl_4 was used in particular for the dissolution of the nuclear wastes, but the products of it were not isolated [1701].

The anodic oxidation of metal (method 2) has been successfully applied for the preparation of uranium (IV) ethoxide [1701]. Cyclooctatetraene (cot) derivatives of uranium ("II") were obtained by the alcoholysis of corresponding borohydrides [64], and hexaalkoxides of uranium (VI) by that of dialkylamides [856] (method 4). The exchange reaction of halids with the alkoxides of alkali metals or silicon (method 5) was successfully applied for the preparation of uranium (III–VI) derivatives, using $UCl_3(THF)_3$, $UCl_4(THF)_2$, $[PyH]_2UOCl_5$, $UO_2Cl_2Py_2$, $UO_2Cl_2(OPPh_3)_2$, and UF_6 as initial reagents (see Table 12.20). Ethoxides of uranium (IV and V) and uranium (VI) methoxide were used as initial reagents in the preparation of different homologues using alcohol interchange reaction (method 6) [204, 221, 527, 856]. The scheme illustrating the preparation of uranium (V and VI) derivatives from uranium (IV) alkoxides applying redox transformations (method 7) was given in Section 2.7.

12.19.2. Properties

Practically all the uranium alkoxides, excluding the polymeric derivatives of uranium (IV) and those of dioxouranium (VI), are rather highly soluble in both polar and nonpolar organic solvents (Table 12.20). Lowvalent ("II"–III) derivatives are not volatile because of redox transformations that apparently accompany the heating. The volatility of alkoxoderivatives increases from tetravalent to hexavalent ones and in each homologous series with the increase in the size and ramification of the radical.

On consideration of the properties of $U(OAlk)_4$ — viscous liquids and amorphous solids — there arises a question about their individuality, especially if we take into account the recent data on the studies of their Zr analogs (see Section 12.12) and also the formation of $U_3O(OBu^t)_{10}$, a structural analog of the corresponding Zr compound.

Polymeric oxoalkoxocompounds disproportionate on heating releasing the more volatile alkoxide derivatives into the gas phase:

$$UO(OR)_3 \xrightarrow{t°C} U(OR)_5\uparrow + UO_{1+x}(OR)_{3-2x}$$

The disproportionation into forms with different oxo-content has been observed for the derivatives of uranium (VI) even at room temperature. Thus on reaction of UO_2Cl_2 with $KOBu^t$ in THF it was $U_3O_4(OBu^t)_{10}$ that was isolated and not the dioxocomplex. The authors of [277] supposed that its formation takes place due to decomposition of the initially formed $UO_2(OBu^t)_2$ according to the following scheme:

$$2UO_2(OBu^t)_2 \longrightarrow UO(OBu^t)_4 + UO_3$$
$$UO_2(OBu^t)_2 + 2UO(OBu^t)_4 \longrightarrow U_3O_4(OBu^t)_{10}$$

An important feature of the alkoxide complexes containing uranium atoms in different oxidation states is their relative stability to redox transformations, $U(cot)(OR)_2$, which can be formally considered as the complexes of uranium ("II") should better be treated as the derivatives of uranium (IV), as the configuration of the alkene ligand is corresponding rather to the cot^{2+} anion. The latter acts also as a **π-acceptor,** which ensures the further stabilization of the molecule [64]. Alkoxocomplexes of uranium (III) can be easily transformed into the derivatives of uranium (IV) on action of different oxidants [79]:

$$2U(OAr)_3 + I_2 \longrightarrow 2UI(OAr)_3$$
$$2U(OAr)_3 + N_2O \longrightarrow U(OAr)_3{-}O{-}U(OAr)_3 + N_2$$

The reaction with oxygen in contrast to that with nitrous oxide doesn't lead to the formation of oxoalkoxides, due probably to the intermediate formation of peroxocomplexes in this case. The reaction products are then alkoxides of uranium (IV) and uranium (IV) oxide:

$$4U(OAr)_3 + O_2 \longrightarrow 3U(OAr)_4 + UO_2$$

The oxidation of uranium (IV) complexes has already been mentioned on discussion of the synthesis of U (V) derivatives. They can even be transformed directly into the U(VI) compounds on action of strong dielectron oxidants in the basic media [432]:

$$U(OMe)_4 + 2\,LiOMe + Pb(OAc)_4 \xrightarrow{THF} U(OMe)_6 + 2LiOAc + Pb(OAc)_2$$

The highest oxidation state (+6) appears not to be the most stable one for the alkoxides. Uranium hexaethoxide is easily converted into pentaethoxide on action of different reducing agents such as ethylmercaptane, diethylamine, and so on. Its interaction with uranium tetraethoxide leads to coproportionation [856]:

$$U(OEt)_6 + U(OEt)_4 \longrightarrow 2U(OEt)_5$$

The reduction of U(VI) into U(V) is observed also on photolysis of $U(OR)_6$ [1154]:

$$U(OMe)_6 \xrightarrow{hv} U(OMe)_5 + MeO^{\bullet} \quad [1154]$$
$$2MeO^{\bullet} \longrightarrow MeOH + CH_2O$$

Photolysis is carried out on IR laser irradiation and is isotope selective reaction, as the molecules containing ^{238}U turn to be more sensitive to its action and the samples become finally ^{235}U**-enriched.**

It is of importance that uranium atoms remain electropositive even in rather high oxidation states. The M–OR bonds remain polar, and the molecules can act as the donors of alkoxide anions in the reactions with HC1 and organic halids, such as, for example, acylbromide [147]:

$$U(OEt)_5 + nRCOBr \longrightarrow U(OEt)_{5-n}Br_n + RCOEt$$

The alkoxide is then transformed into alkoxide halide.

The stereochemistry of uranium alkoxides is very diverse, and it is possible to conclude that the geometry of the metal atom is independent on its oxidation state and the coordination numbers are in general lower than those observed for the inorganic compounds. In the series of monomeric U(IV) molecules — e.g., $[U(OC_6H_3Bu^t_2\text{-}2,6)_4]$ **[1669]**, $[UI_2(OC_6H_3Bu^t_2\text{-}2,6)_2THF]$ **[79],**

Table 12.20. Uranium and transuranium alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
U(II)				
U(cot)(OR)$_2$, R= Et, Pr^i (2 10-vertex polyhedra sharing a (OR)$_2$ edge), Bu^t	4	or. cr., s. in hc.	IR, ^{1}H, X-r	64
U(III)				
U(OC$_6$H$_3$Me$_2$-2,6)$_3$(THF)	5	dark bl. sld., s. in THF	^{1}H	385
U(OC$_6$H$_3$Pr$^i_2$-2,6)$_3$, piano stool sharing a (μ-OR-η^6-Ar)$_2$ edge	4	dark purple cr., s. in THF, hc.	IR, X-r	1669
U(OC$_6$H$_3$Bu$^t_2$-2,6)$_3$ ·nBu^{t}CN, n=1, 2	4	grn. sld., s.in THF, RCN, α= 1 bl., grn. cr., s. in RCN, hex.	IR, ^{1}H	79, 1669
U(IV)				
U(OMe)$_4$	4, 5	light grn. sld., dec., s. in ROH	-	221, 856, 855
U(OEt)$_4$	2, 4, 5	grn. sld., 220/0.01 (subl.)	IR, electr.sp.	221, 856, 855, 1701
U(OPr^n)$_4$	5	grn.visc.liq., 240/0.1 →U(OR)$_5$↑; s. in ROH	-	221
U(OPr^i)$_4$	5	grn. visc. liq., 160/0.01(b.)	-	221

«$U(OBu^t)$»=$U(OR)_5$+ $U(OR)_6$	4, 5	grn. cr., s. in ROH, petr. eth.	IR, ^1H, electr. sp.	40, 143, 221, 856, 1669
$U_2(OBu^t)_8(^tBuOH)$ +H_2O →**$U_3O(OBu^t)_{10}$**= $U_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_6$], trian., 3 oct. sharing [O(OR)] edges	4	grn. cr., s. in hc.	IR,^1H, electr. sp., magn. prop., X-r	419, 1669
$U(OCHBu^t_2)_4$	5	purple sld., 105 (m.), 90/10^{-3} (subl.), s. in ROH, μ_{eff}=2.59	IR, magn. prop.	1533
$U(OAr)_4{\cdot}nNH_3$, n=1, 2 ; Ar=Ph, C_6H_4Me-1, -2, $C_{10}H_7$-α, -β; **$U(OAr)_4{\cdot}2ArOH{\cdot}Am$**	5	red-brn. or blk.-brn. powd., s. in THF, Diox, ins. in hc.	-	594, 1070
$[U(OPh)_4(Dmpe)_2]{\cdot}C_7H_8$, dodecahedron	4, 5	grn. cr., s. in hc.	^1H,$^{13}C\{^1H\}$,^{13}P, X-r	520
$U(OC_6H_3Pr^i_2\text{-}2,6)_4$	4	or.-brn. (grn.) cr., s. in hex.	IR,^1H, electr.sp.	143, 157
$U(OC_6H_3Bu^t_2\text{-}2,6)_4$, tetrah.	4	or. cr., s. in THF	IR, ^1H, electr. sp.	143, 1669, 79
$[U_2(OC_6H_3Bu^t_2\text{-}2,6)_6O]$ 2 tetrah. sharing common O vertex	7	yel. cr.	X-r	
$U(OC_6H_3Ph_2\text{-}2,6)_4$	5	brn. sld..	-	157
$U[OCH(CF_3)_2]_4(THF)_2$	5→7	bl.-grn..sld., 238 (m., dec.), μ_{eff} = 3.01, s. in eth., RHal	^{19}F	40
$U[OCH(CF_3)_2]_4(Tmeda)$	5	grn. sld., 265 (m.)	^{19}F	
$U[OC(CF_3)_3]_4(THF)_2$	5	grn. sld., 80/vac. (subl.), 210 (m.,dec.), μ_{eff}=2.91,s.in eth.	^{19}F, magn.prop.	
$UCl_3(OR){\cdot}2L$, R=Me, Et, L=ROH,Dipy,Phen **$UCl_2(OEt)_2{\cdot}$ 0.5EtOH**		dark grn. sld.	IR, ^1H, electr.sp.	594, 615, 1701

$UCl_n(OCBu^t_3)_{4-n}\cdot 2THF$, n=2, 3		or. cr., s. in THF	^1H	122
$[UI_2(OPr^i)_2(^iPrOH)]_2$-*cis*$]_2$ 2 oct. sharing a (μ-OR)$_2$ edge		grn. cr, s. in ROH	IR, ^1H, X-r	1669
$[UI_2[O(CH_2)_4I]_2(Ph_3PO)_2]$, oct.		cr., s. in tol. (b.)	IR, ^1H, X-r	79
$[UCl_2(OC_6H_3Me_2$-2,6$)_2]$		yel cr., s. in hc.	-	759
$[UHal(OC_6H_3Bu^t_2$-2,6$)_3]$, Hal=F,Cl, Br, I, tetrah.		blk.(F), yel (Cl, Br), grn..(I)cr.	IR, X-r	79, 759
$[UI_2(OC_6H_3Bu^t_2$-2,6$)_2THF]$, trig. bipyr.		yel. cr.		
$[LiTHF_4]^+[U(OC_6H_3Pr^i_2$-2,6$)_5]^-$, anion- trig.bipyr.		bl.-grn. cr., s. in THF	X-r	157
$KU_2(OBu^t)_9\cdot C_6H_{14}$ trian., U-oct. share a common face, CN K= 4		grn. cr., s. in hex.	IR, ^1H, electr. sp., X-r	143, 419, 1669
$[LiTHF_3U(OC_6H_3Pr^i_2$-2,6$)_2Cl_3]$, trig. bipyr. U and tetrah.Li sharing a (μ-Cl) vertex		yel.red. cr.	X-r	157
$Na_4[U(\eta^2$-$C_6H_4O_2$-1,2$)_4]\cdot 21H_2O$, dodecahedron		grn. cr.	IR, X-r	1529
$UO(OPh)_2\cdot 4PhOH\cdot NR_3$		red sld.	-	1070
$U[Al(OPr^i)_4]_4$ (?) [19]				
U(IV,V)				
$U_2(OBu^t)_9$, 2 oct. sharing (OR)$_3$ face	7	dark brn. dichroic cr., s. in hex.	^1H, electr. sp., X-r	419, 1669
U(V)				
$U(OMe)_5$	5, 6, 7	red cr., 140/10^{-2} (subl.), α=3	ebul.	204, 855

$U(OEt)_5$	4, 5, 7	brn. liq., 161/0.05 (b.), 170 (dec.), d^{25} 1.71; α=1.9, μ_{eff} =1.12	IR, ^1H, ^{13}C, ^{19}F, ebul., magn. prop.	197, 204, 221, 855, 527, 699, 888
$U(OPr^n)_5$	4, 5, 6	brn. liq.,181/0.07 (b.), α=1.95	ebul.	204, 221, 855
$[U(OPr^i)_5]_2$, 2 oct. sharing common $(OR)_2$ edge	4, 5, 6	golden. cr., 320 (m.,dec.), 160/ 0.01(subl.)	IR, ^1H, ^{13}C, ^{19}F, X-r	204, 419, 527, 855
$U(OBu^n)_5$	4, 5, 6	brn. liq.,192/10^{-3} (b.), α=1.94	ebul.	204, 855
$U(OBu^i)_5$	4, 5, 6	brn. sld.,100 (m.),192/0.01(b.)	-	204, 855
$U(OBu^s)_5$	4, 5, 6	brn. sld., 85(m.), 175/10^{-2} (b.)	-	855.
$[U(OBu^t)_5]_2$, 2 oct. sharing common $(OR)_2$ edge	4, 5, 6	red-brn. cr., 120/0.05 (subl.), α=1.35	IR, ^1H, ^{13}C, ^{19}F, X-r	221, 419, 527, 855
$\cdot{}^tBuOH$, Py	6	brn. cr.,130/ 0.05 (subl.)	-	221
$U_2(OBu^t)_n(OEt)_{10-n}$, n=5, 6, 8	6	brn. cr.,150/ 0.1 (subl.) (n=5)	-	221
$U(OC_5H_{11}{}^n)_5$, $U(OC_2H_4Pr^i)_5$, $U(OCH_2CHMeEt)_5$	6	brn.liq., 246/, 225/, 220/0.05 (b.), α=2	ebul.	204, 221
$U(OC_5H_{11}{}^{neo})_5$, $U(OCHEt_2)_5$	6	sld., 160/, 180/0.1 (subl.)	-	221
$U(OCHMePr^n)_5$	6	liq., 175/0.1 (b.)	-	221
$U(OCHMePr^i)_5$, $U(OC_5H_{11}{}^t)_5$	6	sld.,160/, 130/0.05(subl.), α=1.3	ebul.	221
$U(OCMe_2Pr^n)_5$, $U(OCMe_2Pr^i)_5$	6	liq., 200/0.1 (subl.), dec	-	221
$U(OCMeEt_2)_5$, $U(OCMeEtPr^i)_5$, $U(OCEt_3)_5$	6	brn. sld., dec.,200/, 210//0.1 (subl.); α=1	-	221
$U(OPh)_5$	6	brn. sld.,165 (m.), 140(dec.)	IR, ^1H, ^{13}C, ^{19}F	527
$U(OPh)_4(OEt)$	6	blk. sld., s. in bz., $CHCl_3$	IR, electr.sp.	90

$U(OCH_2CH{=}CH_2)_5$	6	liq., 175/0.01(b.)	-	855
$U(OCH_2CF_3)_5$, $\cdot$2-3Am	4, 5, 6	grn.cr., 130/10^{-2} (subl.); liq.	m-s, tensim.	855, 1461
$U[OCH(CF_3)_2]_4(OEt)(EtOH)$	6	grn.-brn. sld.	IR, ^1H, ^{13}C, ^{19}F	527
$[U(OC_4F_9^t)_4(OEt)(EtOH)]$-*cis*, oct.	6	grn.-brn. cr., 130 (dec.)	IR, ^1H, ^{13}C, ^{19}F, X-r	527
$U(OC_6F_5)_5(EtOH)$	6	red-brn. cr., 160 (m.,dec.)	IR, ^1H, ^{13}C, ^{19}F	527
$U(OSiMe_3)_5$ $U(OSiMe_nEt_{3-n})_5$, n=1, 2 $U(OSiEt_3)_5$	6	brn. cr., 140/ 0.1(subl.), α=1.8 or. cr.,155/ 0.1 (subl.), α=1.31 brn. cr. 170/ 0.1 (subl.), α=1	ebul.	221
$U(ArO_2)_2[ArO(OH)]$, $U(ArO_2)_2(OEt)$ $U_2(ArO_2)_3[ArO(OH)]_4$, Ar=$MeC_6H_3O_2$-2,3, -3,4	6	blk. cr., ins. in common org. solv.	IR, electr. sp.	90
$UF_3(OMe)_2\downarrow$		yel.-grn. sld.		1398
$UHal_n(OEt)_{5-n}$, Hal=Cl, Br, n=1-3		grn.-brn. liq. or sld., s. in hc.	IR, electr. sp.	247, 147, 855
$UCl(OPr^n)_4$		grn. liq.,186/0.1(b.)	-	855
$UCl(OPh)_4 \cdot 2Dmfa$		brn. paste	IR, electr. sp.	90
$M[U(OEt)_6]_n$, M=Na, Ca		grn cr.,200/10^{-3} (Ca, subl.), s. in ROH, eth.	-	855
$[Et_4N][U(OEt)_2Hal_4]$, Hal=Cl, Br			IR, X-r powd.	247, 247
$UO(OR)_3$, R= Et, Pr^i, Bu^t (?), $\cdot$3ROH	5	brn. slds., s. in petr. eth., $t \rightarrow U(OR)_5\uparrow$+..	-	143, 204, 221
$Al[U(OEt)_6]_3$ [855]				

U(V, VI)				
$[U_2O_3(OPh)_5(THF)_2]_2$, $[Ti(OMe)_4]_4$ struct. type, CN U=7 (pentag. bipyr.)	5	dark red-brn. cr., invol.	IR, ^1H, X-r	1813
U(VI)				
$U(OMe)_6$, oct.	5, 6, 7	red cr.,69 (74 ?) (m.), 87/0.01 (b.), p-T (polytherm), s. in hc.	IR, Raman, ^1H, electr. sp.and struct.; photochem.	279, 432, 856, 855, 980
$U(OEt)_6$	5, 7	red liq., -62(m.), $72/10^{-3}$(b.), d=1.563, s. in bz., eth.	IR	19, 197, 856, 855, 980
$U(OPr^n)_6$	6	red liq., $107/10^{-3}$ (b.)	-	856
$U(OPr^i)_6$	5, 6	red cr., 167(m), $135/10^{-3}$ [$65/10^{-2}$] (subl.), α=1	-	204, 856, 855
$U(OBu^n)_6$	6	red liq., $206/10^{-2}$ (b.)	-	1671
$U(OBu^s)_6$, $U(OBu^t)_6$, $U(OC_5H_{11}{}^{neo})_6$, $U(OC_5H_6{}^t)_6$	6	red sld., $75/10^{-2}$,100/, $120/10^{-1}$ (subl.), α=1, exp.	-	204, 221
$U(OCH_2CF_3)_6$	6, 5, 4	red sld., $2/10^{-3}$ (subl.), p-T (polytherm)	m-s, tensim.	1461
$U[OCH_2(CF_2)_3H]_6$	5	sld., 60 (subl.),200 (dec.),s. in org.solv., p-T (polytherm)	IR, ^1H, ^{19}F, electr. sp., tensim.	1003
$U(OSiMe_3)_6$, $U(OSiEt_3)_6$, $U(OSiMe_nEt_{3-n})_6$, n=1, 2	6	or.-red cr., 145/, 195/, 160/0.1 (subl.), α=1	-	221
$UF_5(OMe)$	rot-brn. sld., -60 (dec.)			1698

$UCl(OEt)_5$	red liq., $104/10^{-2}$(b.)			855
$UO(OPr^i)_4(^iPrOH)$ **$U_2O_5(OPr^i)_2(^iPrOH)_2$ (?)**	dec.	red-brn. sld.; t→$U(OR)_6$↑ +...	-	204
$UO(OBu^t)_4\cdot{}^tBuOH$	6	red cr., s. in hc., 100/0.01→ $U(OR)_6$↑+$U_2O_5(OR)_2$	-	204
$UO_2(OR)_2$, R=Me, Et, Pr^n, Bu^n, Bu^i, $C_5H_{11}{}^i$, $C_5H_{11}{}^t$ ↑ t/vac. **·n ROH↓**	5, 6, 7	red-brn. sld.; R, n, dec./10^{-2}: **Me,** 1, 100, yel.; (dec.); **Et,** 2-3, 80, yel.; **Pr^i,** 1, 40, red; **Bu^n,** 4, red; t→$U(OR)_6$↑ +..	-	204, 855
$[UO_2(OBu^t)_2(OPPh_3)_2]$- *cis,* oct. **$U_3O_4(OBu^t)_{10}$,** linear chain of 3 oct., $[UO_2][U(\mu\text{-}O)(\mu\text{-}OR)(OR)_4]$	5 5	or. cr., s. in THF or.-red cr., s. in THF	IR, ^1H, X-r	277
$UO_2(OAr)_2\cdot n$ Am, Ar=Ph,C_6H_4Me-2, -4; Am=Py, Phen, Dipy; n=1-4	4, 5, 6	yel.-brn., red slds., 152 (m., Ph), s. only in Am, α=1	IR	594, 1058, 1070
$[UO_2(OC_6H_3Pr^i{}_2\text{-}2,6)_2Py_3]$-*trans*, pentag. bipyr.	5	dark red cr.	IR, ^1H, X-r	104
$UO_2(C_6H_4O_2\text{-}1,2)(H_2O)$	3	bl.k. sld., >300 (dec.)	-	1182
$[UO_2]_3(C_6H_3O_3\text{-}2,4,6)(H_2O)_7$	3	brn. sld., 155(dec.)	-	1182
$M_2[UO_2(OAr)_4]$, Ar= Ph, MePh-2, -4; M=Et_3NH, Et_2NH_2, Na, K	red-brn. sld., s. in ArH, α=1		ebul., conductom.	594, 1058
$[NaTHF_3]_2[UO_2(OC_6H_3Me_2\text{-}2,6)_4]$, angular mol., oct. $[UO_2(OR)_4]$ sharing a $[(\mu\text{-}O)(\mu\text{-}OR)]$ edge with 2 $[NaO_5]$	dark red-brn.. cr.		IR, ^1H, X-r	104

Np				
$Np(OMe)_4\downarrow$	5	brn. amor. sld.	IR,electr. sp.	1390
$Np(OEt)_4 \cdot nEtOH$, n=2- 4	5	red cr.,200(dec.), s. in CCl_4	IR,electr. sp.	1390,1512
$NpBr_n(OEt)_{4-n}$, n=1, 2		s. in CCl_4	electr. sp.	1390
$NpBr(OEt)_4$		grn. sld., +MOR→Np(IV)	electr. sp., ESP	1390
Pu				
$Pu(OPr^i)_4 \cdot {}^iPrOH$, $\cdot Py$ -ROH→ **"$Pu(OPr^i)_4$"**	5	grn. cr., 220/0.05 (subl. ?) grass-grn. sld.	- -	216
$Pu(OBu^t)_4$, $Pu(OCEt_3)_4$	6	grn..sld., 112/, 150/0.05 (subl.)	-	216
$Pu(OC_6H_3Bu^t_2\text{-}2,6)_3$	4	sld., α=1 (?)	-	1671

and $[U(OPh)_4(Dmpe)_2]\cdot C_7H_8$ [520] — the CN of the metal atom increases from 4 (tetrahedron) to 5 (trigonal bipyramid) and 8 (dodecahedron). The dimeric $[UI_2(OPr^i)_2(^iPrOH)]_2$-*cis*$]_2$ molecule (2 octahedra sharing a common edge) [1669] is a structural analog of the known isopropoxides of Zr, Hf, Sn, and other quadrivalent metals (Fig. 4.1 *b*). Among the quinquevalent derivatives it is necessary to mention the monomeric $[U(OC_4F_9^t)_4(OEt)(EtOH)]$-*cis* (octahedron) [527], dimeric $[U(OR)_5]_2$ (R = Pr^i, OBu^t [419]) pairs of octahedra sharing common edges. Homoleptic hexavalent alkoxides are monomeric octahedra (the structure of $U(OMe)_6$ [432] has been investigated). The uranyl derivative $[UO_2(OC_6H_3Pr^i_2\text{-}2,6)_2Py_3]$ is a pentagonal bipyramid with a *trans*-arrangement of the oxoatoms [104]. The presence in the coordination sphere of U of a number of bulky OR-groups decreases the CN to 6. The example is provided by an octahedral anion $[UO_2(OC_6H_3Me_2\text{-}2,6)_4]^{2-}$ [104].

Among the alkoxides of transuranium elements there are known only derivatives of neptunium and plutonium — mainly in the +4 oxidation state. $Np(OR)_4$ (insoluble in alcohols) were obtained by metethesis of $NpCl_4$ with LiOR [1390], and soluble $Pu(OPr^i)_4\cdot{}^iPrOH$ by reaction of $[PyH]_2PuCl_6$ with ammonia in alcohol [216] (method 5). It can be supposed that plutonium isopropoxide solvate is isostructural to the analogous derivatives of Zr, Hf, Sn, Ce, Th, and so on. M(IV) and consists of dimeric molecules — pairs of edge-sharing octahedra with two intramolecular hydrogen bonds each. In analogy with those derivatives, the desolvation of $Pu(OPr^i)_4\cdot{}^iPrOH$ should be accompanied by solvolysis with formation of oxoalkoxides as products (and not $Pu(OPr^i)_4$, as it was supposed in [216], Section 12.12). Its alcohol interchange with ^tBuOH yields volatile $Pu(OBu^t)_4$. Oxidation of $Np(OEt)_4$ with bromium in the presence of NaOEt provides unstable $NpBr(OEt)_4$ [1390].

$Pu(OC_6H_3Bu^t_2\text{-}2,6)_3$ phenoxide complex was obtained on alcoholysis of the corresponding trimethylsilylamide (it is mentioned only in the review [1671]).

12.20. Manganese alkoxides

The methoxide of manganese (II) was described by Kandelaki [874] and first obtained and described in the individual state by the group of Martin in the late 1960s along with a series of methoxide derivatives of the divalent 3*d*-transition metals [6].

A comprehensive study of Mn (II) derivatives was then published by Horvaths in 1979, describing preparation, spectra, and magnetic properties of a large variety of derivatives [770]. The isolation and X-ray characterization of soluble derivatives of Mn(II) with branched alcohols was investigated by Power *et al.* [114]. The mixed-valence Mn(II)–Mn(III) and monomeric Mn(III) species possessing interesting magnetic properties were studied by Christou *et al.* since the late 1980s [1411]. The hydrolysis pathways for bimetallic complexes of Mn(II) were investigated in 1990 by Westin *et al.*[1733].

12.20.1. Synthesis

The metathesis reaction of metal chloride with alkali alkoxides (method 5) was historically the first approach applied, and it remains the main route to both mono- and bimetallic derivatives of Mn(II). The most efficient approach to Mn(II) derivatives is, however, provided by the alcoholysis of the corresponding silylamide (method 4). The derivatives of Mn(III) and mixed-valence Mn(II,III) were obtained by alcoholysis of Mn(III) acetate by polyatomic phenols in the presence of 2,2'-dipyridil accompanied by reduction in the latter case (methods 4 and 4+7).

12.20.2. Properties

The alifatic derivatives of Mn(II) are colorless or pale-colored polymeric solids as indicated by IR and magnetic data. They are insoluble in organic solvents and decompose without melting on heating. The compounds derived from very branched R (like CPh_3) and phenols are pale-colored crystalline matters possessing good solubility in hydrocarbons. The most prominent feature of all Mn(II) alkoxide compounds lies in their facile oxidation by the traces of molecular oxygen, making their isolation and treatment a very complicated problem and demanding the application of carefully degassed solvents. These difficulties led to a certain confusion in description, especially of soluble heterometallic complexes. Thus, brown liquids reported by Mehrotra [1110], appear in fact to be the decomposition products of the Mn(II) alkoxides. The structural chemistry of these derivatives has not been excessively studied, but the existing data (as for $Mn_2Sb_4(OEt)_{16}$ [140]) indicate clearly its likeness to that of small divalent metal atoms. The isolated derivatives of Mn(III) and $C_6H_4C_6H_4(OH)_2$-2,2' are dimeric or monomeric species with a tetragonal pyramidal coordination of the central atom due to the Jahn-Teller distortion of the d^4 electron configuration [1411] (Table 12.21). The alkoxoantimonates of Mn(II) were investigated as precursos of Bi_2O_3-based Mn-doped varistor ma-

Table 12.21. Manganese alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
Mn(II)				
$Mn(OMe)_2$↓, struc. type $Mg(OH)_2$, $[MO_{6/3}]$- oct.,$[OM_3]$- trig. pyr.	5	light pink sld., 300 (dec.), μ_{eff}= 5.96	IR, electr. sp., magn. prop.	6, 7, 1365
$Mn(OR)_2$, R= Et, Pr^i, Bu^n, Bu^s, Bu^t, $C_5H_{11}{}^n$, $C_5H_{11}{}^s$, $C_5H_{11}{}^{neo}$, $C_6H_{13}{}^n$, $C_7H_{15}{}^n$,$C_8H_{17}{}^n$, $C_9H_{19}{}^n$, $C_{10}H_{21}{}^n$, $C_{14}H_{21}{}^n$, $C_{18}H_{29}{}^n$, $C_{19}H_{15}{}^n$	4	colrl. sld., 300 (dec.), μ_{eff} < 5.9, visc. liq. ($C_{19}H_{15}$), pyrophoric (Bu^n, $C_5H_{11}{}^{neo}$)	electr. sp., magn. prop.	500, 770
$Mn(OR)_2$, R= Ph, $PhCH_2$.	4	colrl.cr., s. in.hc., μ_{eff}~ 6	^1H, ”	770
$Mn(OR)_2$·2THF, R= $C_{14}H_{21}{}^n$, $C_{18}H_{29}{}^n$	4	«		
$[Mn(OCHBu^t{}_2)]_3$, central tetrah. $[MnO_4]$ sharing (μ-OR)$_2$ edges with 2 $[MnO_3]$ trian.	4	pale pink cr., 244 (m.), v. s. in hc., eth., α=3	IR, ESR, electr. sp., X-r	167, 1185
$[Mn(OCPh_3)_2Py_2]$, oct in which 2 equ. gr. are missing, 2 Py-equ., 2 OR- ax.	4	colrl. cr.,μ_{eff}=5.8 s. in.tol.	IR, ^1H, ESR, magn. prop., X-r	114
$Mn(OAd\text{-}1)_2$↓, Ad=adamantyl($C_{10}H_{15}$) **$Mn(OCH_2Ad\text{-}1)_2$↓**	4	pale beige cr., 350 (dec.); μ_{eff} =5.44	IR, ^1H, ESR, m-s	166
$[Mn(OC_6H_2Bu^t{}_3\text{-}2,4,6)_2]_2$· 0.5PhMe 2 trian. sharing (μ-OR)$_2$ side	4	yel. cr., 90(234 ?, m.),228 (dec.), s. in hc., μ_{eff}= 3.6	IR, ^1H, ESR, magn. prop., X-r	114, 770
$[Mn(OC_6H_2Bu^t{}_3\text{-}2,4,6)_2L_2]$·2 MeCN, L= MeCN, Py, tetrah.	4, 5	colrl. cr., s. in eth, THF, hc. μ_{eff}=5.8	IR, ^1H, ESR, magn prop., X-r	114, 1148
$Mn[OC(CF_3)_2]_2$·$2H_2O$	5	yel. cr.	-	195

$[Mn[OC_6H_2(CF_3)_3\text{-}2,4,6]_2THF_3]$ tetrag. pyr.	4	colrl. cr., 133 (m.), μ_{eff}= 5.8, s. in hex.	IR, magn. prop., X-r	1361
$Mn_5(C_3H_5O_3)_3[C_3H_5O(OH)_2]$	4	wh. sld., μ_{eff}= 5.9	IR, magn.prop.	1329
$[Mn_2(O_2Ar)_2Py_6]$, Ar=1,2-$C_6H_2Bu^t{}_2$-3,5, 2 oct. sharing (μ-OR)$_2$ edge **$[Mn_4(O_2Ar)_4Py_6]$,** cube, 2 oct. $[MnO_4N_2]$, 2 trig. bipyr. $[MnO_4N]$	4	yel. cr., 290 (m., dec.), s. in Py >300(m. dec.), s. in Py, tol.	IR, ^{1}H, ESR, X-r	1475
$M_2Mn\{[OC(CF_3)_2]_2\}_2$, M=K, Cs		μ_{eff}= 5.2, s. in H_2O	magn. prop.	26
$Li_2[Mn(\mu\text{-}Br)_2(\mu\text{-}OCBu^t{}_3)_2THF_2]$, linear chain, central $[MnBr_2O_2]$ tetrah., tetrah. $[LiBr_2THF_2]$, trian. $[LiO_2Me]$		pink cr., 145 (m.)	X-r	1185
$[Mn_2M_2(OBu^t)_8]$, M=Ge, Sn [1683, 1681, 1684]; **$MnAl_2O_2(OR)_4$,** [1244] **$Mn_2Sb_4(OEt)_{16}$; $Mn_7Sb_4O_4(OEt)_{18}(EtOH)_2$; $Mn_8Sb_4O_4(OEt)_{20}$** [1733, 140]				
Mn(II, III)				
$[Mn_2(\eta^2\text{-}ArO_2)_2(ArO_2H)(\eta^2\text{-}Dipy)_2]$, $\cdot 3CH_2Cl_2$, R= $C_6H_4C_6H_4$-1,2. oct. and tetragon. pyr. sharing (μ-OR)$_2$ edge	4-7	blk. cr., μ_{eff}=9.19 (5 K), 7.82 (302 K)	IR, UV, magn. prop., X-r	117, 1411
$[Mn_3(1,2\text{-}O_2C_6H_2Bu^t{}_2\text{-}3,5)_4Py_4]$, angular mol., central oct.. $[Mn(\mu_3\text{-}OR)_4Py_2]$ - *cis*, peripheral - tetragon. pyr. $[Mn(\mu\text{-}OR)_4Py]$	7	red-brn. cr., 250 (m., dec.), s. in Py	IR, ^{1}H, ESR, X-r	1475
Mn(III)				
$[Et_3NH]_2[Mn(\eta^2\text{-}RO_2)_2(\eta^2\text{-}RO_2H)]$, R= $C_6H_4C_6H_4$-α,α, anion - oct. of 3 cycles		blk. cr., μ_{eff}= 4.94 (sld.), 5.30 (s.), s in hc.	IR, electr. sp., magn. prop., X-r	1411

[HDipy][Mn(O_2R)$_2$(Dipy)]·1/2CH_2Cl_2		blk. cr., μ_{eff}= 5.09		
Mn(IV)				
Mn($OCH=CH_2$)$_4$· 0.5THF	7	brn-red. cr.	IR, ^1H, magn.prop.	813
[Mn(1,2-$O_2C_6H_2Bu^t_2$-3,5)$_2$Py$_2$]·2Py-*trans*, oct. **[Mn(1,4-$O_2C_6H_2Bu^t_2$-2,5)$_2$]$_4$,** $Ti_4(OMe)_{16}$ struct. type	7 ?	purple cr., μ_{eff}=4.2? grn.cr., μ_{eff}=5.1 (d^3)	electr.sp., magn. prop , X-r	1037
Mn(VII)				
Mn(=NBu^t)$_3$(OR), R=C_6F_5 (tetrah.), $CH(CF_3)_2$	5	grn. cr., s. in MeCN	X-r	448

terials[1733].

12.21. Technetium and rhenium alkoxides

This section is actually devoted to the description of rhenium alkoxides, as the technetium ones are rarely studied. The latter are reviewed in a short appendix at the end. The chemistry of rhenium in lower oxidation states is much alike that of ruthenium and therefore even for rhenium, the lower oxidation state complexes with **π-acceptor** ligands are described in this chapter.

12.31.1. Synthesis

The main route to rhenium alkoxides is the interaction of halids and oxyhalids with alkali alkoxides or alcohols in presence of amines (method 5). As the important starting reagents can serve also $Re_2(CO)_{10}$ and Re_2O_7 (method 3) The preparation of rhenium (V) and (VI) oxoderivatives by the anodic oxidation of metal in alcohols has also been described (method 2) (see Table 12.22). The bimetallic alkoxides of rhenium and heavy transition metals can most efficiently be obtained by interaction of rhenium (VII) oxide with the alkoxides of these elements in refluxing toluene:

$$Re_2O_7 + MO(OMe)_4 \longrightarrow Re_{4-x}M_xO_6(OMe)_{12} + \ldots \quad (M= Mo, W)$$

$$Re_2O_7 + Nb(OMe)_5 \longrightarrow Re_2Nb_4O_{10}(OMe)_{14} + \ldots$$

12.21.2. Properties

Nearly all the alkoxide derivatives of rhenium demonstrate rather high solubility in different organic solvents such as hydrocarbons, chlorinated hydrocarbons, alcohols, and ethers. The only exceptions are the oxomethoxides — namely, $ReO_3(OMe)$ **[519]**— demonstarting quite low solubility in hydrocarbons due presumably to its polymeric structure and $Re_4O_2(OMe)_{16}$ **[906]**, which is almost insoluble. The other complex, possessing a very close molecular structure, $Re_4O_6(OMe)_{12}$, is rather sparingly but noticeably soluble in both polar and nonpolar solvents. It should be noted that the rhenium (V) compound is almost stable to hydrolysis. The latter property is usually characteristic of homoleptic phenoxocomplexes like $Re(O_2C_6H_2Bu^t_2\text{-}3,5)_3$ [471] and is quite unusual for alifatic derivatives. The analogous complex of rhenium (VI) and bimetallic complexes of rhenium and molybdenum with close molecular and crystal structures are noticeably less stable and decompose completely in ambient atmosphere in several hours.

All the known rhenium alkoxocomplexes are thermally unstable. In the cases when the partial transition into the gas phase can nevertheless be observed, it is accompanied by disproportionation in both oxidation states and the composition of the oxoforms as it takes place in the case of $Re_4O_2(OMe)_{16}$ [906] — for example,

$$Re_4O_2(OMe)_{16} \longrightarrow ReO(OMe)_3 + Re(OMe)_4 + ReO_3$$

The chemistry of the alkoxoderivatives of rhenium is very diversified due to the existence of the compounds corresponding to practically all the possible oxidation states. The transitions between them occur usually quite easily, being characterized by comparably low values of redox potentials as it takes place, for example, for rhenium (VI) cateholates [471]:

$$Re^{VI}(ArO_2)_3 \xrightarrow[+0.36V]{e^-} [Re^{V}(ArO_2)_3]^- \xrightarrow[-0.59\ V]{e^-} [Re^{IV}(ArO_2)_3]^{2-},\ Ar = Cl_4C_6H_2\text{-}1,2$$

The observed E_0 values in this case indicate the highest stability of rhenium (V) derivatives in this series. The comparison of the preparative data published indicates that these are the +5 and +6 oxidation states that appear to be most stable for the alkoxocomplexes of rhenium. The low-valent (+1 – +3) complexes should either be stabilized by **π-acceptor** ligands (CO, PR_3, NO, unsaturated hydrocarbons) or contain multiple **M–M** bonds [321, 586, 729, 762,]. The compounds of rhenium (VII) are very unstable and decompose at room temperature in several minutes when isolated. They can be isolated and kept for several days as the complexes with N-donor ligands such as Tmeda or Py [533, 519, 1358]. The decomposition products of rhenium (VI) and (VII) alkoxides are often described in literature as a “black tar.” The compound with this kind of appearence turned to be the major product of the anodic oxidation of rhenium in methanol (at high current density) and was shown by the X-ray single crystal study to be $Re_4O_2(OMe)_{16}$ [906].

The other feature that enriches but also complicates the chemistry of rhenium alkoxides is their ability to use different kinds of decomposition processes, not leading to the changes in the oxidation state. That is first and foremost the ether elimination from the rhenium (V-VII) derivatives. It leads to the formation of oxocomplexes, as, for example [168]:

$$-3HCl \qquad\qquad -Et_2O$$

$$ReCl_5 + 3\ EtOH \longrightarrow Re(OEt)_3Cl_2 \longrightarrow ReO(OEt)Cl_2$$

The other decomposition pathway discovered for the rhenium (III) isopropoxide is the elimination of an acetone molecule via **β-hydrogen** transfer and appears to be a reversible reaction [762]:

$$Re_3(OPr^i)_9 \leftrightarrow Re_3(OPr^i)_8H + MeCOMe$$

The hydride derivative thus formed is comparably stable and was structurally characterized. The elimination of an acetone molecule in this case therefore does not lead to changes in the oxidation state.

12.21.3. Bimetallic alkoxides of rhenium

In addition to the bimetallic complexes of rhenium and alkaline metals formed as byproducts in the exchange reactions of rhenium halids with alkali alkoxides (such as, for example, $LiReO(OPr^i)_5 \cdot xLiCl(THF)_2$ [519]) there has been recently prepared a number of bimetallic complexes of rhenium and molybdenum, rhenium and tungsten, and rhenium and niobium [904, 1451]. The latter are formed either due to the formation of a metal-metal bond, arising due to combination of a free electron pair on rhenium (V) and a vacant orbital of molybdenum (VI) atom or via insertion of molybdenum or tungsten atoms into the molecular structure characteristic of rhenium (V and VI) oxoalkoxides. The formation of the compounds with variable composition becomes possible in the latter case.

12.21.4. Application

Rhenium alkoxocomplexes are of interest as homogeneous catalysts of olefine metathesis [519]. They have also been used for the preparation of fine powders of rhenium and rhenium alloys for catalytical and powder metallurgical use [1452].

12.22. Iron alkoxides

The preparation of iron (III) ethoxide was first reported in 1929 simultaneously by Meerwein [1101] and Thiessen [1577]. The aim of the first of these studies was to obtain a new reagent for reduction of carbonyl compounds, and the aim of the second was to obtain a precursor for the preparation of iron hydroxydes and their colloid solutions. The derivatives of the $Fe(OAlk)_3$ series were obtained then by Bradley *et al.* in 1958 [228], and their magnetic properties and UV-vis spectra were studied in detail in the 1960s by the group of

Table 12.22. Technetium and rthenium alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
Tc				
$[Na(MeCN)_2Tc^I_3(CO)_9(OMe)_4]_\infty$, chains of cubes $[NaTc_3(\mu_3\text{-}OR)_4]$, $[Tc(CO)_3(OR)_3]$ -oct.		colrl. cr., s. in ROH, MeCN, ins. in H_2O, hc.	IR, ^{1}H, ^{90}Tc, m-s, X-r	733
$K_2Tc^{IV}(OMe)_6$ **$K_2Tc^{IV}[(\text{-}CH_2O)_2]_3 \cdot 3EtOH$** **$K_2Tc^{IV}[OCH_2CH(O)C_2H_4O]_2 \cdot MeOH$**		light-grn. cr., s. in ROH colrl.cr., s. in ROH, MeCN	IR, electr. sp.	20
$[Tc^VOCl_2(OR)Py_2]$, R=Me, Et **$Tc^VOCl(OCHRCHRO)$**, R=H (oct.), Pr^n, Bu^n, Ph, C_2H_3		grn. cr., s.in $CHCl_3$-MeCN grn. cr., s.in CH_2Cl_2, α=1	IR, ^{1}H, ^{99}Tc m-s, X-r	1287
$[Bu_4N]\{Tc^VO[(\text{-}CH_2O)_2]_2\}$		vlt. cr., s. in ROH, THF, bz.	IR, ^{1}H, ^{13}C	240, 778
$Tc^{VII}O_3(OSiMe_3)$		colrl. sld., s. in $(SiMe_3)_2$	^{1}H, ^{13}C	1222
Re(I)				
$[Re(CO)_3(OR)]_4$, R= Me, Et, $[M_4(OR)_4]$-cube, · **n PMe_3**, n=2, 3	3	dark cr., 275(m.), 270 (dec.)	IR, Raman, ^{1}H, ^{13}C, X-r	729, 1491
$[Me_4N][Re_2(OMe)_3(CO)_6]$, 2 oct. sharing a $(\mu\text{-}OR)_3$ face **$[Me_4N][Re_3(\mu\text{-}OMe)_4(CO)_9]$**, anion - trian. $[Re_3(\mu_3\text{-}OR)(\mu\text{-}OR)_3(CO)_9]$		wh. cr., 290(dec.), s. in. ROH, eth., MeCN	IR, ^{1}H, ^{13}C, X-r	738
$M[(CO)_3Re(\mu\text{-}OR)_3Re(CO)_3]$, M=K, Cs, R_4N		colrl. sld.	IR, Raman, ^{1}H	586

Re(III)				
$Re(OEt)_3$	5	brn. cr., s. in ROH	-	500
$[Re_3(OPr^i)_9]\cdot 1/3\ ROH$ **$[Re_3H(OPr^i)_8]$**, trian. $[M_3(\mu\text{-}OR)_3(OR)_5]$, $\cdot L$, L=PMe_3, Py **$[Re_3(OC_5H_{11}{}^{neo})_9]$, $\cdot PMe_3$** $=[Re_3(\mu\text{-}OR)_3(OR)_6L]$, trian., Re=Re 2.38	5 7 5	grn cr., s. in hc. light grn cr., $70/10^{-2}$(subl.), s. in CH_2Cl_2, olive grn. grn cr., s. in CH_2Cl_2	^1H, $^{13}C\{^1H\}$ ^{31}P, X-r	762, 1809 1809
$[Re_3H(OCHEt_2)_8]$= $[Re_3(\mu\text{-}OR)_3H(OR)_5]$	5	brn. powd., s. in THF	^1H, ^{13}C	762
$[ReO(OR)(RC'\equiv CR')]$, R= Me, Et, Ph Pr^i, Bu^t, $SiMe_3$, pseudo-tetrah.	5	yel.-grn. cr., 35-60 (subl.), <100(dec.), s. in hc.	IR, ^1H, ^{13}C, ^{31}P, m-s, X-r	533
$[Re_3(\mu\text{-}OPr^i)_3ClH(OPr^i)_4(PMe_3)]$, trian., Re=Re 2.38		grn.cr., s.in CH_2Cl_2-MeCN	IR, ^1H, ^{13}C, ^{31}P, X-r	1809
$[Re_3Cl_3H(OPr^i)_5]_2$		grn. powd.	^1H, ^{13}C	762
$[Re_3(\mu\text{-}Cl)_3(OBu^t)_6]$, trian., Re=Re 2.44		grn. cr.	^1H, ^{13}C, X-r	1758
$[Re_3(OPr^i)_7Cl]_2Cl_2$= $[Re_3(\mu\text{-}OR)_3(OR)_4Cl]_2(\mu\text{-}Cl)_2$		dark red cr., s. in CH_2Cl_2	IR, "	1809
$[Re_3Cl_2(OC_5H_{11}{}^{neo})_6(PMe_3)_2]$= $[Re_3(\mu\text{-}Cl)Cl(\mu\text{-}OR)_2(OR)_4L_2]$, trian., Re=Re 2.48		grn. cr., s. in THF	IR, ^1H	1809
$[Re_3(\mu\text{-}Cl)Cl(\mu\text{-}OR)_2Cl(OR)_5]$, R= $OC_{10}H_{19}$ (menthoxide), trian., Re=Re 2.37 (2 bonds), 2.42 (1 bond)		brn. cr.	X-r	1758
$[Et_4N]^+{}_4[Re_4Cl_8(\mu\text{-}O)_2(\mu\text{-}OMe)(\mu\text{-}X)]^{4-}\cdot THF$, CH_2Cl_2, X=Cl, OMe, anion - square $[Re_4Cl_8]$, 2 bonds Re≡Re 2.26, 2 bonds Re-Re 2.55			X-r	336
Re(II-IV)				

$(RO)_2Hal_2Re^{IV}\equiv Re^{II}Hal_2(PPh_3)_2$, Hal= Cl, Br, R= Me, Et, Pr^n, Pr^i, cluster - 2 tetragon. pyr., Re-ax., Re-Re 2.23		red cr., s. in ROH, CH_2Cl_2, diamagn.	IR, ^1H, ^{31}P, ESR, electr. sp., X-r	321
Re(IV)				
$Re(OPh)_4(PMe_3)_2$-*trans*, oct.	5	brn. cr., s. in eth., CH_2Cl_2	X-r	519
$Re(OC_6H_3Me_2\text{-}2,6)_4$, **$\cdot RC\equiv CR$**, R=Me, Et, Ph	5	brn. sld., eth., CH_2Cl_2, α=1, μ_{eff} =1.37 μ_{eff} =1.78-1.89	^1H, ^{13}C, ESR, magn. prop.	617
$Re(OC_6H_3Pr^i_2\text{-}2,6)_4$, square	5	brn. cr., α=1, μ_{eff} =1.50	" X- r	617
Re(V)				
$[Re(OMe)_5]_2$, 2 oct. sharing a (μ-OR)$_2$ edge	5	red cr., s. in hc., ROH	^1H, X-r	262
$ReCl_n(OEt)_{5-n}$, n=2, 3, 4		brn., brn., grn. liq.	IR	168
$NaRe(OEt)_6$		vlt.powd., s. in ROH	IR	168
$Re_4O_2(OMe)_{16}$ = $[Re_4(\mu\text{-}O)_2(\mu OR)_4(OR)_{12}]$, planar rectangular $[Re_4]$, gr. $[Re_2O]$- linear	2	blk. cr., 182 (dec.), v. low s. in MeOH, tol.	IR, m-s, X-r	906
$[ReOHal_2(OR)L_2]$, R=Me,Et; Hal=Cl,Br,I; L= Py, PR_3 **$[ReOCl_2(OEt)Py_2]$**, **$[ReOI_2(OEt)(PPh_3)_2]$-*trans, trans***, oct.		grn. or purple cr. 150-190 (dec.)	IR, ^1H, ^{13}C, ^{31}P	378,846, 673, 1024, 1459
$ReOCl(\text{-}CH_2O)_2Phen$		red-brn. cr., s. in MeOH	IR, ^1H, m-s	1287
$M[ReO(\eta^2\text{-}O_2C_6H_4\text{-}1,2)_2]$, M=$Ph_4N$, Me_4N		grn. cr.	IR, ^1H, ^{13}C, electr. sp	481
$ReOMoO(OMe)_7$, 2 oct. sharing a (μ-OR)$_3$ face		red cr., 62/0.01 (b.)	IR, m-s, X-r	904
Re(V, VI)				

$Re_4(O,OMe)_4(\mu\text{-}O)_2(\mu\text{-}OMe)_4(OMe)_8$, planar rectangular $[Re_4]$, Re-Re 3.45	2	grn. cr., 182 (dec.), s. in b. tol., diamagn., t→ ReO_3 $+Re(OR)_4+ReO(OR)_3$	IR, mass-sp, magn. prop. X-r.	906
Re(VI)				
$Re(OMe)_6$	5	or. cr., 59 (m.), paramagn.	IR, Raman, ^1H	812,
$(ReO)_2O(OMe)_6$, 2 oct. sharing a $[O(OR)_2]$ face, Re=Re 2.56	5	or.-red cr., s. in eth., diamagn.	IR, ^1H, m-s, magn. prop., X-r	519
$Re_4O_6(OMe)_{12}$ $= (ReO)_4(\mu\text{-}O)_2(\mu\text{-}OR)_4(OR)_8$, planar rectangular $[Re_4]$	2	reddish blk. cr., diamagn.	IR, X-r	1454
$ReO(OBu^t)_4$	5	bl. cr., 0 (dec.), s. in eth., paramagn.	IR, ^1H, ESR, magn. prop.	519
$ReO(\eta^2\text{-}1,2\text{-}O_2C_6H_{12})_2$, square pyr.	3	red cr.,120 (dec.), μ_{eff}=1.7	IR, m-s, , X-r	521
$ReO(O_2C_{12}H_{20})_2$, square pyr.	3	red cr.,166 (dec.), μ_{eff}=1.7	IR, m-s, , X-r	521
$Re(\eta^2\text{-}1,2\text{-}O_2C_6H_2Bu^t_2\text{-}3,5)_3$, oct. with 3 chelate 3 cycles	7	purple cr., μ_{eff}= 1.18	IR, electr. sp., ESR, m-s, X-r	471
$[LiReO(OPr^i)_5 \cdot LiCl(THF)_2]$, $Ti_4(OMe)_{16}$ - struct. type		grn.cr., 50 (dec.),s. in petrol. eth.,paramagn.	IR, ^1H, ESR, magn. prop., X-r	519
$Re_{4-x}M_xO_{6-y}(OMe)_{12+y}$, M= Mo, W; $0.05<x<2.5$, $0<y<2$		blk. cr.	IR, m-s, X-r	904, 1451
Re(VII)				
$ReO(OEt)_nF_{4-n}$, n=1, 2	3	-	NMR	168
$[ReO_2(OSiBu^t_3)]$ **$[ReO_2(OSiMe_3)(\eta^2\text{-}OCMe_2CMe_2O)]$**, trig.bipyr.	3	colrl. cr.	IR, m-s, X-r	738, 1723

M[ReO$_2$(η^2-RO$_2$-1,2)$_2$]-*cis*, M=Et$_4$N, Ph$_4$P, R= C$_6$H$_4$, C$_6$H$_3$ Bu^t-4, C$_6$H$_2$Bu$^t{}_2$-3,5, anion - oct. with 2 chelate cycles		red. cr., s. in CH$_2$Cl$_2$-eth.	IR, ^{1}H, ^{31}P, elecr. sp., X-r	481
ReO$_3$(OMe), · Py, THF, Tmeda	5	colrl. sld., dec. r. t.	IR, ^{1}H, ^{13}C	519
[ReO$_3$(OMe)(MeOH)]$_2$, 2 oct. sharing a (OR)$_2$ edge	3, 6	colrl. sld.	IR, ^{1}H, ^{13}C, X-r	738
ReO$_3$(OMe)(Tmen)	3, 6	colrl. cr., 114 (dec.)	IR, ^{1}H, ^{13}C	519
ReO$_3$(OBu^t), **· Py, THF, Tmeda**	3, 5, 7	colrl. cr., -4 (dec.), s. in CCl$_4$, CH$_2$Cl$_2$ - stab.	IR, Raman, ^{1}H, ^{13}C	519, 1358
ReO$_3$(OSiMe$_3$),	3	colrl. cr.	"	1222, 1358, 1427
[ReO$_3$(OSiBu^{t}O)]$_4$ planare cycle [Si$_4$O$_4$], [O$_3$ReO(Si)]-tetrah.	3	colrl. cr., 138 (dec.), s. in MeCN (b.)	IR, ^{1}H, ^{29}Si, m-s, X-r	1753
[ReO$_3$(η^2-OCMe$_2$CMe$_2$OMe)], trig. bipyr. **ReO$_3$(η^2-OCMe$_2$CMe$_2$OH)],** trig. bipyr.	3 3	colrl. sld. colrl. cr., 73 (dec.)	IR, m-s, X-r IR,^{1}H,^{13}C, X-r	738 738
ReO$_3$(OC$_6$H$_{12}$OH)(HOC$_6$H$_{12}$OH), trig. bipyr.	3	colrl. cr., 74 (m., dec.)	"	521
ReO$_3$(OC$_{12}$H$_{20}$OH), trig. bipyr.	3	wh. cr., 90 (dec.)	"	521
Re$_2$Nb$_4$O$_{10}$(OMe)$_{14}$, planar [Nb$_4$(μ-O)$_2$(μ-OMe)$_4$] core, 2 ReO$_3$(μ-O)-ligands		colrl. cr.	IR, X-r	1451

Martin and Winter in Australia [7, 5]. The scarce structural studies of $Fe(OR)_3$ have been carried out since 1985.

The very oxidation-sensitive iron (II) derivatives turned out to be much less accessible. The studies of $Fe(OR)_2$ (along with the other polymeric $M(OR)_2$) were started in 1966 by the same group from Australia [6, 7]. An important step was connected with the application by Lehmkuhl [1005] of the electrochemical synthesis for the preparation of $Fe(OR)_2$, which permitted researchers to obtain the samples free from impurities arising from oxidation. The first studies of oligomeric phenoxides with sterically crowded ligands were carried out by Bartlert *et al.* [114] in 1991.

12.22.1. Synthesis

The preparation of $Fe(OR)_3$ was achieved nearly exclusively via metathesis of chloride with NaOR or NH_3 in alcohol-benzene media (method 5) and also via alcohol interchange [228] or transesterification [1466] from ethoxide or isopropoxide (method 6). The introduction of $FeCl_3$ into the reaction with NaOR as an ether solution or suspension in benzene (i.e., elimination of the risk of alcoholysis before the contact with NaOR) permitted of the increase of the yields of $Fe(OR)_3$ to nearly quantitative [1647, 1365, 1648]. It is interesting to note that the anodic oxidation of iron in 2-methoxyethanol leads to the formation of $Fe(OC_2H_4OMe)_3$ [1652, 1514] in contrast to that in alifatic alcohols, which gives the derivatives of iron (II) [1005]. In addition to the electrochemical techniques (method 2), the alcoholysis of $Fe[N(SiMe_3)_2]_2$ [114, 1475] or $[FeEt_2Dipy_2]$ [941] (method 4) and even the metathesis of $FeCl_2$ with lithium methoxide (to obtain the polymeric iron (II) methoxide [6]) were applied for the preparation of $Fe(OR)_2$.

12.22.2. Properties

The alkoxides of iron (III) are reddish-brown solids or viscous liquids. All of them except for $Fe(OMe)_3 \cdot MeOH$ are soluble in alcohols and hydrocarbons. The molecular complexity in a benzene solution is equal to 3 for the derivatives of primary, 2 for derivatives of secondary, and 1 to 1.5 for derivatives of tertiary alcohols [228]. $Fe(OR^s)_3$ and $Fe(OR^t)_3$ are volatile, while $Fe(OR^n)_3$ are not transmitted into the gas phase [1365] in contradiction to [228].

An X-ray single crystal study of the repeatedly reported "crystals of iron ethoxide" has shown that this compound (as well as isomorphous to it "crystalline aluminium ethoxide") is actually an oxocomplex- $[Fe_5O_2(OEt)_{11}]_2 \cdot 3EtOH$ (Fig. 6.4) [1365, 1785]. The fragmentation products of such big molecules were detected in the mass-spectra [954]. The "true" $Fe(OEt)_3$ (an amorphous polymer getting on storage a structure of the $Al(OH)_3$ gibbsite type) was obtained on the action of titanium or niobium alkoxides on solutions of iron oxoethoxide [1365, 1366]. The following equilibrium

$$[FeO_x(OEt)_{3-2x}]_n + Ti(OEt)_4 \leftrightarrow Fe(OEt)_3\downarrow + TiO_x(OEt)_{4-2x}$$

is apparently shifted to the right due to the formation of a precipitate (and stability of titanium oxoethoxide complexes). The samples of "$Fe(OEt)_3$", obtained on evacuation of solutions, do contain supposedly both of the forms (oxo- and homoleptic), their ratio being dependent on the separation conditions — the solvent, concentration, temperature, time of storage, and so on. Therefore, the melting points and solubility in alcohol for different samples can vary in a rather broad range (80 to 120°C, 3 to 15% "$Fe(OEt)_3$") (see also Chapter 6).

The same picture observed for the samples of $[Fe(OPr^i)_3]_n$ is caused by the presence of aggregates with different molecular complexity (h = 2, 3, and ∞). The former 2 kinds are present in the overcooled brown melt; the large reddish-brown crystals formed from diluted solutions in alcohol consist of trimeric molecules (m. 117°C). The yellow powder obtained as residue after extraction of the more soluble forms with alcohol is a polymer (m. 157°C). On action of benzene its color darkens, the molecular complexity turns to be 3, and the melting point varies in the 120 to 150°C interval [1647]. The scheme of the occurring transformations is summarized in the Fig. 12.3.

The iron methoxide precipitates from the solutions in alcohol only as insoluble $Fe(OMe)_3 \cdot MeOH$, which easily loses solvating alcohol yielding $Fe(OR)_{2.6}O_{0.2}$ [1365, 1432]. It can therefore be supposed that the "$Fe(OMe)_3$" samples described in the literature [5-7, 867, 228], that were obtained by long-term drying *in vacuo*, did contain oxoligands.

The magnetic moments for the majority of $Fe(OR)_3$ are significantly lower than 5.9 μB (only-spin value for the high-spin d^5 configuration), which is connected with the existence of stable aggregates not only in the solid state but also in solutions. The results of magnetic measurements [5-7], and UV-vis and Mössbauer spectroscopic studies [1065] did not permit an unambiguous conclusion about the structure of the aggregates and the coordination of the metal atoms. The data of the later publications [1065] are in contradiction with the earlier proposed [7] model of the $Fe(OR)_3$ trimer structure with tetrahedrally coordinated iron atoms. The results of the X-ray structure determinations

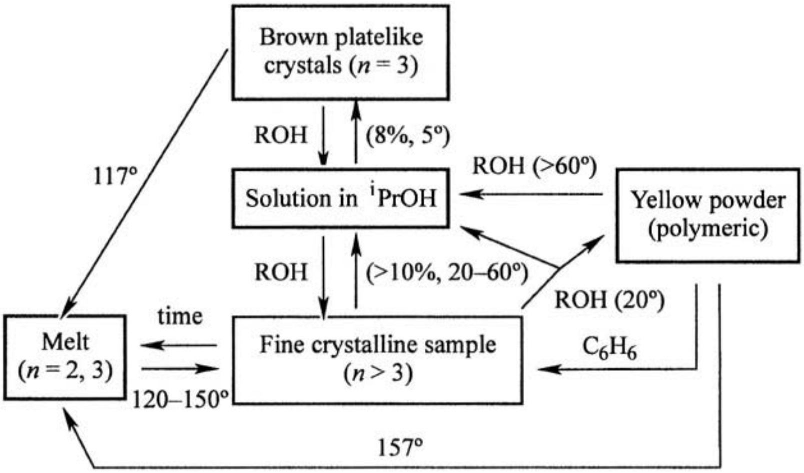


Fig. 12.3. Mutual transformations of the $[Fe(OPr^i)_3]_n$ species [1647]

indicate that in the majority of cases the atoms of iron (III) demonstrate octahedral coordination when surrounded not only by such ligands as OMe or OEt, — as in the structures of $FeO(OMe)_\infty$ [916], $[Fe_6O_2(OMe)_{12}[N(C_2H_4NH_2)_3]_2]^{2+}$ [1188], $Na_2Fe_6O(OMe)_{18}(MeOH)_6$ [724] (Fig.4.10 *a*), $[Fe(OEt)_3]_\infty$ [1366, 1365], but even in the case of more branched radicals like in $\{Fe_6O[MeC(OCH_2)_3]_6\}^{2-}$ [724], $[Fe(\eta^2\text{-}C_6H_4O_2\text{-}1,2)_3]^{3-}$ [42], $(FeO)_2(OCH_2\text{-})_2$ [1329]. The tetrahedral coordination is described only for $[Fe(OC_6HMe_4\text{-}2,3,4,6)_4]$ ~ [933] and $[LiFe(OCHBu^t_2)_4(HOCHBu^t_2)]$ [167]. In the pentamers, decanuclear $[Fe_5O_2(OEt)_{11}]_2{\cdot}3EtOH$ molecules consisting of 2 cyclic 6 iron atoms have trigonal bipyramidal coordination, 2 — tetrahedral and 2 — octahedral (Fig. 6.4) [1365, 1785].

The known $Fe(OAlk)_2$ are green polymeric substances. The diffuse reflectance spectrum of $Fe(OMe)_2$ indicates the octahedral coordination of iron atoms [6]. According to the X-ray powder data its structure is isomorphous to those of other divalent metals, — i.e., resembles that of $Fe(OH)_2$ ($Mg(OH)_2$ type) [1656]. The solubility is characteristic only of the derivatives of rather branched radicals — CH_2Ph, CPh_3 [114, 941] — or of the phenoxides solvated by such bulky ligand as Dipy [941]. The octahedral coordination is observed not only for the methoxide but quite unexpectedly for the derivatives 3,5-sustituted pyrocatechine containing 6 molecules of Py — $[Fe_2(1,2\text{-}O_2C_6H_2Bu^t_2\text{-}3,5)_2Py_6]$ [1475]. In the molecule of $[Fe_2(1,2\text{-}O_2C_6H_2Bu^t_2\text{-}3,5)_2Py_4]$ the coordination number of iron atoms is decreased to 5 (tetragonal pyramid) [1475]. The trigonal bipyramidal coordination is observed in the polymer structure of $[FeC_3H_5O_2(OH)]_\infty$ [1329]. The tetrahedral arrangement is observed only with such sterically crowded ligands as $OCPh_3$ or $OC_6H_2Bu^t_3\text{-}2,4,6$ [114].

The tetranuclear iron alkoxide halides (see Table 12.23) were supposed to possess the cubane-like or $Ti_4(OMe)_{16}$ type structures. The Mössbauer spectroscopy indicated the presence of 2 types of iron atom coordination in $Fe_4Hal_6(OMe)_6 \cdot 4MeOH$ and only one kind of octahedral arrangement in $FeCl(OR)_2$ and $Fe_4Hal_3(OMe)_9$. For the 2 latter products the layered structures of the $Al(OH)_3$ type were also proposed [867, 1065].

The data on the existence of solid bimetallic $MFe(OR)_4$ derivatives, M = Li, Na, K, R = Me, Et, Pr^i [1101, 817, 1432, 1031], and $Ba_nFe_m(OMe)_x(OH)_{2n+3m-x}$ [1432] were not confirmed in the studies of the solubility isotherms in the corresponding tricomponent systems. The formation of complexes of 1:1 and 1:3 composition was observed only in solutions in EtOH. The stability of the former (more stable ones) increases in the series K < Na < Li < Ba. The formation of glasses is observed between these two compositions. In the systems having polymeric $Fe(OMe)_3$ MeOH as component no complex formation is observed [1365]. It can be supposed that the crystalline sodium and barium alkoxoferrates described by Scholder [1432] are in fact oxoalkoxide complexes, such as, for example, $Na_2Fe_6O(OMe)_{18}(MeOH)_6$ [724]. The oligomeric $Fe(OPr^i)_3$ also forms bimetallic complexes (with 1:2 and 1:3 compositions) only in solution with, for example, "$Y(OPr^i)_3$" (the glass formation is observed in the solid phase between these compositions). The data on existence of a volatile liquid $Fe[Al(OPr^i)_4]_3$ [1493] were not confirmed either: both in the condensed and in the gas phases the samples were, with the aid of IR and mass-spectroscopy, shown to contain only the 2 homometallic alkoxides [1365]. The question of the existence of bi-, tri- and tetrametallic alkoxides of iron (III) and *3d*-transition metals is discussed in the Sections 12.12, 12.16, and so on.

In general, it can be concluded that the stability of alkoxoferrates (III) is much lower compared with the analogous complexes of other transition metals or aluminium. The structurally characterized compounds are limited to the

Table 12.23. Iron alkoxides

Chemical composition. Structure	Synt. route	Properties	Investig. methods	Ref.
Fe(II)				
$[Fe(OMe)_2]_\infty\downarrow$, $Mg(OH)_2$ struct. type, oct.$[MO_{6/3}]$	2,4, 5	grn. sld., ins. in org. solv., 200 (dec.), μ_{eff}=5.14	IR, magn.prop. prop., electr. sp., X-r	6, 7, 816, 941, 1005, 1656
$[Fe(OEt)_2]_\infty\downarrow$, $\cdot$Dipy	2	grn., 170 (dec.), pyrophor	IR	941, 1005
$Fe(OPr^i)_2\cdot$Dipy	4	grn. sld.., 185(dec.), s.in THF	IR	941
$[Fe(OBu^n)_2]_\infty\downarrow$	2	olive-grn. powd.	-	1005
$[Fe(OBu^t)_2]_\infty\downarrow$	2	olive-grn.sld., low s. in eth.	-	1005
$Fe(OCH_2Ph)_2\cdot$Dipy	4	grn.sld.,210(dec.), s.in THF	IR	941
$[Fe(OCPh_3)_2THF_2]$, oct . 2 equ. gr. are missing, 2 THF - equ., 2 OR- ax.	4	colrl. cr., s. in THF-hex., μ_{eff}=5.2	IR, ^{1}H,ESR, X -r magn.prop.	114
$Fe(OPh)_2\cdot$Dipy **$Fe(OC_6H_4R\text{-}4)_2\cdot$Dipy**, R=Me, Ph	4, 5	grn. powd., s. in THF	IR, ^{1}H	941
$[Fe(OC_6H_2Bu^t_3\text{-}2,4,6)_2]_2\cdot 0.5C_6H_{14}$ 2 trians. sharing $(\mu\text{-}OR)_2$ edge	4	yel. cr., 90 (m., dec.), s. in tol., μ_{eff}=3.4	IR, ^{1}H, ESR, magn.prop., X-r	114
$[Fe_2(1,2\text{-}O_2C_6H_2Bu^t_2\text{-}3,5)_2Py_6]$ 2 oct. sharing a$(\mu\text{-}OR)_2$ edge **$[Fe_2(1,2\text{-}O_2C_6H_2Bu^t_2\text{-}3,5)_2Py_4]$** 2 tetragon. pyr. sharing $(\mu\text{-}OR)_2$ edge	4	blk.-red cr., 137 (m.), 270 (dec.) blk.-red cr.	IR, ^{1}H, ESR, X-r	1475

$[Fe_4(1,2\text{-}O_2C_6H_2Bu^t_2\text{-}3,5)_4Py_6]$, cube, oct.$[FeN_2O_4]$, in RO_2 - 1 at. μ-O, 1 at. μ_3-O		or. cr., 147 (m.), s. in tol.		
$[FeC_3H_5O_2(OH)]_\infty$↓, layers of 5-membered cycles $[MO_2C_2]$, $[MO_5]$ - trig. bipyr.	4	cryst. plates, dec. by H_2O(t), μ_{eff}=5.00	IR, magn. prop., X-r	1501, 700, 1329
$FeAl_2O_2(OR)_4$, R= Pr^i, Bu^n, Bu^s,Bu^t [1244]				
Fe(III)				
$Fe(OMe)_3{\cdot}MeOH$↓ **«$Fe(OMe)_3$»** ↓	5, 6 6	light yel. cr., 60/vac → $Fe(OMe)_{2.6}O_{0.2}$ yel.-or. sld.,s. in ROH, bz., μ_{eff} = 5.86 (4.51); α=2.9	IR, electr. sp., magn. prop., X-r Mössb.	1365, 1432 6, 7, 5, 228, 867, 1065
$[Fe_6(\mu_4\text{-}O)_2(\mu\text{-}OMe)_8(OMe)_4[N(C_2H_4NH_2)_3]_2]^{2+}(CF_3SO_3)^-_2{\cdot}2MeOH$, cation - 2 tetrah. $[Fe_4]$ sharing $[Fe_2]$ edge	3, 4	or. cr., s. in ROH, Dmfa, μ_{eff}=8.61	magn. prop., Mössb., X-r	1188
$FeO(OMe)$↓, layered struc. of CdI_2 type (struc. analog of γ-FeO(OH)	5	red-vlt. cr., 290 (dec.), stab. to hydrol.	IR, TGA, X-r, Mössb.	916
$[Fe(OEt)_3]_\infty$↓, struc. type of $Al(OH)_3$ - gibbsite, oct.$[MO_{6/2}]$	-	light yel. powd., invol., 185 (m., dec.)	IR, electr.sp., X-r powd.	1366
↑$Ti(OEt)_4$ $[\text{-}TiO_n(OR)_{4-2n}]$ **$[Fe_5O_2(OEt)_{11}]_2{\cdot}3EtOH$ ("$Fe(OEt)_3$")** struct. analog of $[Al_5O_2(OEt)_{11}]_2$	5	brn. cr., s. in bz., hex., in ROH(3%), 100-120 (m), invol., μ_{eff} =4.37; α=2.9(bz.)	IR, cryosc., m-s, X-r, X-r powd.	7,5, 228, 1101, 1365, 1577, 1785

$[Fe_9O_3(OEt)_{21}]\cdot EtOH$, 2 five-member rings connected by the common Fe atom and μ_3-O and μ-OR gr.	5	brn. cr., 90 (m.), 200/0.01 (b.), α=1/3 (bz.), μ_{eff}=13.4, ferromagn.	cryosc., magn. prop., X-r	1680a
$Fe(OPr^n)_3$	5, 6	brn. sld., 162/0.1 (subl.) (?), α=3	ebul.	228
$Fe(OPr^i)_3$	5	red wax, 88-100(m.), s. in ROH 1-15%,α=2(s.), 3(m-s), μ_{eff} =3.55 ↑↓ teim; ROH(20°), yel. powd., 157 (m.), 170(dec.), ins. in ROH, s. in hc., THF- ∞, μ_{eff} = 4.40	IR, electr. sp., magn. prop., ebul., m-s, X-r powd.	228, 1647
$Fe(OBu^n)_3$	5, 6	red liq., s. in hc., ROH, invol.; μ_{eff} = 4.35; α=3	IR, electr. sp., cryosc.	7, 5, 228, 1365, 1466
$Fe(OBu^i)_3$, $Fe(OBu^s)_3$, $Fe(OBu^t)_3$	5, 6	brn.sol.,173/, 159/, 136/ 0.1 (subl.), α=3, 2, 1.5	ebul.	228, 1466
$Fe(OC_5H_{11}{}^n)_3$	5, 6	red visc. liq., 178/0.1(b.?); α=3	ebul.	228, 1466
$Fe(OC_2H_4Pr^i)_3$ $Fe(OCH_2CHMeEt)_3$ $Fe(OC_5H_{11}{}^{neo})_3$ $Fe(OCHMePr^n)_3$	5 , 6	brn. sld., 200/, 178/, 159/, 165/0.1 (subl.); α=3,3,2, 2	ebul.	228
$Fe(OCHMePr^i)_3$, $Fe(OCHEt_2)_3$, $Fe(OC_5H_{11}{}^t)_3$	6	brn. sld., 162/, 163/, 131/ 0.1 (subl.); α=2, 2, 1.5	ebul.	228
$Fe(OCMeEt_2)_3$, $Fe(OCMe_2Pr^i)_3$, $Fe(OCEt_3)_3$	6	brn. visc. liq.,135/0.1(b.); α=1	ebul.	228

$Fe(OPh)_3$	6	bl.-blk. sld., ins. in bz.	-	1466
$Fe(OAd\text{-}1)_3$ $Fe(OCH_2Ad\text{-}1)_3$, Ad= $C_{10}H_{15}$	4	light yel. cr., μ_{eff} =4.69, α=2	IR, ^1H, ESR, m-s	166
$Fe(OCH_2CF_3)_3$ **·2L,** L=Py, Hmpa,Dmfa, Dmso, RCOOR'	5	brn.sld.,>260(m.),μ_{eff}=2.9, μ_{eff}=4.0-5.8, α=2	IR, Mössb., electr.sp.,magn..	317
$Fe(OSiMe_3)_3$	5	grn cr., 179 (m.,dec.), 130/1 (subl.) , α=2	IR, ^1H, cryosc.	1418
$Fe(RO_2\text{-}1,2)(RO_2H)$Tmeda, R=$C_6F_4$	4	blk.sld., s. in ROH, μ_{eff}=6	IR, ^{19}F, Mössb.	1044
$Fe(OC_2H_4OMe)_3$	2, 5	red liq., invol.	IR	1514, 1652
$(FeO)_2(OCH_2\text{-})_2\downarrow$, isostr. with FeO(OMe)	5	red-vlt. cr., stab. to hydrol.	IR, Mössb., X-r	916
$Fe_5(O_3C_3H_5)_3\downarrow$	4	grn. cr., H_2O, μ_{eff} = 4.37	IR, magn prop.	1329
$Fe_4Hal_3(OMe)_9\downarrow$, Hal=Cl, Br	yel. slds., μ_{eff}=4.1; 4.2		IR, Mössb.	867, 1065
$Fe_4Hal_6(OMe)_6$·4MeOH= $[FeHal_2(ROH)_4]^+[FeCl_4]^-$ (?), Hal=Cl, Br	or.(Cl), red (Br) cr., s. in MeCN, μ_{eff}=4.4; 4.7; α=1		IR, Mössb., magn. prop.	867, 1065
$[FeCl(OR)_2]_\infty$, R=Me, Et	grn. slds., 300(dec.), μ_{eff}=3.67		IR, Mössb., X-r	636
$FeHal(OPr^i)_2$, $FeHal_2(OPr^i)$, ·0.5·AcOPr^i	light brn. slds., ins. in bz.		-	1466
$FeHal(OBu^t)_2$, Hal=Cl,Br **$FeCl_2(OBu^t)_8$**	reddish-brn. slds.		-	1466
$FeCl_n(OCH_2CCl_3)_{3\text{-}n}$, n=1, 2 **·L,** L=Diox, Dmso,Dipy/2 etc.	red-brn. visc. liq. ,μ_{eff}=3.47 brn.sld.,>100 (m.), μ_{eff}=4.5-5.5		IR, ^1H, m-s sp., magn. prop.	317
$[Na_2Fe_6O(OMe)_{18}(MeOH)_6]$, struct. analog of $[W_6O_{19}]$, 2 oct. Na- ax.	yel.-grn. cr., s. in MeOH		X-r	724

$[LiFe(OCHBu^t_2)_4(HOCHBu^t_2)]$, tetrah. for Fe and trig. pyr. for Li sharing $(OR)_2$ edge	yel. cr.,144 (m.), s. in eth., in m-s $Fe(OR)_3^+$	IR, electr.sp., ESR, m-s, X-r	167
$M_3Fe\{[OC(CF_3)_2]_2\}_3$, M=K, Cs, Ag	μ_{eff}=6.0 (K)	magn. prop.	26
$[Me_4N]^+_2\{Fe_6O[MeC(OCH_2)_3]_6\}^{2-}\cdot 4MeOH$ in anion – oct. $[M_6]$, struc. analog of $[W_6O_{19}]^{2-}$	brn. or yel. cr., s. in MeOH, 20° (dec.)	X-r	724
$[Et_4N]^+[Fe(OC_6HMe_4\text{-}2,3,4,6)_4]^-$, anion - tetrah.	red-or. cr., s. in EtOH	X-r	933
$M[Fe(OSiMe_3)_4]$, M=Li, Na↓, K↓ **$[SbMe_4][Fe(OSiMe_3)_4]$,** anion- tetrah.	yel. cr., 200 (dec.), slowly → Fe_2O_3; 193 (m.,subl.)	IR, ^1H, X-r	1418, 1738
$M[Fe(\eta^2\text{-}C_6H_4O_2\text{-}1,2)_3]^{3-}\cdot 1.5H_2O$, M=K, $[C_5H_{12}N]_3^+$ anion–oct. of 3 cycles	dark red-brn. cr.	X-r	42, 1336
$Al_2FeO_2(OR)_4$, R=Pr^i, Bu^n, Bu^s, Bu^t	red liq., invol.,s.in hc., α=1-2	^{13}C, electr., m-s	1244
$Ba_2[Fe(OH)(C_3H_5O_3)_2]\cdot 2H_2O$, **$BaFe[C_6H_6O_5(OH)]\cdot nH_2O$** (derivative of glucose, mannose)	yel. cr.	-	1596
$[Bu^t_3PH]^+_2[Fe_2Cl_6(\mu\text{-}OEt)_2]^{2-}$ anion - 2 trig. bipyr. sharing $(\mu\text{-}OR)_2$ edge	yel.-or. cr., μ_{eff}=4.07	IR, electr. sp., magn. prop., X-r	1715

derivatives of sterically crowded radicals such as $LiFe(OCHBu^t_2)_4(HOCHBu^t_2)$ [167], $K_3Fe\{[OC(CF_3)_2]_2\}_3$ [26], and $[Et_4N][Fe(OC_6HMe_4\text{-}2,3,4,6)_4]$ [933].

Among the heteroleptic derivatives of special interest is the decanuclear cyclic molecule of $[Fe(\mu\text{-}OMe)_2(ClCH_2COO)]_{10}$ — the "iron ring" with the effective diameter of ~12 Å. All the 10 iron atoms are situated in the same plane and connected with each other by pairs of $(OMe)_2$-bridges [1554]. Hydrolysis of $Fe(OR)_3$ and application in sol-gel method discussed in Chapters 9 and 10.

The traditional area of application of $Fe(OR)_3$ lies in polymer chemistry, where they are used as components of catalytical compositions for, for example, Ziegler reactions [837], stereospecific polymerization of epoxides [93], and, in combination with BF_3 for olefine polymerization [836, 1268]. The bimetallic oxocomplex $FeAl_2O_2(OBu^n)_4$ [1244] was in addition to high catalytic activity in polymerization ring-opening reactions, found also to be a carrier of molecular oxygen (absorbing it at 20 and releasing at 150°C).

They are also used for vulcanization of organosilicon cauchucs, solidifying agents for epoxy resins, additives to pigments, and so on. [715].

12.23. Cobalt and nickel alkoxides

The first attempts to prepare cobalt and nickel ethoxides were reported in 1936 by Meerwein [1102] and Kandelaki [875]. Application of NaOR in the exchange reactions could not, however lead to the obtaining of the pure products of purpose as they were insoluble in the parent alcohol. Application of LiOR for this purpose permitted Adams *et al.* in 1966 to obtain the individual $M(OMe)_2$ — derivatives of 3*d*-transition elements in the series from Cr to Cu [6]. In the 1980s Mehrotra *et al.* have described the homologous series of $Ni(OR)_2$ — from methoxide to *t*-hexyloxide [99], and also $Co(OR)_2$, where R = Me, Et, Pr^i [1108]. On the alkoxylation of $CoH(N_2)(PPh_3)_3$ by esters, phenol, or fluorinated ketones, Hayashi *et al.* [720] have obtained a series of tetrahedral $[Co^I(OR)(PPh_3)_3]$ complexes.

12.23.1. Synthesis

The major route to insoluble $M(OAlk)_2$ is provided by the metathesis reaction of MCl_2 with LiOR (method 5). To increase the solubility of $NiCl_2$ in *s*-

and *t*-ROH the addition of pyridine was proposed. The named reactions are complicated by the formation of stable mono- and bimetallic alkoxide chlorides. The latter can be destroyed only by the dilution of the reaction solutions and prolonged reflux of the products with them. The same problem complicates the preparation of these alkoxides by the anodic oxidation of metals in alcohols (method 2) as alkali halides are applied as electrolytes. The latter method was applied for the preparation of the first representatives of both series and also $\mathbf{M(OC_2H_4OMe)_2}$ [1005, 1367, 1652]. The alcohol interchange reactions starting from $\mathbf{Ni(OPr^i)_2}$ led to hexylate and octylate and also derivatives of unsaturated alcohols (method 6). The preparation of the derivatives of sterically hindered radicals is usually achieved by alcoholysis of silylamides [167, 1484, 1235]; the acetates are used as initial reagents in the preparation of phenoxides [1095] (method 4).

12.23.2. Properties

All the known $\mathbf{M(OAlk)_2}$ derivatives of both metals are insoluble microcrystalline or amorphous powders. The compounds of Co have a reddish violet color. In the $\mathbf{Ni(OR)_2}$ series the color changes from green for the methoxide to light-violet for ethoxide and dark violet for the isopropoxide [1367, 1005]. $\mathbf{Ni(OR^s)_2}$ are violet, and $\mathbf{Ni(OR^t)_2}$ are light blue powders turning rapidly green if left in the open air [99]. The samples of methoxides are single phase and have a polymeric structure of brucite type containing octahedrally coordinated Ni-atoms. The samples of both ethoxide and *n*-propoxide contain metal atoms (according to the diffuse reflactance spectra) in 2 different coordinations — octahedral and tetrahedral (the latter, supposedly, is characteristic of the amorphous part of the samples) — and in case of $\mathbf{Ni(OPr^i)_2}$ only in the tetrahedral coordination. At the same time, all the homologs obtained by metathesis with $\mathbf{NiCl_2}$ and, apparently, containing the admixture of solid hydrolysis products are green colored [99]. Their spectra contain only the bands corresponding to octahedral coordination of nickel (the values of the magnetic moments do not permit the coordinations to be identified unambigously). The derivatives prepared by this route and also by alcohol interchange are, therefore, taken in Table 12.24 in citation signs.

A special role in the chemistry of nickel and cobalt alkoxide derivatives is played by the poorly soluble methoxide halids studied in detail by the group of Winter [964, 865]. According to the diffuse reflectance spectra, the coordination of the metal atoms in CoCl(OMe) and $CoBr(OMe)\cdot 2MeOH$ appears to be octahedral and in CoHal(OMe), where Hal = Br, I, — tetrahedral. The change in coordination on desolvation of the methoxide bromide is testified by the color change from pink to bright blue. It was supposed that the structures of the Ni-complexes contain cubane-like $[Ni_4(OMe)_4]$ aggregates (with octahedrally coordinated Ni atoms), which are connected into a tridimensional net by the extra bridging ligands. In the case of NiCl(OMe) the bridging should occur via Cl-atoms. The magnetic interaction via them is minor, and the compound is ferromagnetic. The magnetic isolation of cubanes decreases in the OR, Br, I series, and the antiferromagnetic interaction increases. The energy splitting of the orbitals (10 *Dq*) increases on the replacement for Cl with OMe (from 7900 to $8500\ cm^{-1}$ for $Ni(OMe)_2$).

The formation of bimetallic complexes is rarely studied for the derivatives of these 2 metals. The structurally characterized derivatives are limited to 2 derivatives of rather branched radicals—$Li(THF)_3Co(\mu\text{-}Cl)(OCBu^t_3)_2]$ [1235], $M_2Ni\{[OC(CF_3)_2]_2\}_2$ [26, 427] and a series of ethoxoantimonate complexes: $Ni_2Sb_4(OEt)_{16}$, $Ni_5Sb_3O_2(OEt)_{15}(EtOH)_4$, $Ni_6Sb_4O_4(OEt)_{16}(EtOH)_4$, and $Ni_6Sb_{14}O_{18}(OEt)_{18}(EtOH)_2$ [140, 1733].

Rather high stability is observed for the nickel and cobalt derivatives containing the $[M_4(\mu_3\text{-}OMe)_4]$ cubane-like core and heteroligands such as acac, OAr, OC_6H_4CHO, $[M(CO)_n]$, and so on [1771, 1097, 698, 642, 276].

12.23.3. Application

The hydrolisis of mixed solutions of Ni and Ti 2-ethoxyethoxide in ROH with subsequent thermal treatment of the dried product at 500 to 700°C was reported as a route to $NiTiO_3$ [1425].

Cobalt glycerate prepared by the reaction of acetate with glycerine at 160°C (in contrast to the samples obtained from water solutions at 20°C) and possessing a layered structure and hydrophobic properties was proposed as a lubricant in alternative to graphite and talcum [700]. The alkoxides of both metals are used as coloring additives to titanium pigments. The insoluble $Ni(OR)_2$ were proposed as additives to the vanadium-containing fuels. They react with V_2O_5 forming nickel vanadate and thus hinder the corrosion [715]. A patent on cobaltocene preparation via reaction of $Co(OEt)_2$ with CpH was registered [1226].

Table 12.24. Cobalt and nickel alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
Co(I)				
$[Co(OPh)(PPh_3)_3]$, tetrah.	4	brn.cr.,s.in tol.,178(m.)	IR, X-r	720
$Co(OCH_2CF_3)(PPh_3)_3$		158 (m.), μ_{eff} =3.0	IR, magn. prop.	720
$Co[OCH(OEt)CF_3](PPh_3)_3$		136 (m.), μ_{eff} =2.6	-	720
$Co(OR)(PPh_3)_x$, $Co(OR)H(PPh_3)_x$, $R=CH(CF_3)_2$, $CHPhCF_3$, $CMe(CF_3)_2$	7	-	^1H, ^{31}P {^1H}	720
Co(II)				
$[Co(OMe)_2]_\infty\downarrow$ isostr. $Ni(OMe)_2$	2, 5	purple (vlt.-bl.) cr., μ_{eff} =5.46	IR, magn. prop., electr. sp., X-r	6, 7, 1108, 1005, 1656
$Co(OEt)_2\downarrow$	2, 5	bl.-vlt. cr.; t→MeCHO+Co	electr. sp.	1005, 1108
$Co(OPr^i)_2\downarrow$	5	purple powd.	electr. sp.	1108
$Co(OBu^n)_2$	2	vlt.sld., low s. in EtOH	-	1005
$Co(OBu^t)_2$	2	vlt.sld., s.in THF	-	1005
$Co(OCHBu^t_2)_2$	4	bl.sld, 130(dec.), α=2-1	IR, electr.sp..	167
$[Co(OCPh_3)_2]_2\cdot{}^nC_6H_{14}$ 2 trian. sharing (μ-OR)$_2$ side **$[Co(OCPh_3)_2THF_2]$**, tetrah.	4	grn. cr., 267 (m.), s. in hex. red cr.,139(m.), s.in tol.	IR, ^1H, electr. sp., X-r	1484

$\{Co[OC(C_6H_{11})_3]_2\}_2 \cdot MeOH \cdot 1/2C_6H_{12}$, THF, 2 trian. sharing $(\mu\text{-}OR)_2$ side	4	grn. cr., 210 (m.), s. in THF, tol.	IR, ^1H, electr. sp., X-r	1484
$Co(OAd\text{-}1)_2$, $Co(OCH_2Ad\text{-}1)_2$, (1) Ad=adamantyl $(C_{10}H_{15})$	4	purple cr., low s. in org. solv., [μ_{eff}=5.09, α=2 **(1)**	IR, ^1H, ESR, magn..prop., m-s	166
$Co[OC(C_6H_5Me\text{-}4)_3]_2THF_2$	4	grn.cr., 105(m.), s. in tol.	electr.sp.	1484
$Co(OPh)_2$	2, 4	vlt.powd., s.in PhOH	-	1005, 1095
$Co(OC_6H_4Me\text{-}4)_2$	4	deep bl. cr.	-	1095
$Co(OCH_2CCl_3)_2 \cdot L$, L=THF, Diox	5	-	IR, ^1H, magn. prop	316
$[Co(OSiPh_3)_2THF]_2$ 2 tetrah. sharing $(\mu\text{-}OR)_2$ edge	4	purpl cr., 194(m.), s. in tol.	IR, ^1H, electr. sp., X-r	1484
$Co(OC_2H_4OMe)_{1.9}Br_{0.1}$	2	brn. (vlt.) amor. sld., s. in eth., α=3-4 (bz.)	IR	268, 1652
$Co(OC_6H_4OMe\text{-}4)_2$	4	purple powd.	-	1095
$[Co(\eta^2\text{-}1,2\text{-}O_2C_6H_2Bu^t_2\text{-}3,5)]_4 \cdot 5.5THF$ cube, 2 oct.$[CoO_6]$ and 2 trig. bipyr. $[CoO_5]$	4	grn. cr., 250 (m., dec.), s. in THF, tol.	IR, ^1H, ESR, X-r	1235
$[CoC_3H_5O_2(OH)]\ \infty\downarrow$, polymer layers of $[MO_2C_2]$ 5-membered rings, $[MO_5]$ - trig. bipyr.	4	red cr., dec. by H_2O (t), μ_{eff} =3.94	IR, magn. prop., X-r, X-r-powder	700, 1329, 1501
$CoCl(OMe)\downarrow$, $CoBr(OMe)$, $\cdot 2MeOH$; $CoI(OMe)$		bl., bl., red, vlt. cr., μ_{eff} =4.7-5.1	electr.sp., magn. prop.	865
$LiCo(OCHBu^t_2)_3$ (?)		purple sld., s. in petrol.	-	167
$[Li(THF)_3Co(\mu\text{-}Cl)(OCBu^t_3)_2]$ tetrah. Li and trian Co sharing a $(\mu\text{-}Cl)$ vertex		bl. cr., s. in THF, eth.	X-r	1235

$CoAl_2O_2(OR)_4$, R= Pr^i, Bu^n [Ouhadi **15**, 865; **95**, 1973]; **$[Co_2M_2(OBu^t)_8]$**, M=Ge,Sn [1683]				
Ni				
$[Ni(OMe)_2]_\infty\downarrow$, $Mg(OH)_2$ type - intermitting [ROMOR]... layers, $[MO_{6/3}]$-oct., $[OM_3]$- trig. pyr.	2, 5	yel.-grn. powd., ins. in org. solv., μ_{eff} =3.38	IR,electr.sp., magn. prop. X-r powd.	6, 7, 99, 1108,1367 1410
$Ni(OMe)_2[\eta^2-(C_6H_{11}^c)_2PCH_2-]_2$	5	red sld.	IR , ^1H,^{31}P	1379
$[Ni(OEt)_2]_\infty\downarrow$, isostr. to $Ni(OMe)_2$	2, 6	vlt.sld., μ_{eff} =3.38; t→MeCHO+Ni	IR,electr.sp., X-r powd.	99, 1005, 1102,1108 1367,1410
$[Ni(OPr^n)_2]_\infty\downarrow$, isostr. to $Ni(OMe)_2$ **$[Ni(OPr^i)_2]_\infty\downarrow$**	2, 5	light vlt. sld. dark vlt. powd., μ_{eff}=3.6	"	99, 1108, 1367
$[Ni(OBu^n)_2]\downarrow$	2, 5, 6	vlt. sld., μ_{eff}=3.38	IR, magn.prop.	99, 1005, 1108
$Ni(OBu^s)_2\downarrow$	5	vlt. sld., μ_{eff}=3.70	"	99, 1108
$Ni(OBu^t)_2\downarrow$	2, 5	vlt. sld., μ_{eff}= 3.61	"	1005,1108
"$Ni(OC_5H_{11}^t)_2$" ↓	5	bl. sld.,μ_{eff} =3.67	"	99, 1108
"$Ni(OC_6H_{13}^n)_2$" ↓	6	light grn. sld.	"	99, 1108
$Ni(OC_6H_{11}^c)_2 \cdot 1/2$ Dmfa↓	2	500(dec.)	-	1410
"$Ni(OCMeEtPr)_2$" ↓	5	bl. sld.	IR, magn. prop.	99
"$Ni(OC_8H_{17}^n)_2$" ↓	6	light grn.	"	99
$Ni(\eta^2-OC_6H_4PPh_2)_2$	4	or. cr., >300(m.)	IR, ^1H, ^{31}P, m-s	1334
***trans*-$[NiH(OPh)(PR_3)_2 \cdot PhOH$**, R=$PhCH_2$, $C_6H_{11}^c$, Pr^i, square planar	5	or. cr., 65 (m.), s. in tol., C_5H_{12} (R=Pr^i, or. oil)	IR, ^1H, ^{31}P, X-r	1456
"$Ni(OCH_2CH=CHR_2)_2$"↓R=H, Ph	6	brn.-yel. powd.	IR, magn. prop	99

$Ni[OC(CF_3)_2]_2L_2$ $L=PR_3$, Tmeda/2, Dipy/2, Phen/2	4	or. cr., 132-208 (m.), diamagn.	^{19}F,electr.sp., magn. prop.	26, 195, 427
$Ni[OC(CF_3)(C_6F_5)]_2$·Tmeda	4	or. cr., opt. isomers	^{19}F, electr.sp.	427
$Ni[OC(CF_3)_2OC(CF_3)_2O]$·Am, Am = Phen, Dipy, Tmeda	5	**Phen**: red cr., 167(m.), s. inCH_2Cl_2	-	195
$Ni(OMe)(OCH_2CCl_3)$	6	cr., $\mu_{eff}=4.08$	IR,magn.prop.	318
$Ni(OC_2H_4OMe)_{1.9}Br_{0.1}$	2	brn. sld., s.in eth., $\alpha=3\text{-}4$	IR, electr.sp.,	268,1652
$Ni(OC_2H_4OEt)_2$	5	yel. gl.,s. in hex., eth, ROH, $\alpha=10$, $\mu_{eff}=3.66$	magn. prop.	1425
$[Ni(\eta^2,\mu_3\text{-}OC_2H_4O)_2]_\infty$, $Ca(OH)_2$ struct. type, layered struc. with cycles $[NiO_2C_2]$ **$[Ni(\eta^2,\mu_3\text{-}OC_2H_4OH)_{0.8}(OH)_{1.2}]$** ∞	3	grey sld.	IR, X-r X-r-powd.	1568
$Ni(C_6F_4O_2\text{-}1,2)L_2$, $L=PEt_3$ *etc.*	4	brn.cr., diamagn.	IR, ^{19}F, electr.sp.	1044
$NiHal(OMe)\downarrow$ (ferromagn.) **$NiCl(OMe)\cdot(1\text{-}2)MeOH\downarrow$,** **$Ni_3Hal_2(OMe)_4\downarrow$; $Ni_3Hal(OMe)_5\downarrow$**,Hal=Cl,Br, I		cr., grn. (Cl-Br), red (I), $\mu_{eff}=3.0\text{-}3.5$;	IR, electr.sp., magn. prop.	99, 964
$NiCl(OR)$, R=Et, Pr^i, Bu^n, $C_6H_{13}{}^n$		cr. powds, yel., yel., brn., light grn., $\mu_{eff}=3.2\text{-}3.37$	IR, electr.sp., magn. prop.	99
$M_2Ni\{[OC(CF_3)_2]_2\}_2$, M=K, Cs		cr., diamagn.	^{19}F, magn. prop.	26, 427
$Na_3NiI_2[OSi(OBu^t)_3]_3$, cube $[Na_3Ni(\mu_3\text{-}O)_4]$		bl. cr., slowly dec.	IR, ESR, X-r	1097
$Na_2[Ni(\eta^2\text{-}C_6H_4O_2\text{-}1,2)_2]\cdot 2Dmfa$, anion - square **$Na_2[Ni(\eta^2\text{-}C_6H_4O_2\text{-}1,2)_2(H_2O)_2]\cdot 12H_2O$,** anion oct., *trans-*		pink cr., diamagn. light grn., $\mu_{eff}=2.93$	^1H, ^{13}C, electr. sp., X-r	257
$Ni[Al(OBu^t)_4]_2$ [1691]; **$[Ni_2Sn_2(OBu^t)_8]$**, [1683] **$Ni_2Sb_4(OEt)_{16}$, $Ni_5Sb_3O_2(OEt)_{15}(EtOH)_4$, $Ni_6Sb_4O_4(OEt)_{16}(EtOH)_4$, $Ni_6Sb_{14}O_{18}(OEt)_{18}(EtOH)_2$** [1733]				

12.24. Alkoxide derivatives of platinum metals

The most important feature of the chemistry of platinum group elements in general lies in their high electronegativity associated with a big number of electrons in the outer shell that leads to a relative reluctance to form derivatives in the higher oxidation states and a need in **π-acceptor** ligands for the formation of stable complexes. As the alkoxogroups are known to be strong **π-donors,** it appears to be practically impossible to prepare corresponding homoleptic derivatives for these elements. The complexes described in the literature do usually contain the carbonyl, phosphine, or unsaturated hydrocarbon ligands necessary for their stabilization. The only exception is the chemistry of osmium (VI), where the high oxidation state is responsible for the central atoms affinity to **π-donors** such as oxide and alkoxide ligands. A good description of the chemistry of the alkoxide derivatives of platinum metals can be found in the review [1115].

12.24.1. Synthesis

The most usual synthetic routes to the derivatives of platinum group metals are the exchange reactions of the complexes containing halide ligands with alkali metal alkoxides (method 5), alcoholysis of the same kind derivatives (usually by phenols, method 4), alcoholysis of hydroxide complexes (method 3), and redox reactions — reduction of chlorides or OsO_4 in alcohol media (method 7) (Table 12.25).

12.24.2. Properties

The molecular derivatives of platinum group metals are usually rather well soluble in organic solvents and volatile in vacuum. At normal pressure they demonstrate very low thermal stability and easily decompose producing fine metal powders. This decomposition occurs more easily for the derivatives of branched radicals as it is based on a **β-hydrogen** elimination process. An important feature of the chemical behavior of these alkoxide complexes is their rather high stability to hydrolysis. Some derivatives can even form outer sphere hydrates when reacted with water in organic solvents. This stability to hydrolysis can at least partially be due to the kinetic inertness of the complexes of this group.

12.24.3. Application

As many other derivatives of the platinum metals the alkoxide ones find their application first and foremost as catalysts in different processes. Thus indium complexes ***trans*-$\mathrm{ROIr(CO)(PPh_3)_2}$ ($\mathrm{R = Me, Pr^i, Pr^n, Bu^t}$)** were reported to catalyze transformation of aldehydes into esters in Tishchenko reaction, carbonylation of alcohols [245], and so on. Rhodium complexes were used in hydrogen or even methyl group transfer, such as [895]

$$\mathrm{[(COD)Rh(OMe)]_2 + 2HCOOMe \longrightarrow [(COD)Rh(HCOO)]_2 + 2Me_2O}$$

Ruthenium derivatives were found to be catalytically active in dehydrogenation of cyclic alkenes [333].

Table 12.25. Platinum Group alkoxides

Chemical composition. Structure	Synth. route	Properties	Investig. methods	Ref.
Ru (I)				
$[(PPh_3)_xRu(OR)]$, $[Ru(OR)H(PPh_3)_x]$, R=$CH(CF_3)_2$, $CHPhCF_3$	4, 6	$+H_2+EtOH \rightarrow$ $CF_3PhCHOH$ (yield~100%)	IR, ^1H, $^{31}P\{^1H\}$	720
Ru(II)				
$[Ru(OR)Dipy_2]_2^{2+}[PF_6]^-_2$, R=Me,Et, cation - 2 oct. sharing a common (μ-OR)$_2$ edge	5	blk. cr., s. in MeCN, ROH (purple)	^1H, m-s, el.-chem. prop., X-r	101
$(Me_3P)_4RuH(OR)$, R= Ph, C_6H_4Me	4	yel. sld., s. in hc.	IR, NMR	1240
$(Ph_3P)_2RuH(OPh)(PhOH)_2$	4	yel. sld., s. in hc.	IR, NMR	405
$[L_2Ru_2(\mu\text{-}OR)_3]X$, R= Me, Et, Ph; X= BPh_4, PF_6; L= C_6H_6, C_6Me_6, $C_{16}H_{16}$;	3, 5	or. cr., s. in MeCN	IR, NMR	67, 529, 666, 918
Ru(III)				
***trans*-$[Ru(OR)ClPy_4]X$**, cation- oct., R=Me, Et, Pr^n,Pr^i, X= PF_6, ClO_4	3	red cr., s. in ROH, μ_{eff}=2.15	IR, ^{18}O, electr. sp., magn. prop., X-r	55
Os(IV)				

$[Os(Dipy)(O_2R)_2]$, R= C_6H_2-3,5-Bu^t_2, C_6Cl_4, oct.	4	purple cr., s. in hc., MeOH	IR, UV, X-r	148
$[OsBr_3(OMe)(PPh_3)_2]$, oct.	4	red cr., s. in MeOH	X-r	753
Os(VI)				
$Os(1,2\text{-}O_2Ar)_3$, Ar= C_6H_4, $C_6H_3Bu^t$-4, $C_6H_3C_8H_{16}{}^t$-4, $C_6H_2Bu^t_2$-3,5	7	dark bl. cr., air stab., s. in hc., H_2O, diamagn., α=1	IR,Raman,^1H, ^{13}C, m-s, magn. prop.	1212
$OsO(O_2R)_2$, R= C_2H_4 **(1)**, C_2Me_4 **(2)**, $(C_6H_{10}{}^c)_2$ **(3)** **$[OsO(O_2(C_6H_{10}{}^c)_2)_2(C_6H_{10}{}^cOH)_2(Ph_3PO)]$**, 2 5-vertex polyhedron sharing a $(\mu\text{-}OR)_2$ edge	7	blk. cr., s. in hex., diamagn., α=1 **(1, 2)**, 2 **(3)**	IR, ^2H, ^{18}O, cryosc., X-r	406, 1006
$OsO(1,2\text{-}O_2C_6H_3R\text{-}4)_2 \cdot nH_2O$, R= Me, Bu^t	7	bl. slds. , s. in Me_2CO	IR, Raman	1212
$[OsO_2(1,2\text{-}O_2R)]_2$, R= C_2H_4, C_3H_6, C_2Me_3Et, $C_5H_8{}^c$, $C_6H_8{}^c$, $C_{10}H_{16}$, **C_2Me_4** (=$[OsO(\eta^2\text{-}O_2R)(\mu\text{-}O)]_2$, 2 tetragon pyr. sharing a $(\mu\text{-}O)_2$ edge)	7	brn. or blk. slds., s. in CH_2Cl_2, diamagn., α=1, 2	IR, Raman, ^2H, ^{18}O, magn. prop., X-r	426, 406, 1212, 1299
***trans*-$[OsO_2(1,2\text{-}O_2R)Py_2] \cdot nH_2O\downarrow$**, R= C_2H_4, C_3H_6, C_2Me_4, $C_5H_8{}^c$	7	brn sld., s. in hc.	IR, ^2H, ^{18}O, cryosc.	426, 406
***trans*-$[OsO_2(OC_2H_4OH)_2Py_2]$** **$[OsO_2(OC_2H_4OH)_2Py_2]$**	7	brn sld., s. in hc., diamagn.	IR, ^2H, ^{18}O	406
$K_2[OsO_2(OMe)_4]$-*trans*, $KOsO_2(OMe)_3$		red slds., s. in MeOH	IR	426,1212

$M_2[OsO_2(1,2\text{-}O_2R)_2]\cdot nH_2O$, M=K, $[PPh_4]$; R= $C_6H_{10}^c$, C_6H_4, $C_6H_2Me_2$, $C_6H_3Bu^t$-4, $C_6H_3C_8H_{16}^t$-4, $C_6H_2Bu^t_2$-3,5, gr. $[OsO_2]$- *trans*		red -brn. or bl. slds., α=1	IR, Raman	426, 1212
Rh(I)				
$[(PMe_3)_3Rh(OR)]$, R=4-MeC_6H_4, CH_2CF_3, $CH(CF_3)_2$, 4-$CF_3C_6H_4$, square; **$\cdot ROH$**	4	yel. or red cr., s. in hc.; $+H_2 \rightarrow$ ROH (yield 90%)	IR, ^1H, $^{31}P\{^1H\}$, X-r	720, 894
$[(\eta\text{-}R_2P(CH_2)_3PR_2)Rh(OR)]_2$, R= Ph, $C_6H_{11}^c$, 2 squares sharing $(\mu\text{-}OR)_2$ edge	ligand exch.	red brn.cr., s. in hc.	IR, NMR, X-r	674
$[(COD)Rh(\mu\text{-}OR)]_2$*, R= Me, Et, Pr^n, CH_2CF_3, Ph *COD= cyclooctadien	5	yel. sld., or. cr. (Pr^n)	IR, NMR	13, 455
$[(COD)Rh]_2[Ti(OPr^n)_6]$ [455]				
Ir(I)				
$(PR_3)_2(CO)Ir(OR')$, R= $C_6H_4CH_3$, R'= Me, $C_6H_4CH_3$, $CH_2C_6H_5$, square	ligand exch.	cr., s. in CH_2Cl_2	IR, NMR, X-r	1153
$[(R_2P(CH_2)_3PR_2\text{-}\eta)Ir(\mu\text{-}OR)]_2$, R= Ph, $C_6H_{11}^c$, 2 squares sharing $(\mu\text{-}OR)_2$ edge	ligand exch.	cr., s. in CH_2Cl_2	IR, NMR, X-r	674
$[Ir(\mu\text{-}OR)(1.5\text{-}COD)]_2$, R= Me,Et,$Pr^i$,$Bu^n$,$Bu^t$,Ph	5	cr., s. in CH_2Cl_2	IR, NMR	1251
$+C_{60} \rightarrow$ **$[Ir_2(\mu\text{-}OR)(\mu OPh)(1.5COD)_2]\cdot C_{60}$,** R=Me,Et,$Pr^n$,Ph, each Ir at has 4 bonds with COD		brn. sld.	X-r	1511

Ir(III)				
$IrH_2(P(C_6H_{11})_3)_2(OCH_2CF_3)\cdot xL$, $L=H_2O,CO$, trig. bipyr. (x= 0),oct.(x= 1)	4	cr., s. in hc.	IR, NMR	1033
Pd(II)				
$[(PPh_3)_2Pd(OPh)_2]$ **$Pd(\eta^2\text{-}OC_6H_4PPh_2)_2$**	5 4	yel. sld., s. in hc. yel. cr., 230 (m.)	IR, ^1H, ^{31}P,m-s	1363 1334
$Pd[OC(CF_3)_2]_2(Me_2PPh)$	4	wt., 157(m.,dec.), s. in MeOH	^{19}F, electr.sp., magn. prop.	427
$[LPdCl(\mu\text{-}OR)]_2$, R=Me,Et, Pr^n,Pr^i ; L= C_8H_{12},$C_{10}H_{12}$	5	yel. slds.	cryosc.	331
$[(C_5F_6HO_2)Pd(\mu\text{-}OMe)]_2$ 2 squares sharing $(\mu\text{-}OR)_2$ edge	4	or. cr., 100(dec.), s. in MeOH	IR, NMR, X-r	1480
Pt(II)				
$[LPt(OMe)_2]$, L= $(MePhP)_2C_6H_4$, $(Ph_2PCH_2\text{-})_2$, square planar	5	yel. cr., s. in CH_2Cl_2/ eth.,THF, 25°→MeOH+$(HCHO)_n$	IR, ^1H, ^{19}F, ^{31}P, m-s, X-r	264
$[LPt(\mu\text{-}OR)]_2$, R= Me, Et, Pr^i, CH_2CF_3, L=1,4,5-η (8-MeO-4-cycloocten-1-yl), 2 squares sharing $(\mu\text{-}OR)_2$ edge	5	wh. cr., dec 140, s. in ROH, CH_2Cl_2	IR, NMR, X-r	640
$(PPh_3)_2Pt(OPh)_2$ **$[PtH(OPh)[P(PhCH_2)_3]\ ]$**	5 5	yel. sld., s. CH_2Cl_2 yel. sld., s. in CH_2Cl_2	IR IR	1363 1363

***trans*-[PtH(OPh)[P(PhCH$_2$)$_3$]$_2$·0.5 PhMe**, square planar	5	yel.sld., 127 (m.), s. in THF, hc	IR, ^{1}H, ^{31}P, X-r	1456
[Pt(η^2-OCMe$_2$CH$_2$PPh$_2$)$_2$]·3.5H$_2$O, square	5	yel. sld., s. in THF, hc.	IR, NMR, X-r	22
Pt[OC(CF$_3$)$_2$](Me$_2$PPh)	4	wt. sld.,174 (m.,dec.)	^{19}F,magn.prop.	427
Pt[η^2-O$_2$C(CF$_3$)$_2$]$_2$(PPh$_3$), **Pt[η^2-[OC(CF$_3$)$_2$]$_2$O](PPh$_3$)**, square	7	colrl. cr., s. in CH$_2$Cl$_2$, ins. in eth.	IR, ^{1}H, ^{19}F, X-r	721, 1165
[Pt(η^2-OCH$_2$CHOCH$_2$OH)·2MeOH·[1,2-(R$_2$P)$_2$C$_6$H$_4$], square planar	6	yel. sld., s. in CH$_2$Cl$_2$	IR, NMR, X-r	57
[QPt(μ-OR)]$_2$, R= Me, Et, Pr^i, CH$_2$CF$_3$ Q= 1,4,5-η(8-methoxy-4-cyclo-octen-1-yl), 2 squares sharing (OR)$_2$ edge	5	wh. cr., dec 140, s. ROH, CH$_2$Cl$_2$	IR, NMR, X-r	640, 1114
(2-Ph$_2$PC$_6$H$_4$O)(2-Ph$_2$PC$_6$H$_4$OH)PtCl	4	yel. sld., 230 (m.)	NMR	1334
Pt(IV)				
Pt(OMe)$_4$, Pt(OMe)$_2$F$_2$	4	yel. sld. ,visc. paste,20(dec.)	IR, electr. sp.	937
M$_2$[PtF$_5$(OMe)], M= Na, K, NH$_4$	4	yel. sld.	IR, electr. sp.	937
[PtMe$_2$L(OR)(H$_2$O)]X, X= OH, ClO$_4$, PF$_6$, BPh$_4$, L= Dipy, Phen; R= Me, Et, Pr^i	4	yel. slds.	IR, NMR, electrochem	1168

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