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Spin Crossover in Transition Metal Compounds I



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Preface

The chapters in this and its two companion volumes deal with an aspect of transition metal chemistry which is fundamental to the application of ligand field theory. The change from a high spin to a low spin ground state which occurs for a particular metal ion when the ligand field is progressively strengthened is one of the most important aspects of the theory. When this occurs within a particular complex merely by the application of some external perturbation without any change in chemical composition a most remarkable and fascinating situation arises – electronic spin crossover or spin transition, the subject of these volumes. As will be evident from the various chapters, the situation is realised in a surprisingly large number of instances and its detection is feasible by application of a great variety of techniques. The perturbations which can instigate a change in spin state, initially confined to a variation in temperature or pressure, now include irradiation with visible light, X-rays and radioactive sources as well as application of a magnetic field.

Spin crossover has been investigated by chemists almost since the beginning of the application of the ideas of ligand field theory. It offers a very diagnostic means of testing many aspects of the theory and its study has revealed features of importance in the understanding of the mechanism of a range of reactions of transition metal complexes e.g. substitution, electron transfer, racemisation and photochemical processes. But its relevance goes beyond this and it is no longer the exclusive domain of chemists. Biochemists and biologists have long had a strong interest in the phenomenon since its role in, for example, the function of certain haem systems is crucial. Similarly its relevance to earth scientists, arising principally from the pressure dependence, has become widely recognised. Because of the remarkable ways in which spin crossover is manifested in solid substances it has attracted the attention of solid-state scientists and it provides a highly responsive probe for the investigation of cooperative phenomena in solids. Thus physicists, theoreticians and others have become attracted to the topic and much of the recent progress in the field can be ascribed to highly effective inter-disciplinary collaborations. A further driving force for both a broader and a deeper interest in spin crossover is the recognition that the spin crossover phenomenon has potential application in switching, sensing, memory and other devices. Hence materials scientists are also now making important contributions to the field. It is particularly noteworthy that spin crossover research has recently been incorporated into the program of the biannual International Conference on Molecular Magnetism (ICMM) with a continually growing participation from researchers in the field. Related to this is the recent estab-

lishment by the German Science Foundation of a *Priority Program* on Molecular Magnetism involving some 50 projects, a quarter of which are directly concerned with spin crossover.

The interest in the practical aspects of spin crossover, together with the discovery of the light-induced spin changes first reported in the early 1980s, the latter also opening up a totally new approach to the study of fundamental aspects of the phenomenon, have resulted in a remarkable, almost exponential, growth in the literature devoted to the field. This growth has been stimulated too by the remarkable advances in techniques, particularly in structure determination. The importance of understanding the structural consequences of a spin state change was recognised early but it was rare, up until the 1980s, to have both spin states characterised structurally. With the improvement in equipment and advances in computing it has become feasible to monitor much more closely the structural changes which occur throughout the course of a transition, even for a transition induced by a change in pressure or by irradiation. Synchrotron radiation sources too have become more widely available and valuable structural information has been provided by application of these, particularly for those systems which are not amenable to X-ray crystallography. The net result is that complex, yet beautifully inter-locked networks containing spin crossover centres have now been characterised and structural details can provide the basis for the understanding of the actual nature of the spin transition in the solid species. An impetus of a different kind has been responsible for much of the increased activity in the field in recent years. In 1998 a four year research program titled Thermal and Optical Switching of Molecular Spin States (TOSS) was established by the European Union, involving ten leading research groups. The results of the efforts of the groups in this program are evident in much of the material covered in the following chapters.

The field of spin crossover is now obviously a very broad one and in these volumes an attempt has been made to present as comprehensive a treatment of the topic as feasible. Over the years there have been many reviews devoted to aspects of the phenomenon of spin crossover, and a few of these have attempted to give a relatively broad treatment. As the literature and the scope of the topic have grown so markedly in recent times, it has become unrealistic to cover the whole area in a single review article. The range of topics covered in the present volumes takes in the most important modern aspects of the spin crossover field and should provide a sound basis for the understanding of the occurrence of the phenomenon and its multi-faceted manifestation. It is hoped that it will stimulate further interest in the area. An overall perspective introduces the first volume of the series (volume 233) and this is followed by the ligand field basis for the occurrence of spin crossover. The emphasis in the subsequent chapters, extending into volume 234, is on the nature of the systems in which the phenomenon is observed. This is followed in volumes 234 and 235 by consideration of some fundamental specific phenomena associated with spin crossover and the techniques applied to monitor them. Theoretical aspects are presented in volume 235 which concludes with a discussion of the practical applications of spin crossover, thereby pointing the way to the likely future emphasis of research in the area.

The authors have been drawn from a truly international source and we thank them for their willingness to contribute so enthusiastically to the volumes. Their

patience and cooperation, together with those of the staff at Springer, have lightened the burden of our own efforts in bringing the project to fruition. Among the names of authors of the chapters in these volumes, those of two of the most prominent contributors to the field of spin crossover are conspicuously absent – Edgar König and Olivier Kahn. While König, a real pioneer and leader in the field for about thirty years, has been pursuing other interests in an active retirement, sadly Kahn died suddenly in 1999 while his activity in the field was at its peak. The rich legacy of the contributions of both of them to the field of spin crossover is reflected in the extent to which their names appear in the reference lists of many of the chapters of these volumes.

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March 2004

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Spin Crossover—An Overall Perspective

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Abstract In this chapter an outline is presented of the principal features of electronic spin crossover. The development of the subject is traced and the various modes of manifestation of spin transitions are presented. The role of cooperativity in influencing solid state behaviour is considered and the various strategies to strengthen it are addressed along with the chemical and physical perturbations which affect crossover behaviour. The role of intermediate spin states is discussed together with spin crossover in five-coordinate systems. The various techniques applied to monitoring a transition are presented briefly. An introduction to theoretical treatments is given and likely areas for future developments are suggested. Relevant review articles in the field are listed and reference to later chapters in the series is given where appropriate.

Keywords Spin crossover · Magnetism · Mössbauer spectroscopy · Cooperativity · Hysteresis

List of Abbreviations

abpt	4-Amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole
bpy	2,2'-Bipyridine
btr	4,4'-Bis(1,2,4-triazole)
C _p	Heat capacity
DSC	Differential scanning calorimetry
EPR	Electron paramagnetic resonance
HS	High spin
LS	Low spin
LIESST	Light induced excited spin state trapping
mephen	2-Methyl-1,10-phenanthroline
NIESST	Nuclear decay induced excited spin state trapping
NMR	Nuclear magnetic resonance
ox	The oxalate ion
papthH	2-(Pyridin-2-yl-amino)-4-(pyridin-2-yl)thiazole
phen	1,10-Phenanthroline
phy	1,10-Phenanthroline-2-carbaldehyde phenylhydrazone
pic	2-Picolylamine
PM-BiA	N-(2-Pyridylmethylene)aminobiphenyl
ptz	1- <i>n</i> -Propyl-tetrazole
py	Pyridine
SCO	Spin crossover
ST	Spin transition
T _{1/2}	Spin transition temperature (temperature of 50% conversion of all "SCO-active" complex molecules)
TCNQ	Tetracyanodiquinomethane
trpy	2,2':6',2''-Terpyridine
trzH	1,2,4-Triazole
ZFS	Zero field splitting

1 Introduction

For about the past 80 years coordination compounds of certain transition metal ions have been divided into two categories determined by the nature of the bonding, whether it be in terms of ionic and covalent bonding, inner- and outer-orbital bonding or high spin and low spin configurations. It was recognised quite early that this division raised the question of the transition from one type to the other. Would this be a sharp transition, i.e. complexes must be either one kind or the other, or would it be possible for systems to occur in which the nature of the bonding would be subject to change depending on some external perturbation? These questions were addressed in the development of an understanding of the nature of the metal-donor atom bond, most notably by Linus Pauling. In his treatment of the magnetic criterion for bond type, Pauling perceptively recognised that it would be feasible to obtain systems in which the two types could be present simultaneously in ratios determined by the energy difference between them [1]. In fact, this situation had at the time just been realised. The pioneering work of Cambi and co-workers in the 1930s on the unusual magnetism of iron(III) derivatives of various dithiocarbamates led to the first recognition of the interconversion of two spin states as a result of variation in temperature [2]. Work proceeded on the magnetism of various heme derivatives of iron(II) and iron(III) and established that in these naturally occurring systems, as well as in related porphyrin derivatives, the spin state was remarkably sensitive to the nature of the axial ligands. For certain species, intermediate values of the magnetic moment were observed and interpreted in terms of the bonding being in part ionic and in part covalent [3]. Later Orgel proposed for these that there was an equilibrium between an iron(III) species with one, and another with five unpaired electrons [4]. Remarkably, Orgel went on to suggest that in both of the iron(II) systems $[\text{Fe}(\text{phen})_3]^{2+}$ and $[\text{Fe}(\text{mephphen})_3]^{2+}$ the field strength was near, but on opposite sides of, the crossover point in the Tanabe-Sugano diagram for a d^6 ion (shown in Fig. 2, Chap. 2).

The rapid increase in interest in the spin crossover situation that followed more or less coincided with the widespread acceptance by coordination chemists of the value of ligand field theory in understanding the stability, reactivity and structure together with the spectral and magnetic properties of transition metal compounds. Early in the 1960s Busch and co-workers [5] were attempting to identify the crossover region for iron(II) and cobalt(II) and reported the first instance of spin crossover in a complex of the latter ion [6]. Similarly, Madeja and König undertook a systematic variation in the nature of the anionic groups in the iron(II) system $[\text{Fe}(\text{phen})_2\text{X}_2]$ in an attempt to define the crossover region [7]. In this period too the early studies on the iron(III) dithiocarbamate systems of Cambi and co-workers were being extended and included, for example, the crucial experiment of determin-

ing the role of pressure in influencing the spin state in crossover systems. This was the first application of this technique to the spin crossover phenomenon and the predicted effect of favouring of the low spin configuration with increased pressure was observed [8]. The iron(III) dithiocarbamates have continued to attract much attention and these, together with other iron(III) systems, are considered in detail in Chap. 10. It was at about the time of the work of Ewald et al. [8] that the Mössbauer effect (first reported in 1958 [9]) was being taken up by chemists and the application of Mössbauer spectroscopy to the study of the spin changes in the iron(III) dithiocarbamates represents perhaps the first, albeit not the most diagnostic, instance of its value in this area [10]. Mössbauer spectroscopy has come to play a pivotal role in the development and understanding of the spin crossover phenomenon and was the technique which was used to confirm the occurrence of a spin transition as the origin of the unusual temperature dependence of the magnetism in $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, the first example of spin crossover in a synthetic iron(II) system [11].

2

Occurrence of Spin Crossover

The fundamental consideration of the occurrence of spin crossover in terms of ligand field theory, for iron(II) in particular, is given by Hauser in Chap. 2. The change in spin state exhibited by certain metal complexes under the application of an external perturbation is referred to by a number of terms—spin crossover, spin transition and, sometimes, spin equilibrium. The most common perturbation resulting in a change of spin state for a particular complex is a variation in temperature, but pressure changes, irradiation and an external magnetic field can also bring about the change. The origin of the term “spin crossover” lies in the *crossover* of the energy vs field strength curves for the possible ground state terms for ions of particular d^n configurations in Tanabe-Sugano and related diagrams. The term “spin transition” is used almost synonymously with spin crossover but the latter has the broader connotation, incorporating the associated effects, spin transition tending to refer to the actual physical event. Thus for a simple, complete change in spin state, the spin transition temperature is defined as the temperature at which the two states of different spin multiplicity are present in the ratio 1:1 ($\gamma_{\text{HS}} = \gamma_{\text{LS}} = 0.5$). As will be shown below, many transitions are not simple and this definition of transition temperature is not necessarily applicable. The transition temperature is generally represented as $T_{1/2}$ and even in the less straightforward instances this can usually be readily interpreted. For example, for systems in which the transition is incomplete, in either the low temperature region (“residual HS fraction”) or the high temperature region (“residual LS fraction”), or both, the spin transition tempera-

ture can be defined as the temperature at which 50% of the SCO-active complex molecules have changed their spin state. In the early literature the term “spin equilibrium” has been used to describe the temperature dependence of the population of spin states. This term is not suited to most instances of the spin crossover in a solid sample since a straightforward thermal equilibrium based on a simple Boltzmann-like distribution of the energy states is inappropriate to account for the complex nature of the spin changes frequently observed. For systems in liquid solution, however, reference to a spin equilibrium is generally meaningful and appropriate, and is currently used. In dilute solid solutions where the spin crossover centres are incorporated into a SCO-inactive host lattice the cooperative interactions between the spin-changing molecules tend to disappear as the extent of dilution increases and thus the situation is similar to that in liquid solution where, *a priori*, cooperative interactions are assumed to be absent.

Spin crossover is feasible for derivatives of ions with d^4 , d^5 , d^6 and d^7 configurations and is observed for all these in complexes of first transition series ions. Isolated examples are available for the second series, but, because of the lower spin pairing energy for these ions, together with stronger ligand fields, it is unlikely that a large number will be found. For the d^8 configuration, in particular for Ni(II), change in spin multiplicity (singlet $\leftrightarrow$ triplet) generally results in such a major geometrical rearrangement that the process is referred to as a configurational change. The difference between this and what is normally referred to as spin crossover is one more of degree than of kind, but it does tend to be considered separately from spin crossover. An early paper by Ballhausen and Liehr [12] offers some pertinent insight into this distinction.

Of the ions which do show typical spin crossover behaviour the largest number of examples is found for the configuration d^6 and iron(II) accounts for the vast majority of these. For this reason, much of the discussion which follows in this and subsequent chapters refers to transitions in iron(II). The only other d^6 ion for which crossover behaviour has been observed is cobalt(III), but there is a very limited number of examples. The d^6 configuration is relatively easily obtained in the low spin configuration—the spin pairing energy is less than that of comparable ions [13] and the low spin d^6 configuration has maximum ligand field stabilisation energy. Thus for Co(III), which induces a strong field in most ligands, the low spin configuration is almost always adopted, hence the paucity of spin crossover or purely high spin systems for this ion. For the larger Fe(II) ion ligand fields are weaker. Hence spin pairing is not so strongly favoured and it is possible to obtain relatively stable high spin or low spin complexes from a broad range of ligands. Thus it is feasible to fine-tune the ligand field with a fair degree of certainty of bringing it into the crossover region. For the smaller iron(III) ion (d^5) the low spin configuration is again relatively favoured, but not to the extent observed for Co(III), partly because of the relatively low spin pair-

ing energy and higher ligand field stabilisation energy of the latter. Thus the occurrence of spin crossover is much more widespread for Fe(III) than for Co(III). However, conditions are less favourable than for Fe(II), partly because of the tendency of high spin Fe(III) complexes to be readily hydrolysed. For Co(II) (d^7) spin crossover is well characterised, but it is much less common than for Fe(II), possibly because of the higher spin pairing energy and the destabilising effect of the single e_g electron in low spin six-coordinate complexes (SCO in Co(II) complexes is treated in Chap. 12). For Ni(III), also d^7 , SCO has been proposed in only one instance—in salts of $[\text{NiF}_6]^{3-}$ [14]. The occurrence of spin crossover in systems other than those of Fe(II), Fe(III) and Co(II) is considered in detail in Chap. 13.

3

Detection of Spin Crossover

Perhaps the two most important consequences of a spin transition are changes in the metal-donor atom distance, arising from a change in relative occupancies of the t_{2g} and e_g orbitals (see Chap. 2), and changes in the magnetic properties. While the former can be effectively monitored, the changes in magnetism are more conveniently measured. The change from low spin to high spin results in a pronounced increase in the paramagnetism of the system and hence the measurement of this change (as a function of temperature) was the means initially applied to the detection of thermal spin crossover, and remains the most common way of monitoring a spin transition. Measurement of Mössbauer spectra, for iron(II) systems in particular, offers a more direct means of obtaining the relative concentrations of the spin states since these give separate and well defined contributions to the overall spectrum, each spin state having its own characteristic set of Mössbauer spectral parameters (isomer shift and quadrupole splitting). Provided that the lifetimes of the spin states are greater than the time scale of the Mössbauer effect (10^{-7} s) their separate contributions to the overall spectrum can be identified. This is the normal situation for iron(II), with one reported exception for six-coordinate complexes [15]. For iron(III) the rates of interconversion of the spin states are frequently too rapid to enable their separate identification in Mössbauer spectra. When the separate contributions are seen their area fractions can usually be extracted with reasonable accuracy from the Mössbauer spectra. The value of measurements of magnetic susceptibility and Mössbauer spectra in studies of SCO systems is developed below. Their most important application is undoubtedly in the derivation of a spin transition curve which is a visual representation of the course of a spin transition.

3.1 Spin Transition Curves

A spin transition curve is conventionally obtained from a plot of high spin fraction (γ_{HS}) vs temperature. Such curves are highly informative and take a number of forms for systems in the solid state. The most important of these are illustrated in Fig. 1. The variety of manifestations of a transition evident in this figure arises from a number of sources but the most important is the *degree of cooperativity* associated with the transition. This refers to the extent to which the effects of the spin change, especially the changes in the metal-donor atom distances, are propagated throughout the solid and is determined by the lattice properties. The gradual transition (sometimes referred to as a *continuous* transition, but this term can have misleading connotations) illustrated in Fig. 1a is perhaps the most common and is observed when cooperative interactions are relatively weak. This is the course of a transition observed for a system in solution where essentially a Boltzmann distribution of the molecular states is involved. The abrupt transition (sometimes referred to as *discontinuous*, but again this can be misleading) of Fig. 1b results from the presence of strong cooperativity. Obviously, situations intermediate between (a) and (b) exist. When the cooperativity is particularly high hysteresis may result, as shown in Fig. 1c. The appearance of hysteresis, usually accompanied by a crystallographic phase change, associated with a spin transition has come to be recognised as one of the most significant aspects of the whole spin crossover phenomenon. This confers bistability on the system and thus a *memory effect*. *Bistability* refers to the

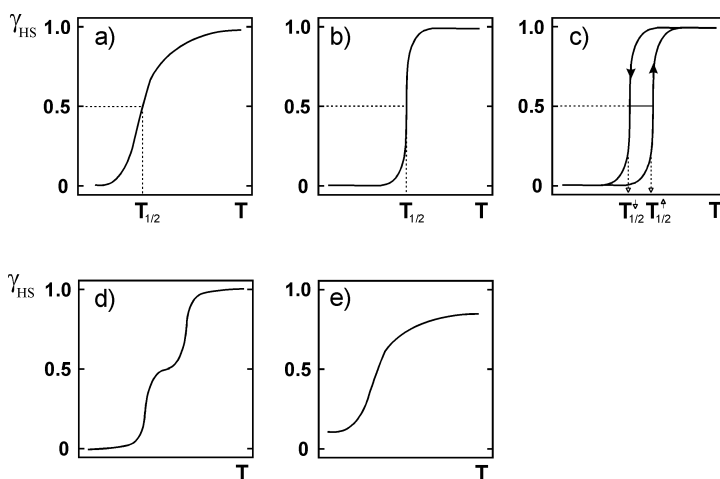


Fig. 1a–d Representation of the principal types of spin transition curves (high spin fraction (γ_{HS}) (y axis) vs temperature (T) (x axis): **a** gradual; **b** abrupt; **c** with hysteresis; **d** two-step; **e** incomplete

ability of a system to be observed in two different electronic states in a certain range of some external perturbation (usually temperature) [16]. The potential for exploitation of this aspect of SCO in storage, memory and display devices was highlighted by Kahn and Martinez [17] and this has driven much of the recent research in the area. The quest for stable systems which display a well-defined, reasonably broad hysteresis loop spanning room temperature and an understanding of the factors which lead to such behaviour is continuing.

There are two principal origins of hysteresis in a spin transition curve: the transition may be associated with a structural phase change in the lattice and this change is the source of the hysteresis; or the intramolecular structural changes that occur along with a transition may be communicated to neighbouring molecules via a highly effective cooperative interaction between the molecules. The mode of this interaction is not always clear but three principal strategies have been adopted in an attempt to generate it: (i) linkage of the SCO centres via covalent bonds in a polymeric system; (ii) incorporation of hydrogen bonding centres into the coordination environment allowing interaction either directly with other SCO centres or via anions or solvate molecules; (iii) incorporation of aromatic moieties into the ligand structure which promote π - π interactions through stacking throughout the lattice. Partial success has been achieved for all three approaches but a full understanding of the factors involved remains one of the major challenges of the area. A further probable origin of cooperativity is the synergism between an order-disorder transition and a spin transition, as has been proposed for the systems $[\text{Fe}(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ [18] and $[\text{Fe}(\text{dppen})_2\text{Cl}_2] \cdot 2(\text{CH}_3)_2\text{CO}$ [19] ($\text{dppen} = \text{cis-1,2-bis}(\text{diphenylphosphino})\text{ethene}$) in which the disorder is associated with solvate molecules and for $[\text{Fe}(\text{biimidazoline})_3](\text{ClO}_4)_2$ where disorder in the anion orientation is considered likely [20]. Disorder involving solvate molecules and anions is relatively common so this relatively little explored aspect to cooperativity offers scope for further development.

Despite the relative lack of predictability, the number of systems now known to display a spin transition curve of type (c) is remarkably high, and highest for iron(II) where, significantly, the change in intramolecular dimensions is the greatest for the ions for which SCO is relatively common (Fe(II), Fe(III), Co(II)).

The transitions of type (c) are defined by two transition temperatures, one for decreasing ($T_{1/2\downarrow}$), and one for increasing temperature ($T_{1/2\uparrow}$). Two-step transitions (Fig. 1d), first reported in 1981 for an iron(III) complex of 2-bromo-salicylaldehyde-thiosemicarbazone [21], are relatively rare and have their origins in several sources. The most obvious is the presence of two lattice sites for the complex molecules. There are several examples of this [22]. In addition, binuclear systems can give rise to this effect, even when the environment of each metal atom is the same—in this instance the

spin change in one metal atom may render the transition in the twin metal atom less favourable. The $[\text{Fe}(\text{diimine})(\text{NCS})_2]_2\text{bipyrimidine}$ series provides the classic examples of this situation [23] (Chap. 7). More generally, two step transitions can be observed in systems in which there is only a single lattice site, this being observed for example in the ethanol solvate of tris(2-picolyamine)iron(II) chloride [24]. This has been interpreted in terms of short range interactions and the preferential formation of HS/LS pairs in the progress of the transition [25].

The retention of a significant high spin fraction (Fig. 1e) at low temperatures may also arise from various sources. A fraction of the complex molecules may be in a different lattice site in which the field strength is sufficiently reduced to prevent the formation of low spin species. It is feasible that for a particular lattice the major structural changes that accompany a complete change in spin state may not be able to be accommodated. There is likely, in addition, in some instances to be a kinetic effect involved—at sufficiently low temperatures the rate of the high spin to low spin conversion becomes extremely small. Because of this, it is possible in a number of instances to freeze-in a large high spin fraction by rapid cooling of the sample [26–29]. This effect is often observed around liquid nitrogen temperature but would obviously be more common at still lower temperatures. It occurs generally when there is a major structural change accompanying the transition over and above the normal intramolecular changes and hence the structural change may proceed at a slower rate than the normal rate for the spin change alone. The retention of a permanent low spin fraction at the upper temperature limit of a transition is less common, because of the much greater density of vibrational states for the high spin species and in addition kinetic factors are not likely to be so relevant in this instance.

3.2

Experimental Techniques

3.2.1

Magnetic Susceptibility Measurements

Measurement of magnetic susceptibility as a function of temperature, $\chi(T)$, has always been the principal technique for characterisation of SCO compounds. The Evans NMR method [30] is generally applied for studies in liquid solution. For measurements on solid samples SQUID magnetometers have progressively replaced the traditional balance methods (Faraday, Gouy) in modern laboratories, because of their much higher sensitivity and accuracy. Alternative instruments being used are Foner-type vibrating sample and a.c./d.c. susceptibility magnetometers. A comprehensive survey of the techniques and computational methods used in magnetochemistry is given by Palacio [31] and Kahn [32].

The transition from a strongly paramagnetic HS state to a weakly paramagnetic or (almost) diamagnetic LS state is clearly reflected in a more or less drastic change in the magnetic susceptibility. The product χT for a SCO material is determined by the temperature dependent contributions χ_{HS} and χ_{LS} according to $\chi(T) = \gamma_{\text{HS}}\chi_{\text{HS}} + (1 - \gamma_{\text{HS}})\chi_{\text{LS}}$. With the known susceptibilities of the pure HS and LS states, the mole fraction of the HS state (or LS state), γ_{HS} , at any temperature is easily derived and is plotted to produce the spin transition curve, as shown in Fig. 1. Alternatively, instead of a plot of $\gamma_{\text{HS}}(T)$, the spin transition curve is frequently expressed as the product χT vs T , particularly in those cases where the quantities χ_{HS} and χ_{LS} are not accessible or not sufficiently accurately known. Expression of the spin transition curve in terms of the effective magnetic moment $\mu_{\text{eff}} = (8\chi T)^{-1/2}$ as a function of temperature has been widely used but is now less common.

Techniques have been developed for measurements of $\chi(T)$ down to liquid helium temperatures with the sample under various external perturbations such as hydrostatic pressure (Chap. 22), light irradiation (Chap. 30) and high magnetic fields (Chap. 23).

3.2.2

⁵⁷Fe Mössbauer Spectroscopy

The *recoilless nuclear resonance absorption of γ -radiation* (Mössbauer effect) has been verified for more than 40 elements, but only some 15 of them are suitable for practical applications [33, 34]. The limiting factors are the lifetime and the energy of the nuclear excited state involved in the Mössbauer transition. The lifetime determines the spectral line width, which should not exceed the hyperfine interaction energies to be observed. The transition energy of the γ -quanta determines the recoil energy and thus the resonance effect [34]. ⁵⁷Fe is by far the most suited and thus the most widely studied Mössbauer-active nuclide, and ⁵⁷Fe Mössbauer spectroscopy has become a standard technique for the characterisation of SCO compounds of iron.

The *isomer shift* δ and the *quadrupole splitting* ΔE_Q , two of the most important parameters derived from a Mössbauer spectrum [34], differ significantly for the HS and LS states of both Fe(II) and Fe(III). Thus, if both spin states, LS and HS, are present to an appreciable extent (not less than ca. 3% in any case) and provided the relaxation time for $\text{LS} \leftrightarrow \text{HS}$ fluctuation is longer than the Mössbauer time window (determined by the lifetime of the excited nuclear state, which is ca. 100 ns for ⁵⁷Fe), the two spin states are discernible by their characteristic subspectra. Even in cases where the subspectra strongly overlap, the area fractions of the resonance lines can be determined with the help of specially developed data fitting computer programs. The area fractions t_{HS} and t_{LS} are proportional to the products $f_{\text{HS}}\gamma_{\text{HS}}$ and $f_{\text{LS}}\gamma_{\text{LS}}$, respectively, where f_{HS} and f_{LS} are the so-called Lamb-Mössbauer factors of the HS and LS states. Only for $f_{\text{HS}} = f_{\text{LS}}$ are the area fractions a direct

measure of the respective mole fractions of the complex molecules in the different spin states, i.e. $t_{\text{HS}}/(t_{\text{HS}}+t_{\text{LS}})=\gamma_{\text{HS}}$. In most cases the approximation of $f_{\text{HS}}\approx f_{\text{LS}}$ is made. This is justified for SCO compounds with gradual spin transitions. For systems showing abrupt transitions, however, f_{LS} tends to be greater than f_{HS} and therefore $\gamma_{\text{HS}}(T)$ would be under-estimated, particularly towards lower temperatures if the above assumption were made. In these cases corrections are necessary for accurate evaluations [35].

Apart from its application in the derivation of a spin transition curve, Mössbauer spectroscopy can provide other valuable information relevant to SCO. The *isomer shift*, δ , is proportional to the s-electron density at the nucleus, and hence is directly influenced by the s-electron population and indirectly (via shielding effects) by the d-electron population in the valence shell. It thus gives information on both the oxidation and the spin state and allows valuable insight into bonding properties (e.g. π -back bonding, covalency, ligand electronegativity) [33, 34]. *Electric quadrupole splitting* ΔE_Q is observed when an inhomogeneous electric field at the Mössbauer nucleus is present. In general, two factors can contribute to the electric field gradient, a non-cubic electron distribution in the valence shell and/or a nearby, non-cubic lattice environment [33, 34]. Thus ΔE_Q data yield information on molecular structure and, in a complementary manner to the isomer shift, oxidation and spin state. *Magnetic dipole splitting* ΔH_M , the third kind of hyperfine interaction of importance in Mössbauer spectroscopy, is generally not observed in SCO compounds, because the valence electron spin and therefore the Fermi contact field are fluctuating sufficiently rapidly such that the magnetic field at the nucleus averages out to zero during the Mössbauer time window. However, magnetic dipole splitting is observed if the sample under study is placed in an external magnetic field. The magnitude of the splitting, ΔH_M , is assigned to different spin states. The value of measurements of Mössbauer spectra in an applied magnetic field has been elegantly exploited for direct monitoring of the spin state in dinuclear iron(II) compounds, which exhibit a striking interplay of antiferromagnetic coupling and spin crossover [36]. This is discussed further in Chap. 7.

Rather sophisticated applications of Mössbauer spectroscopy have been developed for measurements of lifetimes. Adler et al. [37] determined the relaxation times for $\text{LS}\leftrightarrow\text{HS}$ fluctuation in a SCO compound by analysing the line shape of the Mössbauer spectra using a relaxation theory proposed by Blume [38]. A delayed coincidence technique was used to construct a special Mössbauer spectrometer for time-differential measurements as discussed in Chap. 19.

3.2.3

Measurement of Electronic Spectra

While measurement of magnetic susceptibility and Mössbauer spectra remain the principal techniques for the monitoring of a spin transition through the production of a spin transition curve, magnetism being applicable in all instances, several other techniques have been applied to the detection and characterisation of transitions. Thermal ST is always accompanied by a colour change (thermochromism) which is frequently pronounced and visible. This offers a very convenient and quick means of detecting the likely occurrence of a transition by simple observation of the colour at different temperatures. If the visible colour is due solely to the ligand field bands, then for iron(II) a striking change from colourless in the high spin state to violet in the low spin state will be observed, as in, for example, the $[\text{Fe}(\text{alkyl-tetrazole})_6]^{2+}$ systems [39] (discussed in Chap. 2). For many systems bands due to spin- and parity-allowed charge transfer transitions occur in the visible region of the spectrum and these mask the less intense ligand field bands in the same region. While the charge transfer bands may be displaced slightly to lower frequencies with change from high spin to low spin, the more pronounced effect is an increase in intensity and this also will often be a very visible change. For example, the colour change observed for $[\text{Fe}(\text{mphen})_3]^{2+}$ salts, from light orange in the high spin state to deep red-violet in the low spin, arises principally from this effect [40]. A further striking example is the colour change from yellowish in the HS state of $[\text{Fe}(\text{2-pic})_3]^{2+}$ salts to deep brown in the LS state [41].

In ideal situations, optical spectroscopy as a function of temperature for single crystals is employed to obtain the electronic spectrum of a SCO compound. Knowledge of positions and intensities of optical transitions is desirable and sometimes essential for LIESST experiments, particularly if optical measurements are applied to obtain relaxation kinetics (see Chap. 17). In many instances, however, it has been demonstrated that measurement of optical reflectivity suffices to study photo-excitation and relaxation of LIESST states in polycrystalline SCO compounds (cf. Chap. 18).

3.2.4

Measurement of Vibrational Spectra

Accompanying a transition from high spin to low spin there is a reduction, for d^4 , d^5 and d^6 species a complete depletion, of charge in the antibonding e_g orbitals and simultaneous increase of charge in the slightly bonding t_{2g} orbitals. As a consequence, a strengthening of the metal-donor atom bonds occurs, and this is observable in the vibrational spectrum in the region between ~ 250 and $\sim 500\text{ cm}^{-1}$, where the metal-donor atom stretching frequencies of transition metal compounds usually appear [42]. In a series of far-in-

frared or Raman spectra measured as a function of temperature, the vibrational bands belonging to the HS and the LS species can be readily recognised as those decreasing and increasing in intensity, respectively, as the temperature is lowered. In several instances a spin transition curve, $\gamma_{\text{HS}}(T)$, has been derived from the normalized area fractions of characteristic HS or LS bands [43]. Certain internal ligand vibrations have also been found to be susceptible to change of spin state at the metal centre. Typical examples are the N-coordinated ligands NCS^- and NCSe^- , which are widely used in the synthesis of iron(II) SCO complexes to complete the FeN_6 core, as in the “classical” system $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$. The C-N stretching bands of NCS^- and NCSe^- are found in the HS state as a strong doublet near $2060\text{--}2070\text{ cm}^{-1}$. In the region of the transition temperature (176 K), the intensity of this doublet decreases in favour of a new doublet appearing at $2100\text{--}2110\text{ cm}^{-1}$, which arises from the LS state [43]. Recent developments in this area are presented in Chaps. 21 and 24.

3.2.5

Heat Capacity Measurements

As with studies of phase transitions in general, calorimetric measurements (DSC or $C_p(T)$) on SCO compounds (treated in detail by Sorai in Chap. 27) provide important thermodynamic quantities such as enthalpy and entropy changes accompanying a ST, together with the transition temperature and the order of the transition. The ST can be considered as a phase transition associated with a change of the Gibbs free energy $\Delta G = \Delta H - T\Delta S$. The enthalpy change $\Delta H = H_{\text{HS}} - H_{\text{LS}}$ is typically 10 to 20 kJ mol^{-1} , and the entropy change $\Delta S = S_{\text{HS}} - S_{\text{LS}}$ is of the order of 50 to 80 $\text{J mol}^{-1}\text{ K}^{-1}$ [44]. The thermally induced ST is thus an entropy driven process; the degree of freedom is much greater in the HS than in the LS state. Approximately 25% of the total entropy gain accompanying the LS to HS change arises from the change in spin multiplicity, $\Delta S_{\text{mag}} = R \cdot \ln \frac{(2S+1)_{\text{HS}}}{(2S+1)_{\text{LS}}}$, and the major contribution originates from changes in the intramolecular vibrations [45, 46].

The first heat capacity measurements were performed by Sorai and Seki on $[\text{Fe}(\text{phen})_2(\text{NCX})_2]$ with $\text{X}=\text{S}, \text{Se}$ [45, 46]. A few other SCO compounds of Fe(II) [47], Fe(III) [48] and Mn(III) [49] have been studied quantitatively down to very low (liquid helium) temperatures. For a relatively quick but less precise estimate of ΔH , ΔS , the transition temperature and the occurrence of hysteresis, DSC measurements, although mostly accessible only down to liquid nitrogen temperatures, are useful and easy to perform [50].

DSC measurements with a microcalorimeter played a key role in tracing the origin of the step observed in the spin transition curve of $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ [24]. The mixing entropy derived from the measured heat capacity data showed a significant reduction in the region of the step. This has been

interpreted as being due to partial ordering, i.e. preferred LS-HS pair formation extending over domains with a perfect chequerboard pattern [25, 51]. Monte Carlo calculations including such short range interactions have supported this interpretation by successful simulation of the stepwise spin transition, together with its alteration by metal dilution and application of pressure [52].

3.2.6

X-ray Structural Studies

Thermal SCO in solid transition metal compounds is always accompanied by significant changes in the metal coordination environment because of the change in occupancies of the antibonding e_g and the weakly bonding t_{2g} orbitals. For iron(II), where the change in total spin is $\Delta S=2$, the resultant change in the metal-donor atom bond lengths is particularly large and amounts to ca. 10% ($\Delta r = r_{HS} - r_{LS} \cong 220 - 200 \cong 20$ pm), which may cause a 3–4% change in elementary cell volumes [44]. The change in iron(III) SCO compounds, also with $\Delta S=2$ transitions, is somewhat less with $\Delta r \cong 10$ –13 pm, because of an electron hole remaining in the t_{2g} orbitals in the LS state. Δr is even less in cobalt(II) SCO systems ($\Delta r \leq 10$ pm), because only one electron is transferred between the e_g and the t_{2g} orbitals in the $\Delta S=1$ transitions. The size of Δr has important consequences for the build-up of cooperative interactions, and also exerts a strong influence on the spin state relaxation kinetics. Although Δr is the major structural change accompanying a spin transition, other changes, particularly in the degree of distortion of the metal environment are significant [53].

Accompanying the changes within the coordination sphere may be significant positional changes in the crystal lattice. These are less predictable. However, these lattice changes, which may in fact result in an actual crystallographic phase transition, influence strongly the nature of the spin transition curve. When that curve indicates a highly cooperative transition the structural details provide an insight into the origin of the cooperativity. Thus crystal structure determination at variable temperatures above and below the ST temperature is very informative of the nature of ST phenomena in solids. Even if a suitable single crystal is not available for a complete structure determination, the temperature dependence of X-ray powder diffraction data can be diagnostic of the nature of the ST (gradual or abrupt), and of changes in the lattice parameters [54]. It is also possible to ascertain from such data structural details such as the space group by application of the Rietveld method. The appearance of separate characteristic peak profiles in powder diffraction patterns for the high spin and low spin species has been taken as indicative of a phase change within the temperature range of the spin transition. For the system $[\text{Fe}(\text{phy})_2](\text{ClO}_4)_2$ (phy=1,10-phenanthroline-2-carbaldehyde-phenylhydrazone) a curve derived from the measure-

ment of the temperature dependence of the relative intensities of characteristic peaks has been shown to reproduce closely, including the hysteresis, the spin transition curve obtained directly from Mössbauer spectral measurements [55]. It was thus concluded that in this instance the changes in the electronic state and the crystallographic changes occur in tandem.

Experimental equipment for X-ray diffraction methods has improved enormously in recent years. CCD detectors and focusing devices (Goepel mirror) have drastically reduced the data acquisition time. Cryogenic systems have been developed which allow structural studies to be extended down to the liquid helium temperature range. These developments have had important implications for SCO research. For example, fibre optics have been mounted in the cryostats for exploring structural changes effected by light-induced spin state conversion (LIESST effect). Chaps. 15 and 16 treat such studies.

3.2.7

Synchrotron Radiation Studies

EXAFS (Extended X-ray Absorption Fine Structure) measurements using synchrotron radiation have been successfully applied to the determination of structural details of SCO systems and have been particularly useful when it has not been possible to obtain suitable crystals for X-ray diffraction studies. Perhaps the most significant application has been in elucidating important aspects of the structure of the iron(II) SCO linear polymers derived from 1,2,4-triazoles [56]. EXAFS has also been applied to probe the dimensions of LIESST-generated metastable high spin states [57]. It has even been used to generate a spin transition curve from multi-temperature measurements [58].

X-ray absorption spectroscopy (XAS) can be divided into EXAFS and X-ray absorption near edge structure (XANES), which provides information essentially about geometry and oxidation states. Although XAS has not been widely applied to follow spin state transitions, the technique is nevertheless ideally suited, as it is sensitive to both the electronic and the local structure around the metal ion undergoing SCO. Metal K-edge X-ray absorption fine-structure spectroscopy (XAFS) has been used to study the structural and electronic changes occurring during SCO in iron(II) [59, 60], iron(III) [61], and cobalt(II) complexes [60].

EXAFS information is restricted to the first or second coordination sphere around a central atom whereas WAXS (Wide-Angle X-ray Scattering) can yield information on short and medium range order up to 20 Å. It has been applied, for instance, to the important polymeric chain ST material $[\text{Fe}(\text{Htrz})_2\text{trz}](\text{BF}_4)$ (Htrz=1,2,4-triazole), in the LS and HS state and indicated the likely involvement of hydrogen bonding between the anion and the 4-H atom of the triazole ring [62].

Nuclear Forward Scattering (NFS) of synchrotron radiation is a powerful technique able to probe hyperfine interactions in condensed matter [63]. It is related to conventional Mössbauer spectroscopy and is particularly useful when the traditional Mössbauer effect experiments reach their limits. As an example, the high intensity of synchrotron radiation allows NFS studies on very small samples or substances with extremely small concentrations of resonating nuclei, where conventional Mössbauer experiments are not feasible. NFS measurements have been carried out on iron(II) SCO complexes with considerable success [64]. The time dependence of the NFS intensities yields typical “quantum beat structures” for the HS and the LS states, the quantum beat frequency being considerably higher in the HS state due to the larger quadrupole splitting than in the LS state. The temperature dependent transition between the two spin states yields complicated interference NFS spectra, from which the molar fractions of HS and LS molecules, respectively, can be extracted. An additional advantage of NFS measurements over conventional Mössbauer spectroscopy is that they yield more precise values of the so-called Lamb-Mössbauer factor, thereby allowing more accurate determination of the mole fractions of HS and LS species. Furthermore, NFS measurements can be combined with simultaneous Nuclear Inelastic Scattering (NIS) of synchrotron radiation, the latter providing valuable information on the vibrational properties of the different spin states of an SCO compound [65] and thus complementing conventional infrared and Raman spectroscopic studies. Chapter 26 is devoted to applications of NFS and NIS of synchrotron radiation to studies of SCO systems.

3.2.8

Magnetic Resonance Studies

Proton NMR measurements provide a widely used, elegant and relatively straightforward technique for monitoring SCO in solution, the magnetic susceptibility being obtained from the magnitude of the shift induced by a paramagnetic centre in the signal due to a standard component (the Evans method) [30, 66]. The analysis of magnetic data obtained in this way for solutions has frequently provided thermodynamic parameters for the spin transition, treated as a process involving a thermal equilibrium of the complex in the two spin states. The technique was applied first to SCO in iron(II) in the important tris(pyrazolyl)borate systems (Chap. 4) [67]. In contrast to its value in characterising SCO for solutions, NMR spectra of solid SCO systems have contributed little to the understanding of the phenomenon, except to detect the transition itself from the line width change. The numerous, chemically distinct protons in the ligands lead to broad lines, which are difficult or impossible to analyse in terms of the details of the transition. The choice of a very simple ligand system with a small number of chemically distinct protons could be more productive and indeed some meaningful results

have been obtained from lineshape analysis for the relatively simple system $[\text{Fe}(\text{isoxazole})_6](\text{ClO}_4)_2$ [68]. More interesting and promising regarding detailed information of the ST mechanism seem to be the results of T_1 relaxation time measurements. The first attempts in this area were reported by Ozarowski et al. [69], who observed for example that in iron(II) compounds T_1 decreases with increasing distance of protons from the paramagnetic iron centre. A comparative detailed proton relaxation time study on $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ ($\text{ptz} = 1\text{-}n\text{-propyl-tetrazole}$) and its zinc analogue was reported later by Bokor et al. [70]. The authors plotted the measured T_1 relaxation times as a function of $1/T$ and found several minima, which they assigned to tunnelling (at low temperatures) and classical group rotations (at higher temperatures). The corresponding activation energies were derived from the temperature dependence of the NMR spectrum. In a later, similar NMR study the same research group measured the ^{19}F and ^{11}B relaxation times, T_1 , on the same iron and zinc compounds [71] and again found characteristic minima in different temperature regions of the $\ln T_1$ vs $1/T$ plot. They concluded that the SCO takes place in a dynamic environment and not in a static crystal lattice.

EPR spectroscopy has been employed in SCO research more often than the NMR technique. The reason is that for SCO compounds of iron(III) and cobalt(II), which are the most actively studied ones in this context, sufficiently well resolved characteristic spectra can be obtained in both HS and LS states. For iron(III) SCO compounds there is no spin-orbit coupling in the HS (^6S) state and thus the relaxation times are long. EPR signals appear at characteristic g values yielding characteristic ZFS parameters, D for axial and E for rhombic distortions. In the LS state of iron(III) ($^2\text{T}_2$) spin-orbit coupling does occur, but at low temperature the vibrations are slowed down and electron-phonon coupling becomes weak and therefore relaxation times are long. The result is that the EPR spectrum of the LS state of iron(III) exhibits a single line near $g \sim 2$ for a polycrystalline sample. Anisotropy effects can be observed via g_x , g_y , g_z in measurements on single crystals. Thus EPR spectroscopy can be an extremely valuable tool to reveal structural information, which may otherwise be inaccessible for a SCO system. Many examples have been reported, for example by Timken et al. [72] and Kennedy et al. [73]. Direct EPR studies on neat SCO compounds of cobalt(II) are also very informative [74]. As spin-orbit coupling in the HS state ($^4\text{T}_1$) shortens the spin-lattice relaxation times and makes signal recording difficult in the room temperature region, good EPR spectra of cobalt(II) SCO complexes in the HS state are usually obtained at the lowest possible temperatures, i.e. just above the transition temperature. No problem arises in the recording of the LS spectrum, even with an anisotropic g -pattern reflecting axial and rhombic distortion.

For high spin iron(II) spin-orbit coupling within the $^5\text{T}_2$ state leads to spin-lattice relaxation times so short that EPR spectra can only be observed

at 20 K or lower. The Fe(II) ion is coupled to its environment more strongly than any other $3d^n$ ion. However, doping the Fe(II) SCO complex with suitable EPR probes like Mn(II) or Cu(II), first reported by B.R. McGarvey and co-workers [75] for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ (2-pic=2-picolylamine) doped with 1% Mn(II) and later by Vreugdenhil et al. [76] for $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ doped with ca. 10% Cu(II), provides an alternative means of applying the technique by monitoring the changes in the signals of the guest species.

3.2.9

Other Techniques

Positron annihilation spectroscopy (PAS) was first applied to investigate $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ [77]. The most important chemical information provided by the technique relates to the ortho-positronium lifetime as determined by the electron density in the medium. It has been demonstrated that PAS can be used to detect changes in electron density accompanying ST or a thermally induced lattice deformation, which could actually trigger a ST [78].

The muon spin rotation (MuSR) technique was also first applied to the SCO complex $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ [79]. Two species with different spin relaxation functions and rates were observed above and below the ST temperature. Blundell and coworkers have recently reported on MuSR studies of a variety of molecular magnetic materials, among them an Fe(II) SCO compound [80]. They show that muons are sensitive to local static fields and magnetic fluctuations, and can probe the onset of long-range magnetic order. The SCO system under study, $[\text{Fe}(\text{PM-PEA})_2(\text{NCS})_2]$ (PM-PEA=N-(2'-pyridylmethylene)-4-(phenylethynyl)aniline), with π -stacking pm-pea molecules (see Chaps. 15, 30) shows Gaussian and root-exponential muon relaxation in the HS and LS phases, respectively. A combined MuSR and Mössbauer investigation on the SCO system $[\text{Fe}(\text{ptz})_6](\text{ClO}_4)_2$ shows that the two techniques are complementary in various respects [81]. The thermally induced spin transition is tracked via the temperature dependence of the initial asymmetry parameter as well as the relaxation rates. The spectral line broadening observed in the Mössbauer spectra at ca. 200 K is attributed to relaxation phenomena associated with the spin state transition. Dynamic processes are also detected by MuSR as revealed by the pronounced increase of the relaxation of a fast relaxing component above ca. 200 K. Muonium substituted radicals delocalized on the tetrazole ring have been identified from applied magnetic field MuSR experiments.

4 Iron(II) Systems

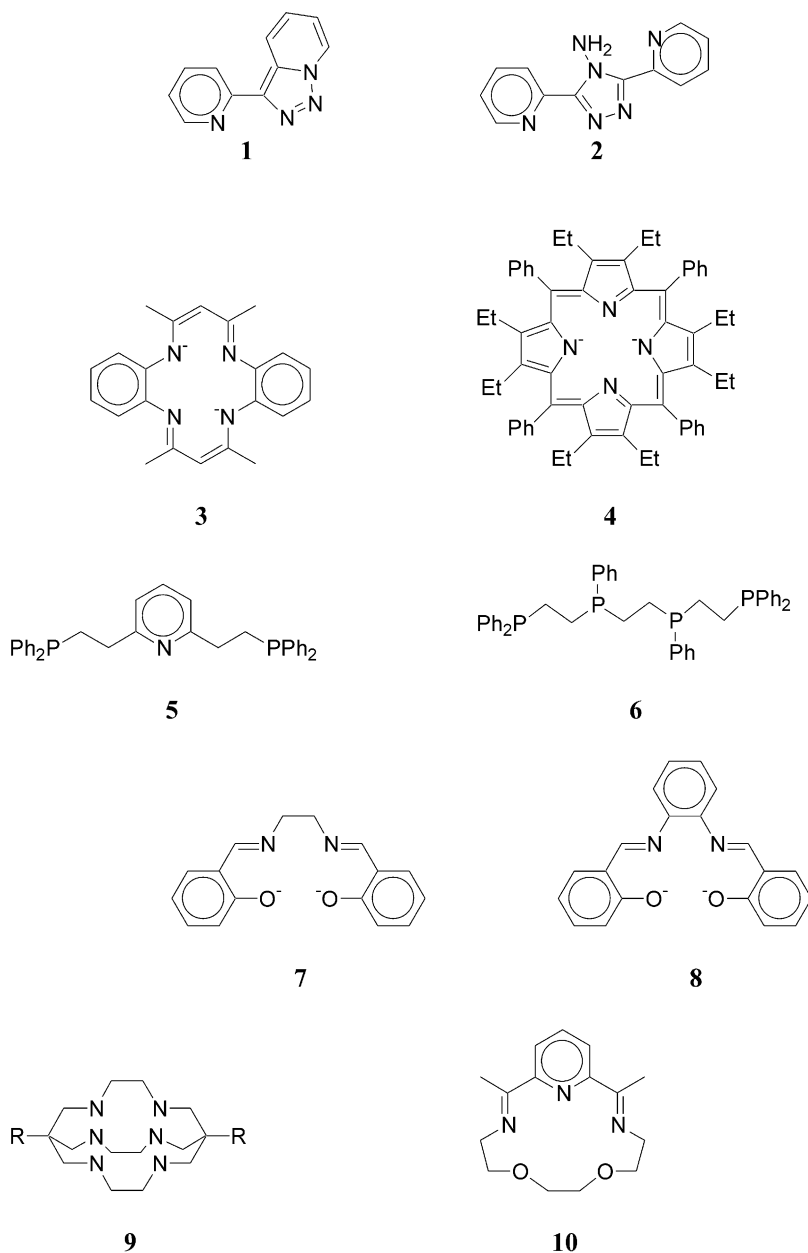
The early work in the spin crossover area quickly became focussed principally on iron(II) systems and was involved in establishing the conditions for spin crossover, its dependence on a number of chemical and physical perturbations and the bases for its theoretical interpretation. This work included the important thermodynamic studies of Sorai and co-workers [34, 35] which demonstrated that a low spin→high spin transition is an entropy driven process, a finding of great significance to the understanding of the behaviour of spin crossover systems, particularly in the solid state. It also follows from this work that it is the high spin state that is always favoured at high temperatures for a thermal transition. In addition, the studies of the dynamics of the spin inter-conversion processes in solution, pioneered by Beattie and co-workers [82], probed the mechanism of the spin changes. Two subsequent developments played a decisive role in a change of emphasis in research in the area. The first was the discovery that light irradiation at low temperatures of the low spin form of a solid spin crossover system generated a long-lived (at low temperatures) metastable form of the high spin species (the LIESST effect, see below and Chap. 17) [83]. This revealed a totally new facet of the spin crossover phenomenon and provided an indication of the likely interest in the phenomenon in photo-switching applications, as well as a means of probing the kinetics of the spin change in solid systems. The second major impetus for an upsurge in interest in the phenomenon was provided by Kahn and Launay [16] who highlighted the implications of the systems where the course of the spin transition follows the abrupt change together with associated hysteresis (Fig. 1c), i.e. those displaying a high degree of cooperativity. They drew attention to the existence of *bistability* associated with systems for which the transition is accompanied by hysteresis, i.e. the properties of a system under a given set of conditions depend on the previous history of the sample. This effectively confers a memory characteristic and highlights the potential for such systems in memory and display devices (developed in Chap. 30). This has led to an emphasis on understanding the origin of cooperativity associated with the transition and the synthesis of systems in which cooperativity is expected to be high.

4.1 [Fe(phen)₂(NCS)₂] and Related Systems

The first report [11] of a spin transition in a synthetic iron(II) system seems to be the result of a well-planned, deliberate strategy to identify the singlet/quintet crossover region by the systematic variation of the field strength of the anionic groups in the six-coordinate species [Fe(phen)₂X₂] [7]. One

member of this family, $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, has become one of the most thoroughly studied and characterised spin crossover systems and it remains of current interest, even from a theoretical viewpoint [84] (see also Chap. 29). It undergoes a very abrupt transition with a narrow hysteresis loop [85]. The structure has been determined above and below the transition temperature [86] as well as at ambient temperature and a pressure of 1 GPa [87]. In addition, the structure of the LIESST-generated metastable high spin species has been probed [88]. It has been the model compound for an extensive series of similarly constituted species. The important aspects of the structure of a series of such species are considered in Chap. 15. When the unusual temperature dependence of its magnetism was first reported it was ascribed to antiferromagnetism [89]. Mössbauer spectroscopy played a pivotal role in the ultimate confirmation of this as the first synthetic iron(II) spin crossover system since a doublet with parameters indicative of HS Fe(II) at room temperature and one characteristic of LS Fe(II) at liquid nitrogen temperature were observed [11]. The significant observation of the co-existence of the two doublets in the region of the transition temperature was reported soon afterwards [90].

The $[\text{Fe}(\text{diimine})_2\text{X}_2]$ model, of which $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ is the parent system, has been adapted in many ways, e.g. by replacement of phen with other diimine ligands, including bridging systems. The general retention of spin crossover behaviour in these modified species is extraordinarily widespread. The behaviour is also observed in related systems in which the anionic groups have been replaced, most commonly by the selenocyanate ion. The somewhat stronger field of this ligand, relative to that of NCS^- , usually results in a displacement of the transition to higher temperatures. In addition, crossover behaviour has been observed when $\text{X}=[\text{N}(\text{CN})_2]^-$ [29], $[\text{NCBH}_3]^-$ [91], TCNQ^- [92] and when $2\text{X}=\text{WS}_4^{2-}$ [93] or $\text{C}_2\text{O}_4^{2-}$ [94]. The majority of the monomeric systems have the *cis* configuration of the anionic groups, which would be favoured because of the steric interference from the hydrogen atoms of the two diimine species if they coordinated in a plane [95]. *trans*-Dianion monomeric structures are known but in these the diimines contain at least one coordinating five-membered heterocycle. The steric effects noted above for the *trans* arrangement are reduced considerably when five-membered rings are present because of their particular geometry. The *trans* configuration has been observed in $[\text{Fe}(\text{tzpy})_2(\text{NCS})_2]$ (tzpy=3-(2-pyridyl)[1,2,3]triazolo[1,5-a]pyridine (1) [96]



and in $[\text{Fe}(\text{abpt})_2\text{X}_2]$ (abpt)=4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (2) when $\text{X}=\text{TNCQ}^-$ [92], NCS^- or NCSe^- [97] and the dicyanamide ion, $\text{N}(\text{CN})_2^-$ [29]. For one system of this kind, in which the 4-amino group in abpt has been replaced by a 4-*p*-methylphenyl group a *trans* $[\text{FeL}_2(\text{NCS})_2]$ complex was obtained which showed SCO but replacement by a 4-*m*-methyl-

phenyl group gave a purely HS complex with the thiocyanate ions in *cis* positions [98].

The $[\text{Fe}(\text{diimine})_2\text{X}_2]$ system has been modified by replacing the diimines by unidentate nitrogen donors. $[\text{Fe}(\text{diimine})(\text{py})_2(\text{NCS})_2]$ is a crossover system when the diimine is 2,2'-bipyrimidine or phen [99] but $[\text{Fe}(\text{py})_4(\text{NCS})_2]$ is purely high spin [100]. However, $[\text{Fe}(\text{py})_4(\text{NCS})_2]$ systems containing substituted pyridine derivatives have been shown to exhibit thermal SCO [101], while 4,4'-bipyridine derivatives are able to bridge Fe(II) centres and form polynuclear structures containing SCO $[\text{Fe}(\text{py})_4(\text{NCS})_2]$ centres [102]. SCO is maintained in certain instances when the diimines are replaced by an N_4 quadridentate [103, 104].

4.2

The Involvement of an Intermediate Spin State

Early in the characterisation of $[\text{Fe}(\text{diimine})_2\text{X}_2]$ species the involvement of a triplet state was proposed. The deep red species formulated as $[\text{Fe}(\text{phen})_2(\text{ox})]$ (ox=the oxalate ion) and several closely related complexes were reported as having an intermediate, essentially temperature-independent magnetic moment, and a Mössbauer spectrum showing only a single doublet with small quadrupole splitting and low isomer shift. This was interpreted as being due to a triplet spin state for iron(II) [105]. The Tanabe-Sugano diagram for octahedral d^6 species shows that the triplet $^3\text{T}_1$ state can never be the ground state (Chap. 2, Fig. 2). Nevertheless, the difference in energy between it and the ground state is a minimum in the region of the quintet $\leftrightarrow$ singlet crossover. If the coordination environment were considerably distorted from O_h symmetry then it was considered that splitting of the $^3\text{T}_1$ triplet state may bring the energy of the $^3\text{A}_2$ component below that of the quintet or singlet and it could in fact become the ground state for a system in which the ligand field is close to that at the crossover [106]. A violet form of $[\text{Fe}(\text{phen})_2(\text{ox})]$ pentahydrate was subsequently prepared by a quite different procedure and shown to undergo a normal singlet $\leftrightarrow$ quintet transition [94]. The originally reported $[\text{Fe}(\text{phen})_2(\text{ox})]$ and other related systems were later shown to be salt-like species containing a low spin iron(II) complex cation, e.g. $[\text{Fe}(\text{phen})_3]^{2+}$ and a high spin iron(III) complex anion, e.g. $[\text{Fe}(\text{ox})_3]^{3-}$ [107]. There have been several other instances over the years where the involvement of a triplet state in six-coordinate iron(II) has been invoked to explain apparently anomalous results [108]. Singlet $\leftrightarrow$ triplet transitions, and also a singlet $\leftrightarrow$ triplet $\leftrightarrow$ quintet (double mode) transition have been proposed for six-coordinate adducts of the neutral iron(II) complex of the macrocyclic di-anion **3** [109]. The involvement of the triplet state has not been unequivocally demonstrated in any of these instances.

An early report [110] of the occurrence of a singlet $\leftrightarrow$ triplet transition in an apparently six-coordinate complex has recently been shown to be a fur-

ther example of a system containing a low spin iron(II) cation together with a high spin iron(III) anion, the latter being oxo-bridged and antiferromagnetism accounting for the nature of the temperature dependence of the magnetism [111].

An intermediate spin state (a quartet) has been proposed as being involved in transitions involving six-coordinate iron(III) derivatives of substituted dithiocarbamates but again definitive evidence is lacking [112]. Somewhat more convincing evidence exists for a doublet $\leftrightarrow$ quartet transition in a mixed ligand complex of iron(III) containing a macrocyclic quadridentate and a 1,2-benzenedithiolato ligand. In this instance EPR and Mössbauer spectral evidence supported the involvement of a quartet state [113]. The occurrence of a doublet $\leftrightarrow$ quartet transition in the pyridine and 4-cyanopyridine adducts of the cationic iron(III) complex of the dianion of octaethyl-tetraphenyl-porphyrin **4** is well documented by structural, EPR and Mössbauer studies. The Mössbauer spectrum of the 4-cyanopyridine adduct in particular clearly reveals separate spectral contributions with parameters indicative of the two spin states. The axial field in these systems is weak, leading to much longer Fe-N_{axial} (2.201 Å) than Fe-N_{equatorial} (1.985 Å) bonds (measured for the pyridine adduct at 298 K), and it is this distortion which renders the quartet state accessible [114].

4.3

Five-Coordination and Intermediate Spin States

An intermediate spin state is feasible for five-coordinate iron(II) and there are isolated instances of its involvement in spin crossover. On the basis of spectral and other data Nelson and co-workers assigned a distorted trigonal-bipyramidal structure to the complexes [Fe **5** X₂] (**5** is the tridentate bis(2-diphenylphosphinoethyl)pyridine) [115]. When X=Cl[−] or Br[−] the species are high spin but when X=I[−] the observed temperature dependence of the magnetism was ascribed to a triplet $\leftrightarrow$ quintet transition. There were no crystal structure data for these systems. Bacci and co-workers proposed a singlet $\leftrightarrow$ triplet transition to account for the strongly temperature dependent magnetic moment of [Fe **6** Br]BPh₄·CH₂Cl₂ (**6** is the quadridentate hexaphenyl-1,4,7,10-tetraphosphadecane). Structural data show that this complex cation has a distorted trigonal-bipyramidal structure and an observed decrease in the Fe–P distances at low temperatures supports the occurrence of a spin transition [116]. Mössbauer and EPR spectral data are consistent with this, but the observation of only one Mössbauer doublet indicates, unusually for iron(II), rapid interconversion of the spin states [117].

An intermediate spin state (a quartet ⁴A₂) similarly is feasible for five-coordinate iron(III) though, as pointed out by Kahn [118], the situation may be more complex. If the states are close in energy then they can interact through spin-orbit coupling to give a so-called spin-admixed ground state.

The extent of this mixing has been correlated with the relative field strengths of axial ligands in tetragonal systems [119]. A doublet $\leftrightarrow$ quartet transition was proposed very early for the nitric oxide adduct of the iron(II) complex of salen (salen is the essentially planar dianion of 1,2-bis(salicylideneimino)ethane (7)) [120]. The very abrupt nature of the transition was noted and in later detailed Mössbauer spectral studies of this and related systems the transition was found to be associated with hysteresis [121]. Interestingly, when salen is replaced by the closely related but more highly conjugated 1,2-bis(salicylideneimino)benzene (8), rapid inter-conversion of the spin states relative to the Mössbauer time scale is observed [122].

There have been other reports of transitions in related iron(III) systems [123] as well as in five-coordinate adducts of bis(ethylenedithiolato)iron(III) derivatives [124]. Remarkably, in these latter systems the transitions occur at extremely low temperatures and their observation at such temperatures is an indication of the relatively rapid inter-conversion of the spin states compared to iron(II) systems for which thermally-driven transitions are only rarely encountered below liquid nitrogen temperature.

4.4

Donor Atom Sets

The majority of the $[\text{Fe}(\text{diimine})_2\text{X}_2]$ systems contain an FeN_6 coordination centre and this is the most widely occurring iron(II) chromophore among spin crossover systems. It is found, for example, in systems in which the coordination is provided by six unidentate donors, most of these being five-membered heterocycles. The most important in this category is the series of $[\text{Fe}(\text{alkyltetrazole})_6]\text{X}_2$ salts [125]. These and other hexakis(azole)iron(II) systems are considered by van Koningsbruggen in Chap. 5. Salts of the $[\text{Fe}(\text{py})_6]^{2+}$ ion are high spin, but there is an intriguing report of a colour change in the hexafluorophosphate salt when it is cooled [126]. This is a system which may reward further attention, particularly pressure studies. Chelated systems are prevalent for bidentate and tridentate groups, the tris(2-picolyamine)iron(II) system in particular having played a prominent role in the development of SCO research [127]. 2-Picolyamine can be considered an intermediate between the purely aliphatic ethylenediamine which gives a HS complex [128], and the aromatic system 2,2'-bipyridine which gives a LS complex. The strong field bipyridine, 1,10-phenanthroline and terpyridine systems have been modified in various ways so as to lead to SCO in iron(II) (Chap. 3). Various multidentate chelate groups have been incorporated into SCO systems, discussed in Chap. 6. SCO was reported quite early for $[\text{FeN}_6]^{2+}$ systems containing sexadentate groups [129], but perhaps the most remarkable example is the cage-like species derived from the encapsulating hexa-amine **9** [130]. This last example, along with salts of the bis(1,4,7-triazacyclononane)iron(II) ion [131] represent the few instances of

spin crossover in an iron(II) $[\text{FeN}_6]^{2+}$ system in which all the nitrogen donors are part of an aliphatic system.

Donor atom sets other than N_6 are known for six-coordinate iron(II) SCO systems. These include N_4O_2 [132, 94] N_4S_2 [133] P_4Cl_2 and P_4Br_2 [19]. There are two examples of the potentially quinquedentate ligand **10** coordinated to iron(II) together with two cyanide ions, giving a seven-coordinate complex in which the donor atom set is $\text{N}_3\text{O}_2\text{C}_2$ [134]. In a recent report the cyanide ions were shown to be able to bridge iron(II) to manganese(II) but the iron(II) centre retains SCO behaviour [135].

5 Perturbation of SCO Systems

5.1 Chemical Influences

5.1.1 Ligand Substitution

Substitution within a ligand may alter drastically the spin state of a system. This is illustrated by the effects of substitution within LS $[\text{Fe}(\text{phen})_3]^{2+}$. Incorporation of a methyl group into the 2-position of phenanthroline results in spin crossover behaviour. This is essentially a steric effect—the close approach of the N_{methyl} donor to the metal atom is hindered and also the methyl groups introduce inter-ligand repulsions. Both effects de-stabilise the singlet state of the complex [136]. A similar effect is caused by a 2-methoxy substituent but in this instance the destabilisation of the singlet state is not so great [137]. On the other hand the bulk of a chloro substituent, coupled with its electron-withdrawing tendency, renders the singlet state inaccessible [138]. This is a form of electronic fine-tuning which could obviously be extended. A similar effect is noted for the $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ system. This shows SCO but $[\text{Fe}(\text{mephen})_2(\text{NCS})_2]$ is purely high spin [139]. On the other hand in $[\text{Fe}(4\text{-mephen})_2(\text{NCS})_2]$ or even $[\text{Fe}(4,7\text{-dimephen})_2(\text{NCS})_2]$, where the substituents present no steric barrier to coordination, SCO behaviour is retained [140].

Substitution of one ligand by another can generate, or alter, spin crossover characteristics. The systems studied early provide the classic illustration of this effect. Thus $[\text{Fe}(\text{py})_4(\text{NCS})_2]$ is high spin at room temperature and does not undergo a thermal spin transition. Substitution of two of the pyridine molecules by a phenanthroline molecule gives $[\text{Fe}(\text{phen})(\text{py})_2(\text{NCS})_2]$ which does undergo a thermal transition [99, 141], as does the species in which the remaining two pyridines are substituted $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$. As would be expected, $T_{1/2}$ for the former complex (106 K) is lower

than that for the latter (176 K). Replacement of the two thiocyanato groups by phenanthroline produces the totally low spin complex cation $[\text{Fe}(\text{phen})_3]^{2+}$. Their replacement by the strong field cyanide ion or the weak field chloride ion produces purely LS $[\text{Fe}(\text{phen})_2(\text{CN})_2]$ or purely HS $[\text{Fe}(\text{phen})_2\text{Cl}_2]$, respectively [7].

5.1.2

Anion and Solvate Effects

A more subtle chemical influence is the variation of the anion associated with a cationic spin crossover system, or of the nature and degree of solvation of salts or neutral species. These variations can result in the displacement of the transition temperature, even to the extent that SCO is no longer observed, or may also cause a fundamental change in the nature of the transition, for example from abrupt to gradual. The influence of the anion was first noted for salts of $[\text{Co}(\text{trpy})_2]^{2+}$ [142] and later for iron(II) in salts of $[\text{Fe}(\text{paptH})_2]^{2+}$ [143] and of $[\text{Fe}(\text{pic})_3]^{2+}$ [127]. For the $[\text{Fe}(\text{pic})_3]^{2+}$ salts the degree of completion and steepness of the ST curve increases in the order iodide < bromide < chloride.

The nature of the solvate molecule in $[\text{Fe}(\text{pic})_3]\text{Cl}_2\cdot\text{solv}$ determines the transition temperature. For the ethanol, methanol and water solvates SCO is observed but there is an increasing stabilisation of the singlet state in the order given [144]. The effect of dehydration on the properties of $[\text{Fe}(\text{paptH})_2](\text{NO}_3)_2\cdot\text{H}_2\text{O}$ is a marked stabilisation of the quintet state and a fundamental change from a gradual transition above room temperature to one accompanied by hysteresis below room temperature [26]. There are many other similar examples in the literature. The effects of the anion and solvation are, however, not always consistent from one system to another and are not readily predictable. In some instances correlations between anion size and transition temperature have been proposed [145] but the generality of this association has not been established. Replacement of the anion or solvent molecule is expected to modify the lattice phonon distribution resulting from different crystal packing geometry or strength of the intermolecular forces. In addition, changes in the chemical composition of the lattice could impose different degrees of “chemical pressure” (also known as “image pressure”) on the spin transition centres and thereby influence the transition temperature. Hydrogen bonding can be a major influence on both the transition temperature (in part at least through a relayed effect on the ligand field strength) and the nature of the transition, providing the structural links for communication between the SCO centres. Thus the extent to which an anion or solvate molecule can hydrogen bond with the SCO centre will likely influence the nature of the transition.

The importance of hydrogen bonding on the SCO behaviour of the tris(picolyamine)iron(II) system was investigated through the effect of iso-

topic exchange (H/D and $^{14}\text{N}/^{15}\text{N}$) in various positions of the ligand and the solvent molecules [146, 147]. Significant changes in the ST curve were observed only when the isotopic substitution took place in positions directly involved in the hydrogen bonding network interconnecting the iron(II) complex molecules. As an example, for the picolylamine complex chloride with $\text{C}_2\text{H}_5\text{OD}/\text{ND}_2$ the ST curve is shifted by ca. 15 K to higher temperatures and no longer shows a step in contrast to the natural system with $\text{C}_2\text{H}_5\text{OH}/\text{NH}_2$. The deuterated positions are in this case both constituents of the hydrogen bonding network. On the other hand, the ST curve of the deuterated system with $\text{C}_2\text{D}_5\text{OH}/\text{NH}_2$, hardly differs from that of the natural compound. In this instance the deuterated positions are located in the ethyl group of the solvent molecule only, and this group is peripheral to the hydrogen bonding pathway.

Hydrogen bonding also seems to play a significant role in changes in SCO behaviour accompanying hydration/dehydration processes. It has been proposed that hydration will generally result in a stabilisation of the LS state, through hydrogen bonding of the water with the ligand [148]. This does indeed seem to be the case for most hydrates, but in a cationic SCO system where the ligand is hydrogen bonded to the associated anion *only* and this in turn is bonded to the water the effect can be the reverse, i.e. *loss* of water can also result in stabilisation of the LS state [149]. Whatever the rationale for the effects, it is clear that variation in the anion or the solvation is a very readily accessible, if not entirely predictable, means of potentially modulating the transition temperature or the nature of the transition.

5.1.3

Metal Dilution

The effect of dilution of spin transition complexes into the lattice of isostructural species which do not or cannot show SCO has proved to be very diagnostic of the function of cooperative interactions in influencing the nature of spin crossover in solids. This was shown first for the mixed crystal series $[\text{Fe}_x\text{Zn}_{1-x}(\text{2-pic})_3]\text{Cl}_2\cdot\text{EtOH}$, with x ranging from 0.007 to 1 [150]. The transition curve is abrupt for the neat compound ($x=1$), but becomes increasingly more gradual with increasing dilution, approaching that indicative of a Boltzmann distribution over all spin states, as is generally found for thermal ST in liquid solutions (Fig. 1a). Moreover, the transition is shifted to lower temperatures, reflecting increasing stabilisation of the HS state. These results clearly support the existence of cooperative elastic interactions between the SCO metal centres as the transition proceeds. The nature of such cooperative interactions is purely mechanical. In a qualitative description, if the spin state in a particular metal centre changes from LS to HS, the molecular volume increases (by $\sim 3\text{--}5\%$) leading to an expansion of the lattice and this causes a change of the “chemical pressure” acting on all complex mole-

cules in the crystal. This facilitates further spin state changes in other centres. With decreasing iron concentration in a crystal diluted with zinc complex molecules, however, the crystal volume change per iron complex decreases, and thus the chemical pressure also decreases. This results in the observed increasingly gradual (less cooperative) nature of the transition and its displacement to lower temperatures. The importance of these elastic interactions is developed by Spiering in Chap. 28.

A different and rather remarkable illustration of the effect of metal dilution has recently been reported. In $[\text{Fe}(\text{trpy})_2](\text{ClO}_4)_2$ ($\text{trpy}=2,2':6',2'$ -terpyridine) the complex cation is low spin, as it is in all its known salts, but when it is incorporated into the lattice of the corresponding manganese(II) species as $[\text{Fe}_{0.02}\text{Mn}_{0.98}(\text{trpy})_2](\text{ClO}_4)_2$ the high spin state can be generated by irradiation at low temperature. This metastable state undergoes thermal relaxation to the stable low spin state at elevated temperatures but has a lifetime of the order of several days at $T < 20$ K, reminiscent of the LIESST effect [151]. A thermally induced transition is not observed for the diluted system and the neat compound shows no evidence for the LIESST effect. This result is not in accord with the “inverse energy gap law”, which would predict for this strong ligand field a much shorter lifetime for the LIESST state by ca. eight orders of magnitude [152]. Clearly, this unexpected but significant observation is not a manifestation of the normal LIESST effect. In this instance the smaller $[\text{Fe}(\text{trpy})_2]^{2+}$ ion experiences a negative chemical pressure within the host lattice of the larger $[\text{Mn}(\text{trpy})_2]^{2+}$ ion and this would be expected to increase the accessibility of the quintet state for the iron species. These results do bear some relevance to the much earlier report that, while pyrites, FeS_2 , is a low spin species, when iron(II) is incorporated into the corresponding disulfide of manganese the iron is high spin, but a pressure-induced transition to low spin was detected by Mössbauer spectroscopy [153].

5.2

Physical Influences

5.2.1

Sample Condition

Mechanical treatment of samples or different synthetic procedures have been shown to influence strongly SCO behaviour. The first observation of the effect of grinding a sample was reported by Hendrickson et al. for an iron(III) SCO complex [154]. This resulted in the flattening of the ST curve with an increase of the residual HS fraction at low temperatures. Similar effects were later observed in other systems. The SCO characteristics may also be influenced by the synthetic procedure, as illustrated for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$. This can be prepared in two principal ways: by precipitation from methanol or by extraction with acetone of a phen molecule from $[\text{Fe}(\text{phen})_3](\text{NCS})_2 \cdot \text{H}_2\text{O}$

[155]. The samples prepared by both methods have the same chemical formula, but exhibit different SCO behaviour. The compound obtained by the first method shows a smooth ST with a significant HS fraction at low temperature, whereas that prepared by the second undergoes a sharp and complete spin transition [85]. The origin of these effects stems from crystal quality considerations, in particular crystal defects introduced during sample preparation either by milling (sheared deformations) or rapid precipitation, the size of the particles playing a minor role. In some cases, polymorphism has also been invoked to account for a difference in the observed magnetic properties. It was assumed to be relevant for $[\text{FeL}_2(\text{NCS})_2]$ ($\text{L}=\text{phen}$, bpy) [156] and later clearly demonstrated for $[\text{Fe}(\text{dppa})(\text{NCS})_2]$ ($\text{dppa}=(3\text{-aminopropyl})\text{bis}(2\text{-pyridylmethyl})\text{amine}$) [104], three polymorphic modifications being identified by X-ray analysis. Two polymorphs, with different space groups, have been characterised for the related complex $[\text{Fe}(\text{PMBiA})_2(\text{NCS})_2]$ ($\text{PMBiA}=\text{N}-(2\text{-pyridylmethylene})\text{aminobiphenyl}$). The method of isolation (slow or fast precipitation together with variations in the concentrations of reactants) determined the structure of the complex isolated. Each of the two phases isolated show distinct SCO behaviour, that of the phase obtained by slow precipitation being abrupt with a narrow hysteresis loop, and that of the phase obtained by rapid precipitation being gradual [157].

5.2.2

Effect of Pressure

The discussion above has been directed principally to thermally induced spin transitions, but other physical perturbations can either initiate or modify a spin transition. The effect of a change in the external pressure has been widely studied and is treated in detail in Chap. 22. The normal effect of an increase in pressure is to stabilise the low spin state, i.e. to increase the transition temperature. This can be understood in terms of the volume reduction which accompanies the high spin $\rightarrow$ low spin change, arising primarily from the shorter metal-donor atom distances in the low spin form. An increase in pressure effectively increases the separation between the zero point energies of the low spin and high spin states by the work term $P\Delta V$. The application of pressure can in fact induce a transition in a HS system for which a thermal transition does not occur. This applies in complex systems, e.g. in $[\text{Fe}(\text{phen})_2\text{Cl}_2]$ [158] and also in the simple binary compounds iron(II) oxide [159] and iron(II) sulfide [160]. Transitions such as those in these simple binary systems can be expected in minerals of iron and other first transition series metals in the deep mantle and core of the earth.

Increase in pressure can affect SCO systems in ways less obvious than the displacement of the transition temperature to higher values. For example, the width of a hysteresis loop, evident in a thermal transition, changes with

application of pressure [161]. A general flattening-out of a transition is also usually observed, with increasing residual fractions of low spin and high spin species at the extremities of the transition. There are even examples where an increase in pressure results in a reversal of the normal stabilisation of the low spin state. In a recent example of this effect it has been ascribed to a pressure-induced phase change, the transition temperature in the new phase being the lower [162].

Somewhat unusual pressure dependence of the nature of the spin transition curve has been found for chain-like SCO systems containing substituted bridging triazole ligands [163, 164]. Although the transition is displaced to higher temperatures with increase in pressure, the shape of the transition curve, unusually, is effectively constant, i.e. there is no significant change in the hysteresis width and the transition remains virtually complete. This has been taken to indicate that the cooperativity associated with the transitions in these and related systems is confined within the iron(II) triazole chains.

5.2.3

Effect of Irradiation

One of the most important developments in spin crossover research was the report that the equilibrium existing between high spin and low spin species in solution could be perturbed by pulsed laser irradiation into the charge transfer band of the low spin species, resulting in bleaching of this absorption and the subsequent rapid decay of the photo-induced high spin species back to the equilibrium conditions [165]. Shortly after this it was shown that irradiation of an SCO system in the solid state at low temperature similarly induced partial or complete conversion of a low spin to a high spin state. Moreover, the metastable high spin state so formed had a virtually infinite lifetime provided the temperature was maintained sufficiently low. This solid state effect became known as the LIESST effect (Light Induced Excited Spin State Trapping) [83, 166]. The subsequent discovery [167] of the effect of irradiation with light of longer wavelength in pumping the metastable high spin species back to the thermodynamically stable low spin species (known as “reverse-LIESST”) highlighted the potential for exploitation of the spin crossover phenomenon in optical switching, storage and memory devices. A novel demonstration of the LIESST effect has recently been reported where the excitation and detection were provided by the one technique, Raman spectroscopy [168]. These topics are taken up by Hauser in Chap. 17 and by McGarvey and co-authors in Chap. 21. A related and more recent development has been the generation of metastable high spin species by irradiation of a low spin species at ~45 K ($[\text{Fe}(\text{phen})_2(\text{NCX})_2]$ X=S, Se) with soft X-rays [169]. When the temperature is raised to 80 K thermal relaxation to the LS state occurs, as expected from LIESST experiments. This phenomenon, called Soft X-ray Induced Excited Spin State Trapping (SOXIESST), occurs at

much higher energy than the LIESST effect, though the two are closely related.

Preceding the reports of the effect of irradiation with visible light were the studies of the products of nuclear decay of ^{57}Co labelled coordination compounds, identified by measurement of Mössbauer emission spectra. In these studies the transient effects of nuclear decay were monitored and it was found that metastable high spin states of $^{57}\text{Fe(II)}$ in the corresponding compounds were produced in instances where the Fe(II) complex possessed a low spin ground state under normal conditions [170]. Over the years these studies have been extended and the relationship between the effects observed with nuclear decay as the intrinsic molecular excitation source and those associated with the LIESST effect has come to be recognized and hence the term NIESST (Nuclear decay-Induced Excited Spin State Trapping) has been adopted. This topic is considered fully by Gütllich in Chap. 19.

With the aim of obtaining optical switching of spin states at or near ambient temperature, Boillot and co-workers have devised an ingenious process called ligand driven light induced spin change (LD-LISC), discussed in detail in Chap. 20. The mechanism of this exploits ligands containing potentially photo-isomerisable groups. The first studies were directed to *cis-trans* photo-isomerisation about an olefinic linkage incorporated into a ligand such as 4-styryl-pyridine (stpy) coordinated to iron in the SCO system $[\text{Fe}(\text{stpy})_4(\text{NCBPh}_3)_2]$ [171]. The complex containing the ligand in the *trans* configuration exhibits an abrupt ST at 190 K, whereas the *cis* derivative remains HS upon cooling. The primary photo-induced isomerisation in the ligand causes a change of the ligand field strength at the iron centre as a secondary step. In general for these systems, in the temperature region where the *spin states of the two isomers differ*, the photo-isomerisation of the ligand directly results in SCO behaviour at the metal centre. In a system in which the isomerisable moiety has been incorporated into 2,2'-bipyridine the triggering of the spin change can be accomplished at room temperature [172]. LD-LISC has so far been observed only for liquid solutions. In the solid state the very pronounced re-organisation of the complex molecules accompanying *cis-trans* isomerisation together with spin state change presumably cannot be readily accommodated by the lattice. This limitation may eventually be overcome by embedding such compounds in a soft matrix such as Langmuir-Blodgett films [173].

Several other light-induced phenomena associated with spin transition systems have recently been reported. These include light induced thermal hysteresis (LITH), which is another example of light induced bistability, discovered for the SCO compound $[\text{Fe}(\text{PMBiA})_2(\text{NCS})_2]$ which undergoes a very abrupt thermal ST around 170 K with hysteresis [174]. Irradiation of the sample at 10 K with green light resulted in the population of the LIESST state. When the temperature was raised to 100 K and lowered back to 10 K under continuous irradiation a wide thermal hysteresis loop resulted. The

same effect was also observed on the mixed crystal system $[\text{Fe}_{1-x}\text{Co}_x(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ with $x=0.3; 0.5; 0.85$ [175]. Desaix et al. have rationalised this effect in terms of the influences of cooperativity on the dynamics of the spin state change [176].

A new photophysical effect, light perturbed thermal hysteresis (LiPTH) was recently found for $[\text{Fe}(\text{phy})_2](\text{BF}_4)_2$ [177]. This compound shows a crystallographic phase transition [178] and undergoes an abrupt ST near room temperature with an associated hysteresis loop. Continuous irradiation with green light during heating and cooling modes in the region of the thermal ST lowers the transition temperatures by ca. 10 K. This observation has been modelled analogously to the theoretical description of the LITH effect. These and other novel optical effects resulting from continuous irradiation are discussed by Varret and co-workers in Chap. 18.

5.2.4

Effect of a Magnetic Field

Perturbation of a spin transition by an external magnetic field is predicted by thermodynamics and the magnitude of the change in transition temperature can be calculated if the magnetic response of the molecules involved is known, which for SCO materials is the susceptibility of the two spin states. A decrease of the transition temperature in an applied magnetic field B is expected because of the decrease in energy of the molecules in the HS state by their magnetic moment $\mu_{\text{HS}} = \chi B$. When the energy shift $-1/2 \chi B^2$ is added to the free energy, the displacement of the transition temperature $\Delta T_{1/2}$ can be calculated as: $\Delta T_{1/2} = -\chi B^2 / 2 \Delta S(T_{1/2})$, where $\Delta S(T_{1/2})$ is the entropy difference between HS and LS states at the transition temperature. Qi et al. [179] were the first to investigate this and measured the shift of the transition curve for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ in an applied magnetic field of 5.5 Tesla. The observed shift of $-0.10(4)$ K was in agreement with the predicted value. More recently, Bousseksou et al. [180] have studied the effect for the same system by the application of an intense, pulsed magnetic field of 32 Tesla, which corresponds to an expected temperature shift at $T_{1/2}$ of 2.0 K. In addition they have reported the effect of a pressure pulse on γ_{HS} within the hysteresis loop of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and this has the expected opposite effect to a magnetic pulse [181]. Their work is considered in detail in Chap. 23.

6

Theoretical Interpretation

There has always been a drive to understand the theory relating to the course of a spin transition. A sound model that can reproduce this can be applied to extract useful data relating to the energetics, dynamics and mech-

anism of transitions, and to have predictive value. A basic model was proposed by Bozza soon after the initial reports by Cambi and co-workers of the spin transitions in the iron(III) dithiocarbamate systems [182]. In their later studies of these systems Ewald et al., recognising the significance of the changes in metal-donor atom distances accompanying a spin change, incorporated the vibrational partition coefficients of the two spin states into a model which was based essentially on a Boltzmann type distribution over all the electronic states, allowing for spin-orbit coupling and Zeeman effects [8]. As research on different spin transition systems developed it became evident that any model had to take into account the large vibrational entropy contribution to the transition as well as the highly cooperative nature of many transitions for solid samples, manifested in the appearance of associated hysteresis. It is now commonly accepted that the presence of both short-range and long-range cooperative interactions are responsible for any significant deviation from a Boltzmann-like ST curve, $\gamma_{\text{HS}}(T)$, irrespective of the dimensionality (mononuclear, chains, layers, or 3-D) of the ST system or of special bonding interactions such as hydrogen bonding and π -stacking.

Various treatments were developed to incorporate interaction between the spin transition centres by Chesnut [183], Wajnsflasz [184], Slichter and Drickamer [185], Bari and Sivardi re [186] and Zimmermann and K nig [187]. In addition, a model, introduced by Sorai and Seki, in which clusters or domains of n molecules, assumed to be completely in the LS or in the HS state, were considered in thermal equilibrium without interactions between the clusters. The cluster size n was treated as a measure for the steepness of the ST curve [46]. The Everett model for hysteresis has been applied to SCO systems with the aim of elucidating the independence or otherwise of domains [188]. The results have been inconclusive. The diagnostic theorem of Everett in this regard is that which states that the areas of inner hysteresis loops produced by scanning between two fixed temperatures within the boundaries of the principal hysteresis loop should be equal, provided that the domains are independent. In the initial report of application of this approach to the system $[\text{Fe}(\text{phy})_2](\text{ClO}_4)_2$ it was found that the areas of two appropriate inner loops were equal to within 3% and hence it was concluded that independent domains do exist [55]. Similar results were reported for $[\text{Fe}(\text{bt})_2(\text{NCS})_2]$ (bt=2,2'-bi-2-thiazoline) [189]. A more extensive study of the areas of relevant inner hysteresis loops constructed for $[\text{Fe}(\text{bpp})_2](\text{BF}_4)_2$ (bpp=2,6-bis(pyrazol-3-yl)pyridine) showed that these were not equal in this instance and this prompted a more detailed examination of the hysteresis in both $[\text{Fe}(\text{phy})_2](\text{ClO}_4)_2$ [190] and $[\text{Fe}(\text{bt})_2(\text{NCS})_2]$ [191]. For the former system, the areas of an extensive range of inner loops showed wide variation. Hence it could be concluded that independent domains were not present but an involvement of domains of like spin molecules could not be excluded. For $[\text{Fe}(\text{bt})_2(\text{NCS})_2]$, on the other hand, the initial observation of equal areas of two appropriate inner loops was found to hold also when the number of

such loops was considerably greater. König et al. [191] noted that the transition in $[\text{Fe}(\text{bt})_2(\text{NCS})_2]$ was particularly abrupt and highly symmetrical, more so than those in the phy and bpp systems, and this led them to suggest that the Everett model may be applicable only to such abrupt and highly symmetrical ones. A recent attempt to obtain direct evidence for the presence of domains of like-spin molecules by deriving spatially resolved spin transition curves has indicated that, if domains are present, they must be smaller than ca. $1\ \mu\text{m}$ [192].

Kambara presented a ligand field theoretical model for SCO in transition metal compounds which is based on the Jahn-Teller coupling between the d-electrons and local distortion as the driving force for a spin transition [193]. The author applied this model also to interpret the effect of pressure on the ST behaviour in systems with gradual and abrupt transitions [194]. By considering the local molecular distortions dynamically this model turned out to be suited to account for cooperative interactions during the spin transition [195].

The theory later developed by Spiering and co-workers [24, 196] takes as its basis changes of volume, shape, and elasticity of the lattice as the main factors influencing the cooperative interactions. This “model of lattice expansion and elastic interactions” has been developed further and is described in detail by Spiering in Chap. 28.

Monte Carlo calculations have been carried out to simulate the spin transition behaviour in both mono- and dinuclear systems [197]. The stepwise transition in $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2\cdot\text{EtOH}$ as well as its modification by metal dilution and application of pressure have been similarly modelled by considering short- and long-range interactions [52, 198, 199]. An additional study of the effect of metal dilution was successfully simulated with the Monte Carlo treatment considering direct and indirect inter-molecular interactions [200]. A very recent report deals with the application of the Monte Carlo method to mimic short- and long-range interactions in cooperative photo-induced LS→HS conversion phenomena in two- and three-dimensional systems [201].

7 Literature

The literature in the SCO field has grown enormously over the past ten years or so. Much of the new material, as well as the older, has been treated in review articles and since these form a very valuable resource, attention is drawn to them here. They are listed below chronologically with their titles.

Barefield, Busch and Nelson (1968) Iron, cobalt and nickel complexes having anomalous magnetic moments [202].

König (1968) Some aspects of the chemistry of bis(2,2'-bipyridyl) and bis(1,10-phenanthroline) complexes of iron(II) [203].

Martin and White (1968) The nature of the transition between high spin and low spin octahedral complexes of the transition metals [204].

Sacconi (1971) Conformational and spin state interconversions in transition metal complexes [205].

Machado (1971–1972) Spin transitions in six-coordinate complexes [206].

Sacconi (1972) The influence of geometry and donor-atom set on the spin state of five-coordinate cobalt(II) and nickel(II) complexes [207].

Drickamer and Frank (1973) Spin changes in iron complexes [208].

Drickamer (1974) Electronic interconversions in transition metal complexes at high pressure [209].

Goodwin (1976) Spin transitions in six-coordinate iron(II) complexes [210].

Sorai (1977) Spin transition in crossover complexes [211].

Gütlich (1979) Mössbauer spectroscopic studies of spin crossover compounds [212].

Drabent and Wajda (1980) Spin equilibrium in six-coordinate iron(II) complexes [213].

Gütlich (1981) Spin crossover in iron(II) complexes [214].

Gütlich (1981) Recent investigations of spin crossover [215].

Scheidt and Reed (1981) Spin-state/stereochemical relationships in iron porphyrins: implications for the hemoproteins [216].

Gütlich (1984) Spin transition in iron complexes [147].

Gütlich (1984) Spin transition in iron compounds [217].

König, Ritter and Kulshreshtha (1985) The nature of spin state transitions in solid complexes of iron(II) and the interpretation of some associated phenomena [54].

Rao (1985) Phase transitions in spin crossover systems [218].

Decurtins, Gütlich, Hauser and Spiering (1987) Light-induced excited spin state trapping [219].

Gütlich (1987) Spin transition in iron(II) complexes induced by heat, pressure, light and nuclear decay [220].

König (1987) Structural changes accompanying continuous and discontinuous spin state transitions [221].

Bacci (1988) Static and dynamic effects in spin equilibrium systems [222].

Beattie (1988) Dynamics of spin equilibria in metal complexes [223].

Kahn and Launay (1988) Molecular bistability; an overview [16].

Maeda and Takashima (1988) Spin state transformation in some iron(III) complexes with Schiff base ligands [224].

Sorai (1988) Thermal properties of complexes showing spin crossover and mixed-valence phenomena [225].

Toftlund (1989) Spin equilibria in iron(II) complexes [226].

Gütllich and Hauser (1989) Thermal and light-induced spin crossover in iron(II) complexes—new perspectives in optical storage [227].

Adler, Hauser, Vef, Spiering and Gütllich (1989) Dynamics of spin state conversion processes in the solid state [228].

Gütllich and Hauser (1990) Thermal and light-induced spin crossover in iron(II) complexes [229].

Hauser (1991) Intersystem crossing in Fe(II) coordination compounds [152].

König (1991) Nature and dynamics of the spin state interconversion in metal complexes [44].

Zarembowitch and Kahn (1991) Spin transition molecular systems; towards information storage and signal processing [230].

Kahn, Kröber and Jay (1992) Spin transition molecular materials for displays and data recording [231].

Zarembowitch (1992) Electronic spin crossovers in solid state molecular compounds—some new aspects concerning cobalt(II) complexes [232].

Kahn (1993) Low spin-high spin transition [32].

Gütllich, Hauser and Spiering (1994) Thermal and optical switching of iron(II) complexes [233].

Gütllich and Jung (1995) Thermal and optical switching of iron(II) compounds [234].

Hauser (1995) Intersystem crossing in iron(II) coordination compounds: a model process between classical and quantum mechanical behaviour [235].

Gütllich, Jung and Goodwin (1996) Spin transitions in iron(II) complexes—an introduction [236].

Kahn, Codjovi, Garcia, van Koningsbruggen, Lapouyade and Sommier (1996) Spin transition molecular materials for display and data processing [237].

Kahn and Codjovi (1996) Iron(II)-1,2,4-triazole spin transition molecular materials [238].

Gütllich (1997) Spin crossover, LIESST and NIESST—fascinating electronic games in iron complexes [239].

Kahn and Martinez (1998) Spin transition polymers: from molecular materials toward memory devices [17].

Gütllich, Garcia, van Koningsbruggen and Renz (1999) Photomagnetism of transition metal compounds [240].

Gütllich, Spiering and Hauser (1999) Spin transition in iron(II) compounds [241].

Hauser, Jeftic, Romstedt, Hinek and Spiering (1999) Cooperative phenomena and light-induced bistability in iron(II) spin-crossover compounds [242].

Real (1999) Bistability in iron(II) spin crossover systems: a supramolecular function [243].

Boillot, Sour, Delhaès, Mingotaud and Soyer (1999) A photomagnetic effect controlling spin states of iron(II) complexes in molecular materials [173].

Linert and Kudryavtsev (1999) Isokinetic and isoequilibrium relationships in spin crossover systems [244].

Kahn, Garcia, Létard and Mathonière (1999) Hysteresis and memory effect in supramolecular chemistry [245].

Spiering, Kohlhaas, Romstedt, Hauser, Bruns-Yilmaz, Kusz and Gütllich (1999) Correlations of the distribution of spin states in spin crossover compounds [199].

Gütllich, Garcia and Goodwin (2000) Spin crossover phenomena in Fe(II) complexes [246].

Kahn (2000) Chemistry and physics of supramolecular magnetic materials [247].

Turner and Schultz (2001) Coupled electron-transfer and spin-exchange reactions [248].

Gütllich, Garcia and Woike (2001) Photoswitchable coordination compounds [249].

Sorai (2001) Calorimetric investigations of phase transitions occurring in molecule-based materials in which electrons are directly involved [250].

Toftlund (2001) Spin equilibrium in solutions [251].

Garcia, Ksenofontov and Gütllich (2002) Spin transition molecular materials: New sensors [252].

Ogawa, Koshihara, Takesada and Ishikawa (2002) New class of photo-induced cooperative phenomena in organic and inorganic hybrid complexes [253].

Boca and Linert (2003) Is there a need for new models of the spin crossover? [254].

Gütllich, Garcia and Spiering (2003) Spin Transition Phenomena [255].

Real, Gaspar, Niel and Muñoz (2003) Communication between iron(II) building blocks in cooperative spin transition phenomena [256].

8 Outlook

It is clear that the field of spin crossover has developed enormously over recent times. Initially it was considered to be little more than a chemical curiosity, albeit a fascinating one, though its fundamental involvement in the function of biological systems was recognized early. It has now developed into a broad inter-disciplinary area which attracts interest from material scientists, physicists, theoreticians, spectroscopists, biochemists, mineral scientists and synthetic chemists. The focus of attention has shifted very much in recent times to potential application of the phenomenon in devices [16] by

exploitation of the basic changes which accompany a spin transition. This has led to an increased effort directed at understanding and predicting the origin and role of the forces promoting the cooperative propagation of the spin changes throughout the lattice of a SCO solid.

The remarkable properties of the iron(II) derivatives of 1,2,4-triazole and the Hoffmann-like arrays of cyano-bridged iron(II) spin transition centres, described in Chap. 9, have highlighted the potential for polymer formation in producing systems exhibiting high cooperativity. Efforts are likely to be concentrated in this area. A totally new field of potential application for the triazole systems as intelligent contrast agents for magnetic resonance imaging has recently been reported and it has been suggested that such spin crossover systems could be used as temperature sensors in hyperthermia treatment of tumours [257]. The incorporation of the iron(II) triazole system into films and the confirmation of both thermal and light-induced transitions under these conditions is significant in terms of potential applications [258]. The original synthetic iron(II) spin crossover systems [Fe(phen)₂(NCS)₂] and [Fe(bpy)₂(NCS)₂] continue to serve as useful models and their modification for incorporation into polymeric systems is being actively pursued [259]. In addition, their potential for producing second order non-linear optical responses has been explored [260]. In a recent report the [Fe(py)₄(NCS)₂] centre has been incorporated into a nanoporous framework species which can reversibly take up guest molecules with an accompanying change in the SCO properties of the host lattice [261]. The scope for application of this property in, for example, molecular sensing is highlighted by Murray and Kepert in Chap. 8. A further new development is the adaptation of a typical iron(III) SCO system to provide the rod-like geometry leading to liquid crystal properties [262]. The scope for practical application of SCO materials with such additional properties for memory, storage and optical devices is attractive. The extension of valence tautomerism (Chap. 14) to the Prussian blue type systems is a very significant development and offers exciting prospects for further electronic switching mechanisms [263]. A somewhat related and novel association of spin crossover and intervalence electron transfer has highlighted a potential new sphere of interest [264]. Alvarez has drawn attention to the crystallisation of certain SCO substances in enantiomorphic space groups and has noted that this opens the way for new studies exploiting the chirality of the metal coordination centres in many instances [53]. There is clearly a bright future for continued interest in the spin crossover phenomenon, probably leading into quite unpredicted areas but certainly building on and exploiting the vast amount of information already accumulated.

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Ligand Field Theoretical Considerations

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Abstract The phenomenon of the thermal spin transition, as observed for octahedral transition metal complexes having a d^4 to d^7 electronic configuration, can be fully rationalised on the basis of ligand field theory. In order to arrive at a self-consistent description of the vibronic structure of spin crossover compounds, it is essential to take into account the fact that the population of anti-bonding orbitals in the high-spin state results in a substantially larger metal-ligand bond length than for the low-spin state. Whereas the electron-electron repulsion is not affected to any great extent by such a bond length difference, the ligand field strength for iron(II) spin crossover compounds can be estimated to be almost twice as large in the low-spin state as compared to the one for the high-spin state. In fact, the dependence of the ligand field strength on the metal-ligand distance may be considered the quantum mechanical driving force for the spin crossover phenomenon.

Keywords Spin crossover · Ligand field theory · Optical properties · Vibronic structure · Configurational coordinate

1 Introduction

The phenomenon of a thermal spin transition was discovered by Cambi et al. [1] on iron(III) dithiocarbamate complexes almost simultaneously to the formulation of ligand field theory, or as it was called then, crystal-field theory, by Bethe [2]. Following Van Vleck's [3] approach to magnetism, it was soon realised that the observations of Cambi et al. could be naturally explained as due to a temperature dependent thermal equilibrium between the two states predicted as possible ground states for an octahedrally coordinated metal ion having five electrons in the d -shell; that is, the low-spin $^2T_{1g}$ state with as many electrons as possible paired up in the t_{2g} sub-shell, and the high-spin $^6A_{1g}$ state with all five electrons unpaired, occupying both the

t_{2g} and the e_g orbitals according to Hund's Rule. But it took more than three decades before Ewald et al. [4] pointed out that the strong dependence of the ligand field strength on the donor atom distance and the resulting large difference in metal-ligand bond lengths between the two states was the actual driving force for the thermal spin transition. In the following, this will be discussed in some detail not for iron(III), but for iron(II), for which by far the largest number of spin crossover compounds are known.

2 Ligand Field Theory

In perfectly octahedral coordination, the five nd orbitals of a transition metal ion are split into a subset of three orbitals, namely d_{xy} , d_{yz} and d_{zx} which are basis to the irreducible representation t_{2g} , and a subset of two orbitals, namely d_{z^2} and $d_{x^2-y^2}$, which are basis to the irreducible representation e_g in O_h [2, 5] (see Fig. 1). The t_{2g} orbitals are basically non-bonding and are therefore at lower energy than the anti-bonding e_g orbitals [6]. The splitting between the two sets is referred to as ligand field splitting and is symbolised by the parameter of the ligand field strength, $10Dq$. The ligand field strength depends upon both the particular set of ligands and the given metal ion [7]. As a semi-empirical parameter, it has to be determined experimentally in each case, for instance from absorption spectra (see below). Therefore, without being explicitly stated, values of $10Dq$ given in tables and reference works [8] usually refer to the ground state geometry. However, and this is going to be of utmost importance in the following, for a given combination of ligands and a metal ion, $10Dq$ depends on the metal-ligand distance as $1/r^n$, with $n = 5-6$ [9]. Therefore, as potential surfaces of different states of a system are plotted, say, along the breathing mode, the corresponding variation of $10Dq$ has to be taken into account.

For systems with more than one d electron, the electron-electron repulsion has to be considered in addition to the ligand field. For iron(II) two ex-

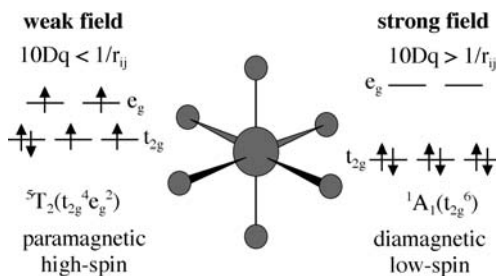


Fig. 1 The electronic configurations of the two possible ground states for iron(II) in an octahedral complex

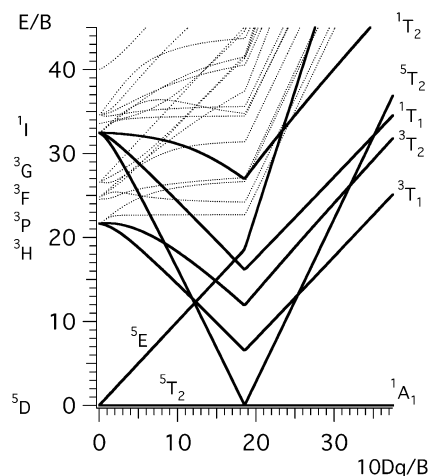


Fig. 2 Tanabe-Sugano diagram for a transition metal ion with six d electrons, showing the energy of the excited ligand-field states in units of the Racah parameter of electron-electronic repulsion B relative to the respective ground state, versus the ligand-field strength $10Dq$ also in units of B . The calculation was performed using the electrostatic matrices in the strong-field basis given in [5]. For the calculation the Racah parameter $C = 4.41B$, as derived from the free ion values of $B = 917 \text{ cm}^{-1}$ and $C = 4040 \text{ cm}^{-1}$ given in [5]

treme cases can be envisaged for placing the six d electrons into the t_{2g} and the e_g orbitals. If the electron-electron repulsion, often referred to as spin-pairing energy Π , is large compared to $10Dq$, then the electrons will enter the five d orbitals according to Hund's rule, with maximum spin multiplicity as for the free ion. This results in a paramagnetic, so-called high-spin $^5T_{2g}(t_{2g}^4e_g^2)$ ground state. If, on the other hand, $10Dq$ is large compared to the electron-electron repulsion, the six d electrons will nicely pair up in the t_{2g} orbitals, resulting in a diamagnetic, low-spin $^1A_{1g}(t_{2g}^6)$ ground state. Classical examples are the $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ complex for the former, and the $[\text{Fe}(\text{CN})_6]^{4-}$ complex for the latter, H_2O and CN^- being ligands at the two extreme ends of Jørgenson's spectrochemical series [9].

According to the Russel-Saunders coupling scheme [10], the electron-electron repulsion between the d electrons of a free transition metal ion results in a series of states characterised by their spin-multiplicity $2S+1$ and their orbital moment L , and denoted by the term symbol ^{2S+1}L . The energies of these states can be calculated as functions of two parameters, the so-called Racah parameters of electron-electron repulsion, B and C [11]. The Tanabe-Sugano diagram [5] for a given electron configuration d^n shows how the electronic states of the free metal ion split under the additional influence of an octahedral ligand field. In Fig. 2, the Tanabe-Sugano diagram of iron(II) with its d^6 configuration is reproduced. It shows the electronic energies of

the excited states relative to the ground state in units of the Racah parameter B as a function of the ligand field strength. The latter is likewise given in units of B . At a nominal ligand field strength of zero, that is on the y-axis, the free ion terms are indicated. The free ion ground state is, according to Hund's rule, a ^5D state. As the ligand field is applied, this state splits into the above mentioned $^5T_{2g}(t_{2g}^4e_g^2)$ high-spin state as ground state of the complex, and a $^5E_g(t_{2g}^3e_g^3)$ excited state. The $^5T_{2g}$ state remains the ground state only up to the critical value of the ligand field strength, where $10Dq$ is equal to the spin pairing energy $\Pi=2.5B+4C\sim 19B$ [8]. Above this value the $^1A_{1g}(t_{2g}^6)$ low-spin state originating from the ^1I free ion term is stabilised relative to the high-spin state and it then becomes the electronic ground state.

The maxima of absorption bands of $d-d$ transitions correspond to vertical transitions in the Tanabe-Sugano diagram, because according to the Franck-Condon principle the geometry of a molecule, and therefore the ligand field strength, do not change within the 10^{-15} s of the actual absorption process. The one absorption band in the near infrared in the spectrum of the weak-field $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ complex (see Fig. 3) can therefore be easily assigned to the spin allowed $d-d$ transition $^5T_{2g}\rightarrow^5E_g$, which is characteristic of a high-spin ground state. It directly gives the value of $10Dq$ as $10,000\text{ cm}^{-1}$. The one band in the UV of the strong-field $[\text{Fe}(\text{CN})_6]^{4-}$ complex, on the other hand, corresponds to the spin-allowed $d-d$ transition $^1A_{1g}\rightarrow^1T_{1g}$, which is characteristic for a low-spin ground state. A second band at still higher energy has been attributed to the $^1A_{1g}\rightarrow^1T_{2g}$ transition [8]. It is somewhat more demanding to extract the ligand field strength in this case as neither of the two bands correspond directly to $10Dq$. But the observation of two bands allows the determination of both $10Dq$ and B from experiment, and for the hexacyanide complex the corresponding values are $10Dq=3300\text{ cm}^{-1}$ and $B=490\text{ cm}^{-1}$ [8]. Such a reduction of the Racah parameter from its free ion value is typical and is known as the nephelauxetic effect [12].

As pointed out above, the values of $10Dq$ correspond to the given combinations of ligands with iron(II) at the respective metal-ligand bond lengths. As a general rule, metal ligand bond lengths of high-spin iron(II) complexes are substantially larger than those of low-spin complexes. This is due to the simple fact that in the high-spin state two of the six d electrons occupy the anti-bonding e_g orbitals, whereas in the low-spin state all six d -electrons reside in the essentially non-bonding t_{2g} orbitals. As a rule of thumb, low-spin bond lengths r_{LS} for Fe-N coordination are found to be between 1.95 and 2.00 Å. With values between 2.12 and 2.18 Å, high-spin bond lengths r_{HS} for Fe-N or Fe-O coordination are typically ~ 0.2 Å longer [13].

In order to understand what happens for ligands with ligand field strengths approaching the crossover point in the Tanabe Sugano diagram, it is essential to remember that a) the ligand field strength depends as r^{-n} on the metal-ligand distance, and b) that the above mentioned difference $\Delta r_{\text{HL}}=r_{\text{HS}}-r_{\text{LS}}$ of ~ 0.2 Å in metal-ligand bond length between the high-spin and the

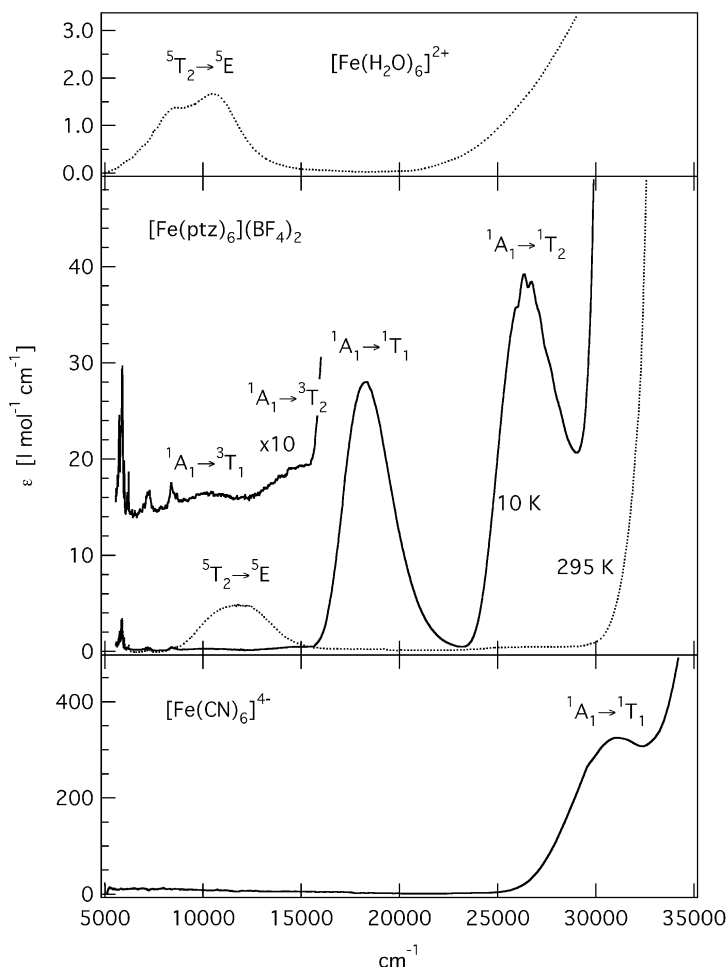


Fig. 3 Absorption spectra of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ in aqueous solution at 295 K, and single crystal absorption spectra of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ at 295 and 10 K

low-spin state also holds for the states within a complex of a given ligand [14]. In a configurational coordinate diagram along the totally symmetric stretch vibration, this means that the minima of the two potential wells are displaced relative to each other, both vertically and horizontally, as depicted in Fig. 4. Based on such a diagram, the condition for the phenomenon of a thermal spin transition becomes apparent: in order for a thermal population of the high-spin state to occur, the zero-point energy difference between the two states, $\Delta E_{\text{HL}}^0 = E_{\text{HS}}^0 - E_{\text{LS}}^0$, has to be of the order of thermally accessible energies, $k_{\text{B}}T$. If such is the case, all complexes will be in the low-spin state at very low temperatures, whereas at elevated temperatures an entropy-driv-

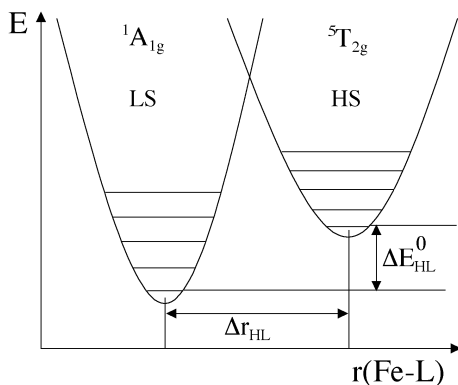


Fig. 4 Adiabatic potentials for the high-spin and the low-spin state along the most important reaction coordinate for spin crossover, namely the totally symmetric metal-ligand stretch vibration denoted $r(\text{Fe-L})$

en, almost quantitative population of the high-spin state may be observed. There are basically two contributions to the entropy difference between the two states, namely the electronic contribution due to the spin degeneracy of the high-spin state, and a vibrational contribution due to the generally lower vibrational frequencies and the resulting higher density of vibrational states in the high-spin state. Note that the low-spin state, in fact, remains the quantum mechanical ground state at all temperatures, but the high-spin state becomes the thermodynamically stable state at elevated temperatures.

What does the ligand field strength do when a complex goes from the low-spin to the high-spin state? During the transition the metal-ligand bond length changes abruptly, and therefore $10Dq$ changes abruptly, too. The ratio of the ligand field strengths in the two spin states is given by the equation

$$\frac{10Dq^{\text{LS}}}{10Dq^{\text{HS}}} = \left(\frac{r_{\text{HS}}}{r_{\text{LS}}} \right)^n \quad (1)$$

with $n = 5-6$. Using average values of $r_{\text{LS}} = 2.0 \text{ \AA}$ and $r_{\text{HS}} = 2.2 \text{ \AA}$, this ratio is estimated to be ~ 1.75 . The well-known spin crossover compound $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ confirms this ratio perfectly. At room temperature, crystals of this compound are colourless. The corresponding absorption spectrum shown in Fig. 2 consists of one band in the near infrared which can be assigned to the ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ transition of the high-spin species. As for the hexa-aquo complex this directly gives $10Dq^{\text{HS}} = 11,800 \text{ cm}^{-1}$. Below 135 K, the crystals turn deep red in colour. The corresponding absorption spectrum now consists of two comparatively intense bands in the visible, assigned to the spin-allowed $d-d$ transitions ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$ and ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$, and two rather weak bands in the near infrared, assigned to the spin-forbidden transitions

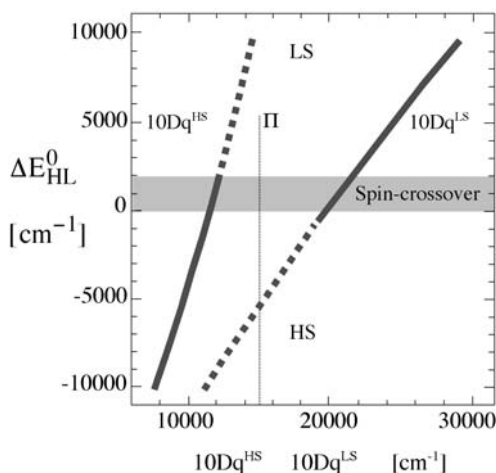


Fig. 5 Regions of stability of either one or the other spin state as a function of the ligand-field strength. The region of spin crossover compounds is indicated by the shaded area. For the calculation, the values of the Racah parameters were taken to be 75% of the free ion values. This corresponds to a typical reduction for iron(II) coordination compounds of the type under consideration

$^1A_{1g} \rightarrow ^3T_{1g}$ and $^1A_{1g} \rightarrow ^3T_{2g}$ [15]. From these bands, values of $10Dq^{LS}$ and B of 19410 cm^{-1} and 740 cm^{-1} , respectively, can be evaluated.

At this stage, a comment on the often encountered statement, that in order to observe spin crossover the mean spin pairing energy Π has to be approximately equal to the ligand field strength $10Dq$, seems to be called for. This statement is misleading and physically unsound. In fact, Π changes very little during the spin transition. If anything, it is slightly larger in the high-spin state because of the smaller nephelauxetic effect for the larger bond length [12]. It is, as shown above, the ligand field strength which changes. It does so in such a way that in the high-spin state $10Dq$ is substantially smaller than Π , and in the low-spin state $10Dq$ is substantially larger than Π . In other words $10Dq^{HS} < \Pi < 10Dq^{LS}$ [4]. In the configurational coordinate diagram, the crossover point of the Tanabe-Sugano diagram for which $10Dq = \Pi$ corresponds to the crossing point of the two potential wells. Under no circumstances whatsoever can this point correspond to the ground state potential minimum of an iron(II) complex.

Based on the bond length dependence of $10Dq$, the fact that Π does not vary to any great extent, and that in a complex the Racah parameters of electron-electron repulsion are typically reduced to 70 to 80% of their free ion values, the zero-point energy difference, $\Delta E_{HL}^0 = E_{HS}^0 - E_{LS}^0$, between the high-spin and the low-spin state can be estimated as a function of $10Dq^{HS}$ as well as of $10Dq^{LS}$ (see Fig. 5). For $10Dq^{HS} < 10,000 \text{ cm}^{-1}$, $\Delta E_{HL}^0 < 0$, that is, the

high-spin state is the quantum mechanical ground state, and, accordingly, the high-spin state is the thermodynamically stable state at all temperatures.

For $10Dq^{LS} > 23,000 \text{ cm}^{-1}$, $\Delta E_{HL}^0 > 2000 \text{ cm}^{-1}$, that is, the low-spin state is the quantum mechanical ground state and will remain the thermodynamically stable state up to very high temperatures. For the narrow range of $10Dq^{HS} \approx 11,000\text{--}12,500 \text{ cm}^{-1}$ and the corresponding range for $10Dq^{LS} \approx 19,000\text{--}22,000 \text{ cm}^{-1}$, $\Delta E_{HL}^0 \approx 0\text{--}2000 \text{ cm}^{-1}$. This is the range of respective ligand field strengths for which the phenomenon of a thermal spin transition can be expected. For a reduction of the Racah parameters to 70–80% of their free ion values, the corresponding value of $\Pi \approx 15,000 \text{ cm}^{-1}$. The above estimates are based on the analysis of the spectroscopic properties of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$. They may therefore be considered valid for iron(II) spin crossover compounds with the most common $[\text{FeN}_6]$ coordination. Special cases, for instance with a different donor set, or with ligands having extreme back-bonding properties, can lie somewhat outside this standard range.

3

Conclusions

The general picture developed above serves as starting point for the explanation of most of the observations discussed in the subsequent chapters of the volumes of “Topics in Current Chemistry” dedicated to the various aspects of spin crossover. Basically, the phenomenon of spin crossover is a property of the isolated complex due to the interplay between the dependence of the ligand field strength on the metal-ligand distance and the electron-electron repulsion. However, secondary effects such as substantial deviations from octahedral symmetry, packing effects in crystal lattices [16] and the thermal contraction inherent to crystalline solids, cooperative interactions [17, 18], and external perturbations such as pressure [19] or magnetic fields [20] may influence the physical and photophysical properties of spin crossover compounds to a non-negligible extent. Indeed, they are responsible for the large variation and the multitude of physical phenomena observed for spin crossover systems [16]. Modern electronic structure calculations, for instance based on density functional theory [21], should not contradict the above ligand field theoretical considerations. But they should provide us with a quantitatively more accurate understanding, particularly of the geometry changes and therefore the reaction coordinate of the spin transition, as well as of the various contributions to the molecular partition function.

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Spin Crossover in Iron(II) Tris(diimine) and Bis(terimine) Systems

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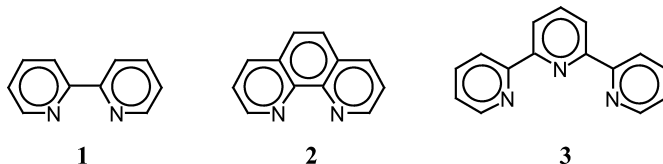
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Abstract Tris(diimine) and bis(terimine) iron(II) complex salts constitute one of the major classes of spin crossover systems. Both electronic and structural modifications can be made so as to bring the ligand field of the parent imines, 2,2'-bipyridine, 1,10-phenanthroline and 2,2':6',2''-terpyridine into the crossover range with some degree of confidence. The resulting imine systems are considered and classified according to their structural types. Among the many crossover systems in this class are several which display a high degree of cooperativity in the solid state, and the incorporation of hydrogen-bonding sites into the ligand structure also strongly influences many solid-state properties

Keywords Diimines · Terimines · Iron(II) · Spin crossover · Spin transition

1 Introduction

The classic low spin $[\text{FeN}_6]^{2+}$ systems are those derived from the bidentate diimines 2,2'-bipyridine **1** (bpy) and 1,10-phenanthroline **2** (phen) and the tridentate terimine 2,2':6',2''-terpyridine **3** (trpy).



The high stability, intense colour and low spin nature of these complexes arise not only from the intrinsically relatively high σ -donor power of the imine systems but also from the availability of empty, low-lying π^* orbitals on the ligand molecules. These are suitably oriented for interaction with the filled d_π orbitals of the metal atom and therefore for strengthening the metal–ligand interaction. These systems, and derivatives of them, have occupied a pivotal position in the development of the spin crossover area right from the early studies involving iron(II) and cobalt(II) systems in the 1960s. In fact, this had been anticipated earlier by Orgel [1] who, before any synthetic iron(II) crossover systems had been characterised, intimated that the field strength in these $[\text{Fe N}_6]^{2+}$ systems should lie near that at the singlet ($^1A_1$) $\leftrightarrow$ quintet ($^5T_2$) crossover for iron(II). This was further indicated by the measurement of the pressure-dependence of the Mössbauer spectra of these systems by Fisher and Drickamer who observed partial population of high spin species for $[\text{Fe}(\text{phen})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ at high pressure [2]. This surprising result was rationalised on the basis of increasing occupancy of the ligand π^* orbitals by ligand electrons as pressure increases and hence reduced availability of these orbitals to metal d_π electrons. It seems reasonable, then, that any modification of these ligands which leads to a small reduction in either their σ -donor and/or π -acceptor character may result in an accessible thermal spin crossover in the $[\text{Fe N}_6]^{2+}$ systems.

A direct measure of the field strength in iron(II) complexes of conjugated diimine and terimine systems is usually not available because of overlap of ligand field bands by intense charge-transfer bands in the electronic spectra. In contrast, the spectra of the corresponding $[\text{Ni N}_6]^{2+}$ complexes generally clearly reveal both the $^3A_{2g} \rightarrow ^3T_{2g}$ and $^3A_{2g} \rightarrow ^3T_{1g}$ (F) transitions, although the latter may sometimes overlap with a charge-transfer transition. Moreover, for (essentially regular) octahedral complexes of nickel(II) there is no change in spin state as the field increases. The frequency of the former transition bears a direct relationship to the ligand field splitting parameter $10Dq(\text{Ni}^{2+})$ and the value of this in the prediction of the likely appearance of a spin transition in the corresponding iron(II) system was first demonstra-

ted by Busch and co-workers [3]. They proposed that ligands which lead to crossover behaviour in the iron(II) systems will have $Dq(Ni^{2+})$ values within the range $\sim 1120\text{--}1240\text{ cm}^{-1}$. While exceptions to this have been noted, the correlation between the value of $Dq(Ni^{2+})$ and the electronic properties of the corresponding iron(II) system has been widely applied as a useful benchmark in understanding the differences in the behaviour of the $[Fe N_6]^{2+}$ derivatives of related ligand systems. Where they are relevant and available, values (as $Dq(Ni^{2+})$) are quoted in the discussion below. Some prudence needs to be exercised in the interpretation of small differences in reported values for different systems, as the conditions for measurement are not necessarily constant and the coordination geometry may vary appreciably. For the strong field ligands 1, 2, 3, the values are 1265, 1270 and 1235 cm^{-1} , respectively [4, 5].

2

Tris(diimine) Systems

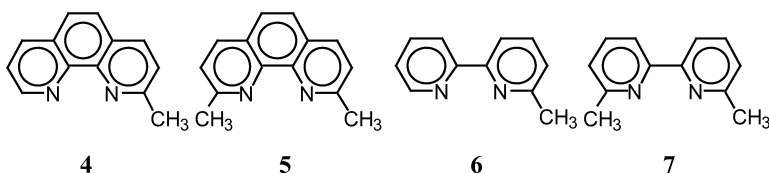
2.1

Effect of Ring Substituents

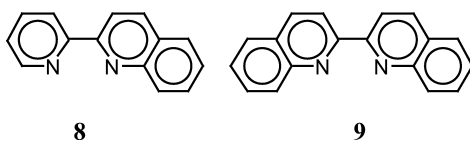
The ligands 1 and 2 lend themselves to modification in various ways, perhaps the simplest being the incorporation of substituents into the rings. Provided that the substituents are at positions relatively remote from the donor atoms no significant change in field strength results and the $[Fe N_6]^{2+}$ species remain low spin [6]. A possible exception is the complex of 5,5'-diethylcarboxylate-2,2'-bipyridine. In this instance it has been suggested that the relatively low stability, the temperature-dependence of the intensity of the charge-transfer transition and the paramagnetism arose from the presence of a "spin equilibrium", but dissociation of the complex could be responsible for these effects [7].

Substitution at sites adjacent to the donor atoms has a more pronounced effect. The field strength of 2-methyl-phenanthroline (mephen) 4 ($Dq(Ni^{2+})=1100\text{ cm}^{-1}$) is significantly less than that for 2 and the $[Fe N_6]^{2+}$ complexes of both 4 [8] and 2-methoxy-phenanthroline [9] are high spin and relatively feebly colored (orange) at room temperature, but become low spin and intensely red-violet at low temperatures. The thermochromism in this instance arises primarily from the intense charge-transfer transition in the visible region for the low spin species. The increase in intensity of this with decrease in temperature has been applied to monitor the transition in $[Fe(mephen)_3](ClO_4)_2$ incorporated into a film of poly-vinyl acetate [10]. In the structure of $[Fe(mephen)_3](BPh_4)_2$, (at 298 K where the complex is high spin) the cation has the *mer* configuration and the average Fe–N distance is $2.21\text{ \AA}$ [11]. This is normal for high spin Fe(II)–N distances and contrasts

with 1.96 Å found in the low spin $[\text{Fe}(\text{phen})_3]^{2+}$ ion [12]. The Fe–N_{Me} distance (average 2.25 Å) is considerably longer than the Fe–N_H (average 2.17 Å), and this indicates a steric barrier to coordination exerted by the methyl substituent. This may be the major factor in reducing accessibility of the singlet state for this system, since such a steric effect would be expected to be enhanced in coordination to the smaller low spin iron(II). The structure does reveal, in addition, considerably greater inter-ligand repulsion in this system than in the unsubstituted and this may also be a factor in de-stabilising the singlet state. Despite the comparable steric bulk of a chloro- and a methyl-substituent, 2-chloro-1,10-phenanthroline yields an $[\text{Fe N}_6]^{2+}$ complex which remains high spin at 4.2 K [13]. When methyl substituents are incorporated at both the 2- and 9-positions 5 a tris(ligand)iron(II) complex could not be isolated [14].

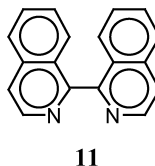
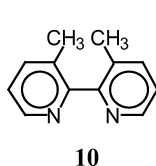


Substitution at the 6- and 6'-positions in 2,2'-bipyridine has similar effects. A singlet $\leftrightarrow$ quintet transition (gradual and incomplete) is observed in salts of the $[\text{Fe } \mathbf{6}_3]^{2+}$ ion ($Dq(\text{Ni}^{2+})$ for $\mathbf{6}=1060 \text{ cm}^{-1}$) and the average Fe_{HS}–N distance is the same as that in $[\text{Fe}(\text{mephen})_3]^{2+}$ [15]. Fusion of a benzene ring on to one of the pyridine rings has a steric effect similar to that of methyl-substitution and again a spin transition is observed in the $[\text{Fe N}_6]^{2+}$ complex of 2-(pyridin-2-yl)quinoline $\mathbf{8}$ ($Dq(\text{Ni}^{2+})=1000 \text{ cm}^{-1}$) [15]. As expected, 6,6'-dimethyl-2,2'-bipyridine $\mathbf{7}$ [14] and 2,2'-biquinolyl $\mathbf{9}$ [16] fail to yield $[\text{Fe N}_6]^{2+}$ derivatives.



For 2,2'-bipyridine the 3,3'-positions have particular structural significance. There is evidence for steric interaction between the hydrogen atoms in these positions in the coordinated molecule [17]. This steric interaction is markedly enhanced by substituents at these positions. These prevent the coordinated molecule from being planar and so both the σ - and π -interactions with a metal ion are reduced ($Dq(\text{Ni}^{2+})$ for $\mathbf{10}=1140 \text{ cm}^{-1}$). In the structure of $[\text{Fe } \mathbf{10}_3]^{2+}$ there is considerable twisting about the inter-annular bridge of the diimine, the planes of the two pyridine rings being inclined at an angle of $\sim 34^\circ$. As a result of this, the quintet state for iron(II) becomes thermally accessible in salts of this cation, which are completely low spin in the solid

state at 90 K (and at 320 K in acetone solution) but show a continuous transition to high spin which is centred close to room temperature [18]. A transition is also observed in salts of the tris(1,1'-biisoquinoline)iron(II) ion where the steric effects of the fused benzene rings in **11** are expected to be comparable to those of the methyl groups in **10** [14].



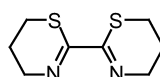
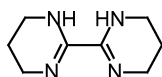
2.2

Effect of Ring Replacement

2.2.1

Replacement with Six-Membered Heterocycles

There are several diimines containing two linked six-membered heterocycles such as 2,2'-bipyrazine, 2,2'-bipyrimidine and 3,3'-bipyridazine. These are mostly strong field systems [19] and it is their $[\text{Fe}(\text{diimine})_2(\text{NCS})_2]$ type derivatives which are of principal relevance to iron(II) spin crossover. For tris(ligand) systems containing diimines in this category spin crossover seems to be limited to the complex of 2,2'-bi-1,4,5,6-tetrahydropyrimidine **12** ($Dq(\text{Ni}^{2+})=1100\text{ cm}^{-1}$), the transition in the complex perchlorate being continuous and centred at about 310 K. The closely related diimine 2,2'-bi-(4*H*-5,6-dihydrothiazine) **13** exerts a stronger field ($Dq\text{Ni}^{2+}=1160\text{ cm}^{-1}$) than the pyrimidine system ($Dq(\text{Ni}^{2+})=1160\text{ cm}^{-1}$) and its $[\text{Fe N}_6]^{2+}$ derivative is low spin at 293 K. Its behaviour at elevated temperatures was not reported [21].

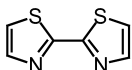
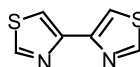


2.2.2

Replacement with Five-Membered Heterocycles

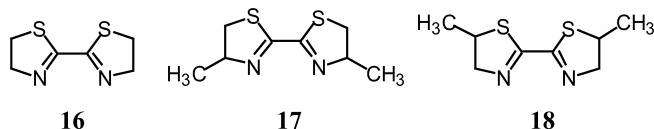
Modification of the field of 2,2'-bipyridine by replacement of one or both of the pyridine rings with five-membered heterocycles is a much more effective means of generating the crossover situation than replacement by six-membered rings. This has resulted in the crossover region being attained in a relatively large number of instances. The incorporation of thiazole moieties il-

illustrates the effects. Both 2- and 4-(pyridin-2-yl)thiazole provide weaker fields than 2,2'-bipyridine, as indicated by the $Dq(Ni^{2+})$ values (1160 and 1200 cm^{-1} , respectively) but still sufficiently strong to yield $[Fe N_6]^{2+}$ derivatives which are low spin [22, 23]. Replacement of the second pyridine moiety by thiazole effects a further reduction in the field and the tris(ligand) complexes of both 2,2'-bithiazole **14** and 4,4'-bithiazole **15** ($Dq(Ni^{2+})$ values 1130 and 1140 cm^{-1} , respectively) undergo spin transitions, the transition in salts of $[Fe 15_3]^{2+}$ occurring above room temperature [24, 25].

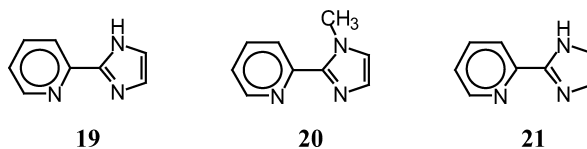
**14****15**

In salts of $[Fe 14_3]^{2+}$ the transition is strongly cooperative, being associated with thermal hysteresis and preliminary results indicate that hysteresis is associated with the transition in $[Fe 15_3](BF_4)_2$ as well [26]. 4,4'-Bithiazole is not strictly a diimine system of the kind present in bipyridine or, for example, in 2,2'-bithiazole. Within the thiazole moieties there is some π -electron localisation, both in the free ligands and in the iron(II) and nickel(II) complexes [24]. As a consequence of this, salts of $[Fe 15_3]^{2+}$ do not contain the typical iron- α -diimine chromophore which normally leads to strong charge-transfer absorption in the visible region. Their pale pink-violet colour (at room temperature) is due to the $^1A_1 \rightarrow ^1T_1$ ligand field transition observed at 18,700 cm^{-1} . The salts are almost colorless at elevated temperatures when they are high spin. In contrast, salts of $[Fe 14_3]^{2+}$ are intensely violet in both their high spin and low spin states. The charge-transfer transition, responsible for this colour, is displaced to considerably lower frequencies in this system than that in the spectra of salts of $[Fe 15_3]^{2+}$. While the iron(II) complex of **14** decomposes in solution, that of **15** is relatively stable and the spin transition can be observed in the solution state. It is found that the transition is displaced to lower temperature for the solution, being centred close to room temperature. This transition is characterised by $\Delta H = 24$ kJ mol $^{-1}$ and $\Delta S = 70$ J mol $^{-1}$ K $^{-1}$, values typical for a $(^1A_1) \leftrightarrow (^5T_2)$ transition in iron(II).

The 2,2'-bi-2'-thiazolines **16** **17** **18** ($Dq(Ni^{2+})$ values 1160, 1120 and 1160 cm^{-1} , respectively) are related to the bithiazoles, and the perchlorate salts of the $[Fe N_6]^{2+}$ derivatives of all three systems are low spin at room temperature but their behaviour above room temperature has not been reported. The low spin configuration for $[Fe 17_3](ClO_4)_2$ in particular appears inconsistent with the behaviour of related systems containing substituents adjacent to the donor atoms, and with its relatively low $Dq(Ni^{2+})$ value. Nelson and co-workers have pointed out that the steric effect here is not so pronounced because the methyl substituents are not coplanar with the diimine group [21].



For five-membered heterocycles other than thiazole, (such as pyrazole [27], imidazole [28], and triazole [29]) the effect of replacement of just one pyridine moiety in **1** is greater and the $[\text{Fe N}_6]^{2+}$ derivatives in these instances show crossover behaviour. The $[\text{Fe N}_6]^{2+}$ derivative of 2-(pyridin-2-yl)imidazole **19** ($\text{Dq}(\text{Ni}^{2+})$ 1150 cm^{-1} [22]) was shown relatively early on to be a crossover system [28]. In solid salts and in solution the transition is continuous and centred above room temperature. The dynamics for the $^5\text{T}_2 \rightarrow ^1\text{A}_1$ relaxation for this system have been investigated by a number of techniques [30–32] and Beattie and McMahon have shown that in solution there is not only a spin equilibrium but also a ligand dissociation process, very reasonably ascribed to the high spin form of the tris complex [32].

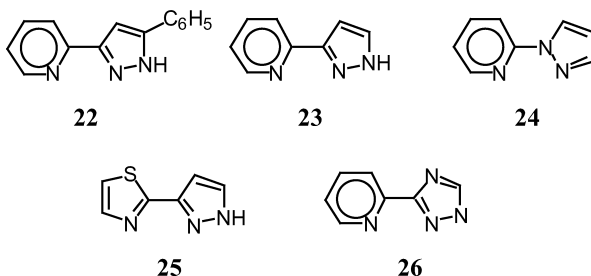


Substitution of a methyl group at the non-coordinating NH site of **19** results in an increase in the ligand field ($\text{Dq}(\text{Ni}^{2+})=1160\text{ cm}^{-1}$ for **20**) and a displacement of the transition in salts of the $[\text{Fe N}_6]^{2+}$ species to higher temperatures [33].

For the complex of the related ligand 2-(pyridin-2-yl)imidazoline **21** ($\text{Dq}(\text{Ni}^{2+})$ 1140 cm^{-1}) spin crossover is also observed [34]. Two forms of $[\text{Fe 21}_3](\text{ClO}_4)_2$ were isolated – one low spin and the other high spin but undergoing an abrupt and time-dependent transition to low spin from about 120 K. This system is of obvious interest and warrants further study.

The pyridyl-pyrazole systems **22**, **23**, **24** are closely related to the pyridyl-imidazoles. $[\text{Fe 22}_3](\text{ClO}_4)_2$ shows a very gradual transition below room temperature [35]. In hydrated complex salts of 3-(pyridin-2-yl)pyrazole **23** the transition is at higher temperatures and moreover the transition temperature is found to increase as the extent of hydration of the salts increases, suggesting an increasing involvement of the ligand $>\text{NH}$ groups in hydrogen bonding to water [36]. For the triflate salt the dihydrate is almost completely low spin at room temperature but the anhydrous salt is high spin. It undergoes an abrupt transition with a thermal hysteresis loop of width 12 K ($T_{1/2\downarrow}=229\text{ K}$ and $T_{1/2\uparrow}=241\text{ K}$) [27]. This behaviour is similar to that noted for salts of $[\text{Fe 58}_2]^{2+}$, **58** being a terimine analog of **23** discussed in Sect. 3.3. In the structure of the triflate dihydrate salt, the three pyrazole $>\text{NH}$ groups of each complex cation are involved in hydrogen bonding, either to the anion or to the solvate water. The average $\text{Fe-N}_{\text{pyridine}}$ and $\text{Fe-N}_{\text{pyrazole}}$ dis-

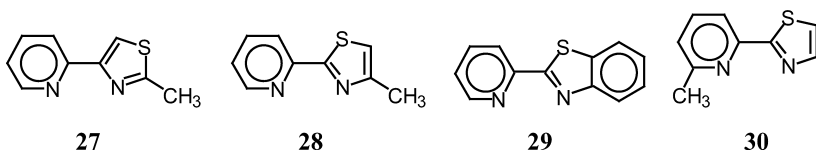
tances are 1.99 Å and 1.94 Å, respectively, consistent with the low spin configuration and reflecting the general trend of shorter Fe–N distances to the five-membered heterocycles. A greater tendency to stabilise singlet state iron(II) is evident for 1-(pyridin-2-yl)pyrazole **24**, and $[\text{Fe } \mathbf{24}_3](\text{BF}_4)_2$ is low spin (at least to 353 K).



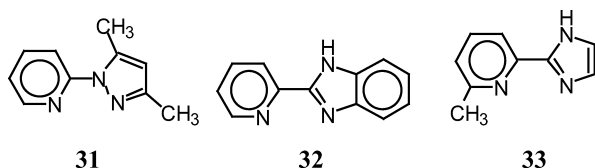
This is consistent with the relative values for $\text{Dq}(\text{Ni}^{2+})$ (1160 and 1170 cm^{-1} for **23** and **24**, respectively) [36]. For 2-(1,2,4-triazol-3-yl)pyridine **26** $\text{Dq}(\text{Ni}^{2+})$ is somewhat smaller, 1130 cm^{-1} , and for this and certain substituted derivatives the spin transitions in the $[\text{Fe N}_6]^{2+}$ derivatives are observed below room temperature [29]. This and related triazole systems are discussed more fully in chapter 5 by van Koningsbruggen.

The mixed thiazole-pyrazole system **25** ($\text{Dq}(\text{Ni}^{2+})=1110 \text{ cm}^{-1}$) yields a tris(ligand) iron(II) complex in which one of the ligand molecules is deprotonated. For the complex perchlorate a complete and fairly abrupt transition occurs below room temperature but no associated hysteresis was observed [27].

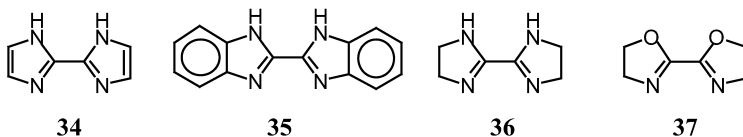
Substitution adjacent to the donor atom of a five-membered heterocycle generally results in a reduction in the ligand field but the effect is not so marked as similar substitution in the pyridine ring. This is due primarily to the geometry of the five-membered ring, which results in substituents being skewed away from the metal atom more than in a coordinated six-membered ring. Therefore the steric barrier to coordination is not so great. The effect is illustrated by the derivatives of the substituted pyridyl-thiazoles. Whereas the unsubstituted ligands yield low spin $[\text{Fe N}_6]^{2+}$ species, substitution of a methyl-group adjacent to the donor nitrogen atom of the thiazole ring as in either **27** ($\text{Dq}(\text{Ni}^{2+})=1120 \text{ cm}^{-1}$) or **28** ($\text{Dq}(\text{Ni}^{2+})=1110 \text{ cm}^{-1}$) [37], or the fusion of a benzene ring as in 2-(pyridin-2-yl)benzothiazole **29** ($\text{Dq}(\text{Ni}^{2+})=1080 \text{ cm}^{-1}$) [38] brings the field into the crossover region. The effect of the substituent in the pyridine ring in **30** is more marked ($\text{Dq}(\text{Ni}^{2+})=960 \text{ cm}^{-1}$) and no spin-pairing in the iron(II) species is observed.



The same effect is observed for the substituted pyridyl-pyrazole and -imidazole systems. While 2-(pyrazol-1-yl)pyridine **24** gives a low spin iron(II) complex a continuous spin transition is observed centred just above room temperature in solid salts of $[\text{Fe}(\mathbf{31})_3]^{2+}$ and just below in solution [39]. Spin crossover occurs in the $[\text{Fe} \text{N}_6]^{2+}$ derivative of 2-(pyridin-2-yl)benzimidazole **32** ($Dq(\text{Ni}^{2+})=1050 \text{ cm}^{-1}$) but not in that of the 6-methyl-pyridyl system **33** ($Dq(\text{Ni}^{2+})=1000 \text{ cm}^{-1}$). Although the transition in salts of $[\text{Fe} \mathbf{32}_3]^{2+}$ is strongly influenced by the nature of the anion and the extent of hydration, suggesting an influence of hydrogen-bonding, in all instances it is continuous [40].



Replacement of *both* pyridine rings of bipyridine by imidazole has a much greater effect than replacement by thiazole and the $[\text{Fe} \text{N}_6]^{2+}$ derivative of 2,2'-biimidazole **34** ($Dq(\text{Ni}^{2+})=1080 \text{ cm}^{-1}$) is purely high spin [41]. The spin-crossover behaviour of tris(2,2'-bi-imidazoline)iron(II) salts seems somewhat unexpected in light of this and the relatively low σ -donor power as indicated by the small $Dq(\text{Ni}^{2+})$ value (1030 cm^{-1}) for **36**.

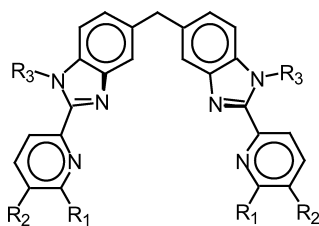
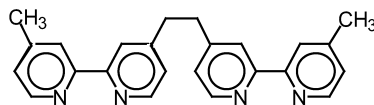


In **36**, however, the delocalization associated with the diimine system will be concentrated within the chelate ring, thereby enhancing the metal-ligand π -interaction. This is not reflected so much in a $Dq(\text{Ni}^{2+})$ value but is important in rendering the singlet state for iron(II) accessible [42]. The $Dq(\text{Ni}^{2+})$ value for 2,2'-bi-2-oxazoline **37** is even smaller (1010 cm^{-1}) and in this instance the $[\text{Fe} \text{N}_6]^{2+}$ species is entirely high spin [43]. There are some features of the spin transition in $[\text{Fe} \mathbf{36}_3](\text{ClO}_4)_2$ which are of particular significance. The transition is abrupt and associated with hysteresis ($\Delta T_{1/2}=6.5 \text{ K}$) and a disorder-order transition in the lattice orientation of the anions. Hydrogen bonding from the $>\text{NH}$ groups of the imidazoline moieties to the

perchlorate anions is believed to be involved in the coupling of the disorder-order and spin transitions [42].

With effectively both imidazole rings in 2,2'-bi-benzimidazole **35** substituted, the characterisation of (purely high spin) $[\text{Fe } \mathbf{35}_3](\text{ClO}_4)_2$ [44], in contrast to the absence of a $[\text{Fe N}_6]^{2+}$ derivative of 2,2'-biquinolyl **9** [16] demonstrates again the difference in the effects of substitution in five-membered and six-membered rings. The reported low spin nature of the $[\text{Fe N}_6]^{2+}$ derivative of 4,4'-dimethyl-bi-2-thiazoline **17** is certainly remarkable and serves to illustrate this point even more strongly [21].

The coordination of the bis(benzimidazole) system **38** is of considerable interest. This leads to a dinuclear species $[\text{Fe}_2\mathbf{38}_3](\text{ClO}_4)_4$. Structural studies show that the bridging **38c** molecules in $[\text{Fe}_2\mathbf{38c}_3](\text{ClO}_4)_4$ are arranged in a triple helix [45].

**38****39**

38a: $\text{R}_1=\text{H}$; $\text{R}_2=\text{Me}$; $\text{R}_3=\text{Me}$

38b: $\text{R}_1=\text{Me}$; $\text{R}_2=\text{H}$; $\text{R}_3=\text{Me}$

38c: $\text{R}_1=\text{H}$; $\text{R}_2=\text{Me}$; $\text{R}_3=\text{Et}$

This complex is low spin with an average Fe–N distance of 1.98 Å, the Fe– $\text{N}_{\text{pyridine}}$ distance (2.00 Å) typically being longer than the Fe– $\text{N}_{\text{benzimidazole}}$ (1.96 Å). The effect of the substituents in **38** is also consistent with trends noted earlier. The complex of **38a** is essentially low spin but shows a small high spin fraction at 330 K, while that of **38b** is high spin in acetonitrile solution. Evidence for a *negative cooperativity effect* within the dimeric unit of such systems has been reported; in other words the low spin $\rightarrow$ high spin change at one iron atom results in a stabilisation of the low spin state for the second atom of the binuclear unit [46]. The bis(bipyridine) binucleating system **39** is related to **38** but $[\text{Fe}_2(\mathbf{39})_3]^{4+}$ is low spin, as expected [47]. Such a system incorporated into $[\text{Fe}(\text{diimine})_2(\text{NCS})_2]$ type species would be expected to lead to crossover behaviour and the degree of cooperativity shown by these should be of interest.

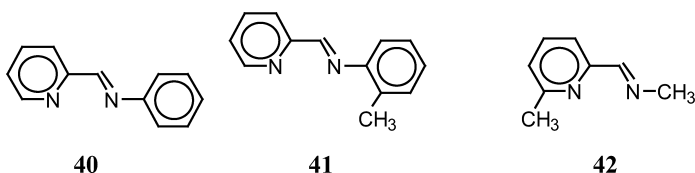
A novel variation of the ligand system **38** has been reported in which one of the terminal benzimidazole moieties has been replaced by a 2-pyridyl-*N,N*-diethylcarboxamide group, providing an NNO tridentate moiety at one end and an NN bidentate at the other [48]. Three strands of the bifunctional

ligand are arranged helically and coordinate to iron(II) through the bis(benzimidazole) bidentate units and to lanthanum(III) through the tridentate units, the latter generating nine-coordination. A gradual and incomplete transition was observed for the $[\text{Fe N}_6]^{2+}$ centre in the solid state (up to 380 K) and in solution (up to 333 K).

2.3

Schiff Base Diimines

The formation of diimine systems by Schiff -base-type condensation of suitable aldehydes and primary amines has been widely applied. Those reported are mostly strong field systems and their relevance to the spin crossover field is generally in systems of the kind $[\text{Fe}(\text{diimine})_2(\text{NCS})_2]$. The effect of the incorporation of substituents likely to hinder coordination has been studied. Robinson and Busch noted a fundamental difference at room temperature in the electronic properties of the $[\text{Fe N}_6]^{2+}$ derivatives of 2-pyridinalmethylhydrazone and 2-pyridinal-dimethylhydrazone, those of the former being low spin and those of the latter high spin [49]. The temperature-dependence of the magnetism of the latter complex was not reported but may well be of interest. However, spin crossover $[\text{Fe}(\text{diimine})_3]^{2+}$ systems have been characterised for systems where the incorporation of appropriate substituents has reduced the ligand field.



This is the case for the $[\text{Fe N}_6]^{2+}$ derivatives of **40** [50], **41** [51], **42** [52] and is consistent with the behaviour of the pyridyl-quinoline or 6-methyl-bipyridine systems. The incorporation of five-membered heterocyclic ring systems in this way could be readily achieved but does not seem to have been exploited in the generation of the crossover situation.

3

Bis(terimine) Systems

The model tridentate terimine system is terpyridine **3** and salts of its $[\text{Fe N}_6]^{2+}$ derivative are low spin, like those of the diimines **1** and **2**, but there are important differences in the bidentate systems on the one hand and the tridentate on the other. Although the average Fe–N distance is virtually the same (~ 1.96 Å) in all three species, in $[\text{Fe}(\text{trpy})_2]^{2+}$ the Fe–N_{central} distances are much shorter than the Fe–N_{distal} and so the $[\text{Fe N}_6]^{2+}$ coordination unit

is tetragonally compressed [53]. This distortion is, at least partly, a consequence of the steric requirements of planar tridentate coordination of the ligand but in addition follows from the nature of the metal-ligand π -interaction [54]. Because of the meridional coordination, this interaction is necessarily concentrated along the $N_{\text{central}}-\text{Fe}-N_{\text{central}}$ axis and simple considerations lead to a prediction of order two for the $\text{Fe}-N_{\text{central}}$ bonds and 1.25 for the $\text{Fe}-N_{\text{distal}}$ bonds, whereas the order predicted for all six $\text{Fe}-\text{N}$ bonds in $[\text{Fe}(\text{bpy})_3]^{2+}$ or $[\text{Fe}(\text{phen})_3]^{2+}$ is 1.5. The observed bond lengths are consistent with these considerations [53]. The uneven distribution of the π -electron density about the metal atom must contribute to the higher quadrupole splitting observed in the Mössbauer spectrum of $[\text{Fe}(\text{trpy})_2]^{2+}$ salts ($\sim 1 \text{ mm s}^{-1}$) compared to that for $[\text{Fe}(\text{bpy})_3]^{2+}$ or $[\text{Fe}(\text{phen})_3]^{2+}$ salts ($\sim 0.3 \text{ mm s}^{-1}$) [55]. It is also significant that the more rigid (when coordinated) tridentate system provides a weaker ligand field than the diimines **1** and **2**. Despite the low spin nature of $[\text{Fe}(\text{trpy})_2]^{2+}$ salts, a long-lived (at $T < 20 \text{ K}$) *high spin* form of $[\text{Fe}(\text{trpy})_2]^{2+}$ has been characterised on photo-excitation of the complex perchlorate doped into a crystal of the corresponding manganese(II) complex [56]. Similarly, a metastable high spin form has been identified in the emission Mössbauer spectrum of the nuclear decay products of certain $^{57}\text{Co}(\text{trpy})_2]^{2+}$ species [57]. This suggests that in $[\text{Fe}(\text{trpy})_2]^{2+}$ the field is quite close to that at the singlet $\leftrightarrow$ quintet crossover and it is perhaps not surprising then that terpyridine has proved a very useful model for fine-tuning the field strength so as to bring it into the thermal crossover region.

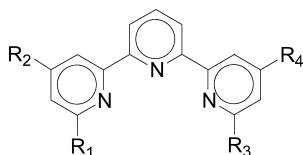
The two principal strategies detailed above for reducing the field strength of diimine systems have also been effectively adapted to bring the field strength of tridentate terimine systems into the crossover region.

3.1

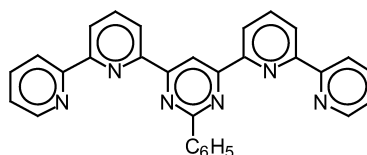
Effect of Ring Substituents

In **43** when $R_1=\text{C}_6\text{H}_5$; $R_2=R_3=R_4=\text{H}$ or when $R_1=R_2=\text{C}_6\text{H}_5$; $R_3=R_4=\text{H}$ the steric bulk of the phenyl substituent adjacent to one of the terminal donor atoms has been shown to bring the field into the crossover region, both a temperature- and pressure-induced transition being observed for the $[\text{Fe N}_6]^{2+}$ systems in solution. For both of these ligand systems solid hexfluorophosphate and perchlorate salts were isolated, the former being high spin ($\mu_{\text{eff}}=5.3 \mu_{\text{B}}$ in the range 40–290 K for $R_1=R_2=\text{C}_6\text{H}_5$) and the latter low spin. A steric influence of the $R_1=\text{C}_6\text{H}_5$ substituent is evident in the structure of the low spin $[\text{Fe } \mathbf{43}_2](\text{ClO}_4)_2$ with the $\text{Fe}-N_{\text{phenyl}}$ distance (average 2.05 Å) being longer than the terminal $\text{Fe}-N_{\text{hydrogen}}$ (average 2.00 Å). The difference in the average overall $\text{Fe}-\text{N}$ bond lengths for the high spin and low spin salts is $\sim 0.23 \text{ Å}$, comparable to that usually observed. When R_1 and R_3 are both either CH_3

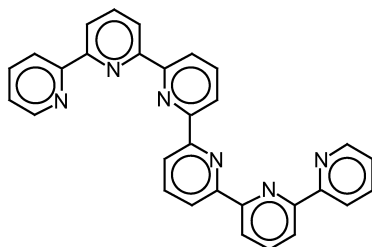
or C_6H_5 the complexes are high spin in both solution and the solid state [58].



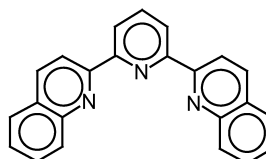
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44



45



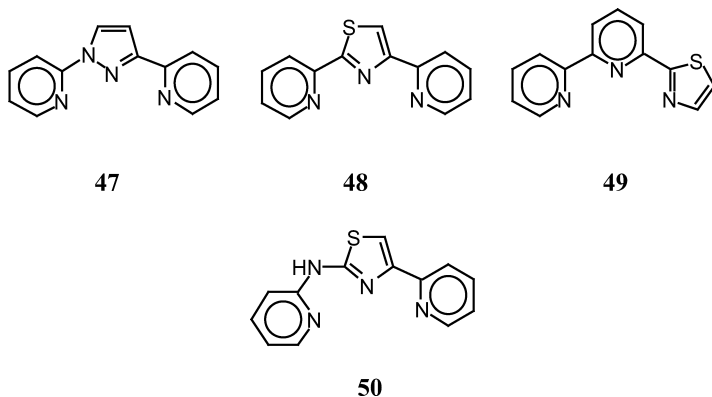
46

In the bis(tridentate) system 4,6-bis(2',2''-bipyrid-6'-yl)-2-phenyl-pyrimidine **44** the phenyl-substituent is adjacent to a terminal donor atom of the two terpyridine-like moieties, and in the grid-like structure of the tetranuclear species $[Fe_4L_4](ClO_4)_8$ temperature- and pressure-dependent populations of singlet and quintet states are observed [59]. Sexipyridine **45**, less constrained than **44**, also acts as a bis(terpyridine) system with each terpyridine unit effectively being substituted adjacent to one of the distal donor atoms. In this instance the more flexible coordination results in a dinuclear double-helical structure, $[Fe_2(sexipyridine)_2]^{2+}$ being paramagnetic in solution and presumably high spin [60], while the hexafluorophosphate salt is low spin in the solid state [61]. 2,6-Bis(quinolin-2-yl)pyridine **46** may be considered a di-substituted terpyridine and in this instance the salts of the $[Fe N_6]^{2+}$ derivative are purely high spin [62]. A spin transition in the complex of 4,4',4''-tris(diethylamino) substituted terpyridine, proposed on the basis of the observation of paramagnetism for the complex in solution at room temperature only ($\mu_{eff}=1.6 \mu_B$) requires confirmation, since temperature-independent paramagnetism of this magnitude may be associated with low spin iron(II) [63].

3.2

Effect of Ring Replacement

A more widely applied approach to modifying the terpyridine system so as to reduce the field has been to replace one or more of the pyridine rings with five-membered rings. The effects of replacement are much more pronounced for the central ring, because of the steric and electronic features mentioned above, and the $[\text{Fe N}_6]^{2+}$ derivative of 1,3-bis(pyridin-2-yl)pyrazole **47**, for example, is high spin [64]. This effect is revealed further by the drastically different properties of the $[\text{Fe N}_6]^{2+}$ derivatives of the isomeric tridentate ligands 2,4-bis(pyridin-2-yl)thiazole **48** ($\text{Dq}(\text{Ni}^{2+})$ 1125 cm^{-1}) and 6-(thiazol-2-yl)-2,2'-bipyridine **49** ($\text{Dq}(\text{Ni}^{2+})$ 1230 cm^{-1}).

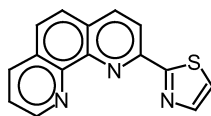


For the former the salts are very susceptible to hydrolysis and are high spin at room temperature but undergo a partial transition to low spin at low temperature [65, 66], while for the latter the salts are low spin and are almost indistinguishable from those of terpyridine [67]. The average Fe–N distances in the $[\text{Fe N}_6]^{2+}$ derivatives of **48** and **49** are $2.20\text{ \AA}$ and $1.94\text{ \AA}$, respectively, the former being somewhat longer than usual for $\text{Fe}_{\text{HS}}\text{--N}$, but in the complex of **48** the central five-membered ring imparts considerable steric strain within both fused chelate rings. The N–Fe–N angles within these rings (70.3° and 74.4°) reflect this effect. In the complex of **49** the average $\text{Fe--N}_{\text{central}}$ distance ($1.89\text{ \AA}$) is the same as that in $[\text{Fe}(\text{trpy})_2]^{2+}$, but the $\text{Fe--N}_{\text{terminal}}$ distances are quite different, the $\text{Fe--N}_{\text{py-terminal}}$ ($1.90\text{ \AA}$) being considerably shorter, and the $\text{Fe--N}_{\text{thiazole}}$ ($2.04\text{ \AA}$) longer than the average $\text{Fe--N}_{\text{terminal}}$ distance in $[\text{Fe}(\text{trpy})_2]^{2+}$ ($1.99\text{ \AA}$). When a terminal ring is replaced by other five-membered heterocycles such as triazole [68] pyrazole [69] or oxadiazole [70], the $[\text{Fe N}_6]^{2+}$ derivatives are similarly low spin.

In **50** the strain resulting from tridentate coordination of **48** is alleviated by the $>\text{NH}$ bridge between the thiazole and one of the pyridine rings, creating one six-membered and one five-membered chelate ring. This is evident from the structure of the high spin fluoroborate salt $[\text{Fe } \mathbf{50}_2](\text{BF}_4)_2 \cdot 3\text{H}_2\text{O}$ in

which the angles at the iron atom are 81° in the six-membered and 76° in the five-membered ring [71]. This system and a number of related ones are of further interest in that, in addition to the cationic complex, uncharged complexes of the deprotonated ligand can be obtained and in both systems a spin transition is observed [72]. The complex $[\text{Fe } \mathbf{50}_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ displays features of the spin crossover phenomenon which are still rather rare. The hydrate is essentially low spin at room temperature but a continuous transition to high spin occurs at higher temperature until the solvate water is lost to give the anhydrous species which is fully high spin at room temperature. The anhydrous salt undergoes a transition to low spin at low temperatures. Despite the gradual nature of this transition it is associated with a thermal hysteresis loop ($T_{1/2\downarrow}=229\text{ K}$ and $T_{1/2\uparrow}=263\text{ K}$). Moreover, metastable high spin species can be thermally trapped by rapid cooling of the substance. Relaxation of this to the thermodynamically stable state occurs only above 150 K [73]. At room temperature the high spin anhydrous salt is quickly converted to the essentially low spin hydrate on exposure to air and the reverse process occurs either at elevated temperature or in a dry atmosphere.

In contrast to 6-substituted-bipyridine systems such as **49**, attachment of a five-membered heterocycle to the 2-position of 1,10-phenanthroline, which is a structural modification similar to the replacement of one of the terminal rings of terpyridine, does generally bring the ligand field into the crossover region and spin transitions have been observed for such systems when the heterocycle is thiazole **51** [74], imidazoline [75], triazole [76], pyrazole [77] and oxadiazole [78].

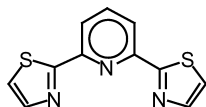
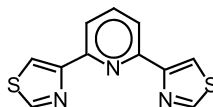
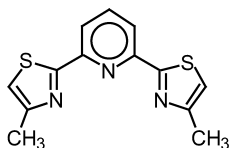
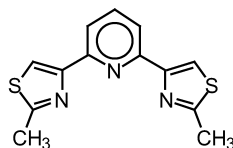


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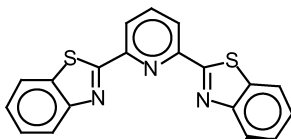
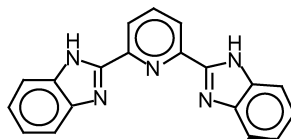
Comparison of the relative field strengths of the corresponding substituted bipyridine and phenanthroline systems reveals a consistently weaker field for the latter; for instance $\text{Dq}(\text{Ni}^{2+})=1230\text{ cm}^{-1}$ for **49** and 1160 cm^{-1} for **51**. The phenanthroline systems are structurally more rigid and the strain inherent in the tridentate coordination of essentially planar terimine systems is greater for these. Structural studies reveal greater flexibility of the bipyridine-based systems, as reflected in the geometry of the chelate rings [79]. This observation appears to conflict with the stronger field of phenanthroline as a simple bidentate compared to bipyridine but a degree of structural flexibility, as exists in the bipyridine systems, is much more pertinent to tridentate coordination.

Replacement of both terminal rings of terpyridine by five-membered heterocycles results in a further reduction of the field compared to that when

only one of these rings is replaced, but still the effect is not as great as replacement of the central ring. Therefore, when both terminal rings of terpyridine are replaced by thiazole moieties (either 2-thiazolyl **52** or 4-thiazolyl **53**) the $[\text{Fe N}_6]^{2+}$ derivatives remain low spin ($\text{Dq}(\text{Ni}^{2+})$ values 1190 and 1220 cm^{-1} for **52** and **53**, respectively) [80, 81].

**52****53****54****55**

Similarly, the tridentate containing two imidazole [82] or imidazoline [80] rings flanking the central pyridine ring gives a low spin derivative. For the bis(thiazolyl) systems further reduction in the field by incorporating substituents adjacent to the N-donor atoms of the thiazole rings brings it into the crossover region. Continuous transitions are observed below and above room temperature for salts of the $[\text{Fe N}_6]^{2+}$ derivatives of **54** ($\text{Dq}(\text{Ni}^{2+})=1160 \text{ cm}^{-1}$) [80] and **55** ($\text{Dq}(\text{Ni}^{2+})=1180 \text{ cm}^{-1}$) [81], respectively. Fusion of benzene rings has essentially the same effect and the $[\text{Fe N}_6]^{2+}$ derivative of bis(benzthiazol-2-yl)pyridine **56** is also a spin crossover system [83], as is that of bis(benzimidazol-2-yl)pyridine **57** [84].

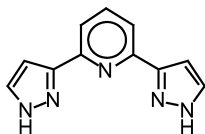
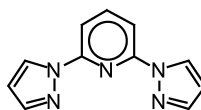
**56****57**

This contrasts with the purely high spin nature of the complex of 2,6-bis(quinolin-2-yl)pyridine [62] **46** and is consistent with the reduced steric barrier to coordination from substitution adjacent to the donor atom within five-membered rings, evident in the diimine systems.

3.3

2,6-Bis(pyrazolyl)pyridine Systems

The incorporation of two terminal pyrazole or triazole rings into the terpyridine framework leads to a diversity of spin crossover behaviour not seen, for example, in the bis(thiazolyl) systems discussed above. It is likely that the presence of a non-coordinating >NH group and its involvement in hydrogen bonding gives rise to the striking effects. For a series of salts of $[\text{Fe}(\text{bpp})_2]^{2+}$ (bpp is 2,6-bis(pyrazol-3-yl)pyridine **58**) a marked dependence of the spin state on the anion and the extent of hydration has been observed [85–88].

**58****59**

In general, the hydrated salts are essentially low spin at room temperature. As the temperature is increased the gradual emergence of a high spin fraction is observed until, at a specific temperature a complete conversion to the high spin state occurs. When the sample is re-cooled to room temperature it remains high spin. This is associated with the loss of solvate water at the elevated temperature and the totally different spin-state behaviour of the dehydrated sample, reminiscent of the properties of $[\text{Fe } \mathbf{50}_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ mentioned above. It has been observed for the fluoroborate, perchlorate [83], bromide, and iodide salts [86]. For all of these salts the role of solvate water is to stabilise the singlet state for iron(II). Structural data for the hydrated tetrafluoroborate and iodide show that the >NH groups of the pyrazole moieties are hydrogen bonded to both the solvate water and the anions. Both of these interactions will result in a strengthening of the σ -donor capacity of the pyrazole N-2 atoms. With the loss of water any hydrogen bonding is limited to weaker interaction with the anions only and so the quintet state for the metal atom will be relatively favoured. For the triflate salt, which crystallises as a trihydrate, the sharp change in electronic properties is observed on the loss of two of the solvate molecules. With the loss of the third a partial restoration of low spin species occurs. The low spin fraction in this anhydrous species increases only gradually with decrease in temperature and levels out at around 0.5 at about 90 K. Again the structure of the low spin trihydrate salt shows extensive hydrogen-bonding of the solvate water to the pyrazole >NH groups [87].

For the high spin species formed on the loss of water, abrupt transitions to the low spin state are observed below room temperature. For the anhydrous iodide and tetrafluoroborate and for the triflate monohydrate these

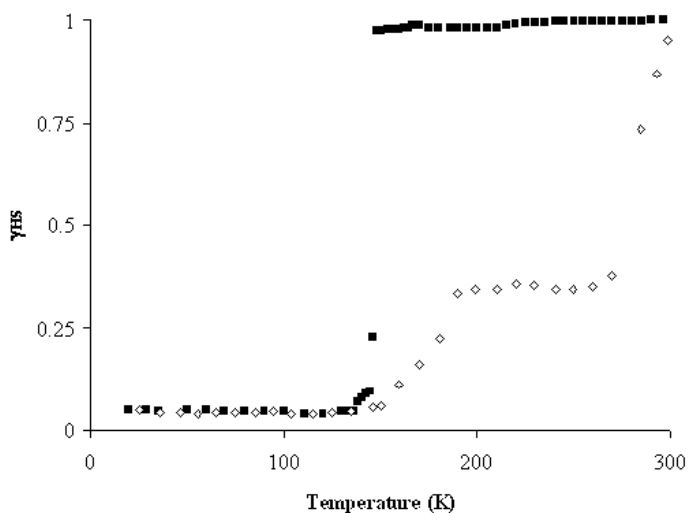


Fig. 1 Plot of high spin fraction (γ_{HS}) vs. temperature for $[\text{Fe}(\text{bpp})_2](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$

are associated with a thermal hysteresis loop, indicative of a structural phase change accompanying the transition. The loss of water results in breakdown of the crystal and structural data from x-ray diffraction could not be obtained.

For both the triflate monohydrate and the anhydrous tetrafluoroborate, metastable high spin species can be frozen-in by rapid cooling of the samples to 77 K, indicating that in the course of the abrupt HS→LS transition a phase change occurs, and rapid cooling results in freezing-in of the high-temperature, high spin phase. Further evidence for this has been obtained by Sung and McGarvey [89]. For the tetrafluoroborate salt, relaxation to the low-temperature thermodynamically stable low spin form occurs as the sample is gradually warmed up from 80 K. In addition, metastable high spin species can be generated by application of the LIESST effect [90]. The relaxation of the LIESST-generated species is initially relatively rapid between 60 and 70 K until the build up of about 5% of LS species and then virtually stops until the temperature reaches about 90 K; complete HS→LS relaxation occurs between 90 and 100 K, remarkably high for such a metastable state which, at least initially, was generated by the LIESST effect. At these temperatures the relaxation kinetics closely follow those of the frozen-in metastable high spin species. Therefore the initial rapid build-up of a small low spin fraction is believed to instigate a phase change to the metastable high spin form produced by rapid cooling and this form persists to the higher temperatures.

The spin transition curve (Fig. 1) for the triflate monohydrate displays some remarkable features [91]. The HS→LS transition is particularly abrupt

($T_{1/2\downarrow}=147$ K), while the LS→HS occurs in two steps and is displaced considerably to higher temperatures with $T_{1/2\uparrow}=285$ K for the major step, leading to an unsymmetrical and extremely broad (~ 140 K) hysteresis loop. Rapid cooling of this species results in trapping of more than 90% of the molecules in the high spin state. Application of the LIESST technique also causes almost complete generation of metastable high spin species. The two-step nature of the LS→HS conversion evident in the spin transition curve is believed to be due to two iron sites (with unequal occupancies) in the lattice presumably resulting from a structural modification below the temperature at which the spin transition (in cooling mode) is complete. This is further indicated by the appearance of two doublets due to high spin iron(II) in the Mössbauer spectrum of the LIESST-generated HS species. The relative intensities of these are comparable to the relative heights of the two spin transition steps (in heating mode). Relaxation of this metastable high spin species occurs in the range 77–85 K and is much faster than that of the thermally generated species, pointing to different mechanisms for the two processes. The decay of the latter species is very similar to that observed for the tetrafluoroborate salt and is influenced by an accompanying structural phase transition. For the LIESST-generated state of $[\text{Fe}(\text{bpp})_2](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ the decay is determined primarily by the HS→LS conversion, unlike in the tetrafluoroborate. For both of these salts reverse LIESST can be observed but the extent of HS→LS conversion is only about 10%, due to the broad-band nature of the excitation source.

The spin transition curve for $[\text{Fe}(\text{bpp})_2](\text{NCS})_2 \cdot \text{H}_2\text{O}$ shows two steps in both the decreasing and increasing temperature directions, thermal hysteresis being associated with both steps ($T_{1/2\downarrow}=247$ K; $T_{1/2\uparrow}=256$ K for the major step; $T_{1/2\downarrow}=193$ K; $T_{1/2\uparrow}=219$ K for the minor step). The transition observed for $[\text{Fe}(\text{bpp})_2](\text{NCSe})_2$ is abrupt but not accompanied by any measureable hysteresis. In the high spin form the average Fe–N distance is 2.16 and 2.17 Å for the thiocyanate and selenocyanate, respectively [88]. The selenocyanate was also obtained as a mixed solvate from nitromethane, $[\text{Fe}(\text{bpp})_2](\text{NCSe})_2 \cdot \text{H}_2\text{O} \cdot 0.25\text{CH}_3\text{NO}_2$. The unit cell for this form contains four independent iron atoms, three of which are low spin (average Fe–N=1.96 Å) and one high spin (average Fe–N=2.16 Å). The difference in the Fe–N distances for the low spin and the high spin state for the different complexes and that for the two spin states in the same complex, the selenocyanate solvate, are virtually the same and consistent with that observed in a variety of iron(II) spin crossover systems.

The only salt of the $[\text{Fe}(\text{bpp})_2]^{2+}$ ion for which crystal structural data have been obtained above and below the transition temperature is the nitroprusside, $[\text{Fe}(\text{bpp})_2][\text{Fe}(\text{CN})_5\text{NO}]$, which crystallises anhydrous. The cation is high spin at room temperature. This salt displays an abrupt transition with a narrow hysteresis loop, $T_{1/2\downarrow}=181$ K and $T_{1/2\uparrow}=184$ K. The transition is accompanied by a phase change; at 298 K the crystal is tetragonal with space

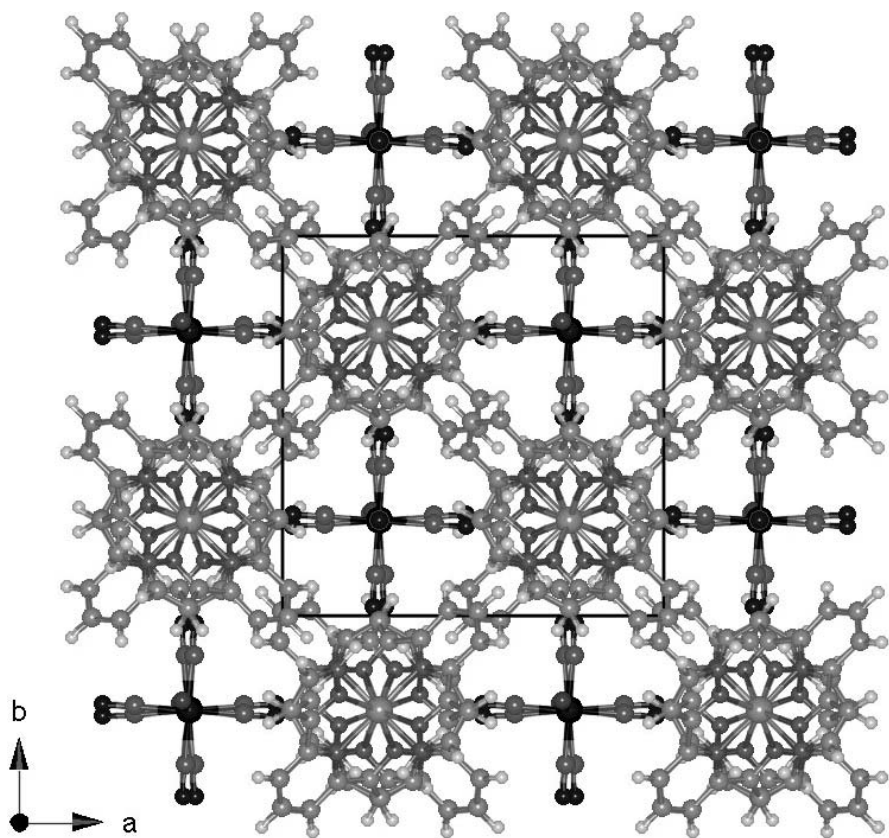


Fig. 2 Representation of two layers in the structure of $[\text{Fe}(\text{bpp})_2][\text{Fe}(\text{CN})_5\text{NO}]$ viewed down c . From [92]. Reproduced by permission of the Royal Society of Chemistry

group $P4/ncc$, while at 130 K it is orthorhombic with space group $Pbcn$. The average Fe–N bond length in the high spin phase is 2.17 Å while that in the low spin is 1.96 Å [92]. This difference is normal for a virtually complete transition and close to that evaluated from EXAFS measurements for $[\text{Fe}(\text{bpp})_2](\text{BF}_4)_2$ (0.19 Å) [93]. The most interesting feature of the structure is the involvement of the nitroprusside ion in hydrogen bonding to the pyrazolyl >NH groups. The structure consists of stacked layers of (4,4) nets. The two-dimensional hydrogen-bonded net consists of two distinct, alternating 4-connectors: each nitroprusside ion hydrogen bonds to four separate complex cations and each complex cation hydrogen bonds to four separate anions. Each of the pyrazole >NH groups is hydrogen bonded to a nitrogen of one of the four equatorial cyano groups of the nitroprusside ion. The axial CN and NO groups are not involved in hydrogen bonding. Two layers of the crystal structure of $[\text{Fe}(\text{bpp})_2][\text{Fe}(\text{CN})_5\text{NO}]$ are shown in Fig. 2 and the hy-

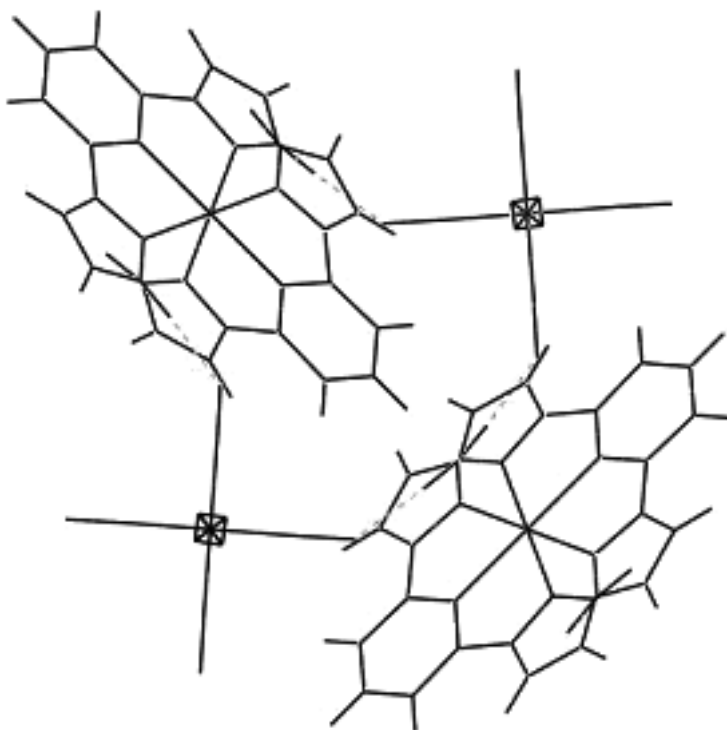


Fig. 3 Representation of the hydrogen bonding in a two-cation, two-anion fragment of $[\text{Fe}(\text{bpp})_2][\text{Fe}(\text{CN})_5\text{NO}]$

hydrogen bonding for a two-cation, two-anion layer fragment is shown in Fig. 3. For $[\text{Fe}(\text{bpp})_2]^{2+}$ the geometrical changes within the complex cation which accompany a change from high spin to low spin are relatively simple. Structural studies show that the N–C(4) axes of the two central pyridine rings coincide and pass through the metal atom in both spin states. The change in spin state is achieved essentially by expansion (LS $\rightarrow$ HS) or contraction (HS $\rightarrow$ LS) along this axis, the iron atom remaining at the centre, with concomitant changes in the bond angles within the chelate rings and in the Fe–N_{distal} distances.

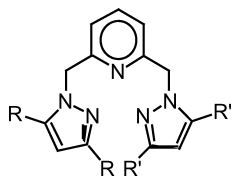
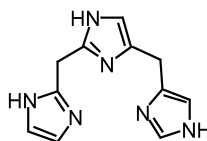
The terimine 2,6-bis(pyrazol-1-yl)pyridine **59** is isomeric with bpp but lacks the hydrogen-bonding potential of the latter. Despite this, the anhydrous tetrafluoroborate salt of its $[\text{Fe}(\text{N}_6)]^{2+}$ derivative shows behaviour remarkably similar to that of $[\text{Fe}(\text{bpp})_2](\text{BF}_4)_2$, an abrupt transition being observed centred at about 159 K with a hysteresis loop, $\Delta T_{1/2}=4$ K [94]. In this instance a suggested origin of the high cooperativity of the transition is a partial ordering of the anion accompanying the HS $\rightarrow$ LS conversion. At 290 K all four fluorines of each anion are crystallographically disordered in

contrast to the situation at 240 K where one F atom in each anion is ordered, the remaining three being disordered by rotation about this one B–F bond. The transition is not accompanied by a change in crystallographic space group but its first order nature is indicated by results of differential scanning calorimetry. The difference in the average Fe–N distance in the HS and LS states (0.215 Å) is virtually the same as that observed for [Fe(bpp)₂] [Fe(CN)₅NO] [92]. A further solvated form of the tetrafluoroborate salt [Fe 59₂](BF₄)₂·2.9CH₃NO₂·0.25H₂O was isolated [95]. This contains two independent cations in the asymmetric unit, both of which are low spin, at 150 K. In one of these one of the ligand molecules is unsymmetrically coordinated, with the Fe–N_{pyrazole} distances differing by 0.040 Å. In contrast to the tetrafluoroborate salt, [Fe 59₂](PF₆)₂ is completely high spin, even down to $T < 25$ K. The structure of this differs significantly from that of [Fe 59₂](BF₄)₂, and also from that of most other bis(terimine)metal systems, in that the N_{central}–Fe–N_{central} sequence is not linear and the planes of the two ligand molecules deviate markedly from the normal orthogonality, the dihedral angle being 62.6° [95]. This form of distortion would obviously have a major impact on the strength of the π -interaction between the metal and the central donors in particular, and would de-stabilise the singlet state. It has been suggested similar distortion may occur in other bis(terimine)iron(II) systems where inconsistencies appear in the magnetism of different salts or in solution and solid-state behaviour.

For the [Fe(bpp)₂]²⁺ system, spin transition behaviour is also observed in acetone solution. For the three salts examined, the tetrafluoroborate, iodide and hexafluorophosphate, the behaviour is virtually independent of the associated anion, unlike the situation in solid samples, and in this instance the molecular process occurs essentially independently of cooperative effects [86]. Analysis of the systems in terms of a simple low spin $\leftrightarrow$ high spin thermal equilibrium gives $\Delta H = 20 \pm 1$ kJ mol⁻¹ and $\Delta S = 80 \pm 4$ J K⁻¹ mol⁻¹ for the forward process, values typical for iron(II) spin crossover systems and similar to those obtained for solid [Fe 59₂](BF₄)₂ ($\Delta H = 24$ kJ mol⁻¹ and $\Delta S = 100$ J K⁻¹ mol⁻¹) from differential scanning calorimetry measurements [94].

2,6-bis(pyrazol-1-ylmethyl)pyridine **60** lacks the conjugation associated with a usual terimine but is related to the systems discussed above. [Fe N₆]²⁺ derivatives of all three ligands **60a–c** are high spin at room temperature but that of **60a** (Dq(Ni²⁺) = 1150 cm⁻¹) undergoes a continuous transition centred at about 220 K [96]. Steric effects influence the coordination of **60b** and **60c** and this is reflected in the values of Dq(Ni²⁺): 1150 cm⁻¹ (**60a**), 1110 cm⁻¹ (**60b**), 1070 cm⁻¹ (**60c**) [97]. The presence of two six-membered chelate rings in the coordination derivatives of **60** drastically influences the structure of the Fe N₆ coordination sphere, as shown for the high spin system [Fe **60b**]₂](ClO₄)₂ [98]. In contrast to the structure of related complexes of terimine systems such as **58** the Fe–N_{central} distance is particularly long (average

2.27 Å) and much longer than the Fe-N_{pyrazole} (average 2.17 Å). Moreover, the iron atom does not lie in the plane of the pyridine ring. In addition, the ligands deviate markedly from overall planarity, though they still coordinate in a meridional plane of the octahedron. The structure of [Fe **60a**]₂(ClO₂)₂, which undergoes a spin transition, would be of particular interest in its low spin form since steric crowding may be expected to be an issue here too, despite the absence of methyl substituents. Significantly, both the lower value for the quadrupole splitting and the higher value for the isomer shift in the Mössbauer spectrum of the low spin form of this complex ($\Delta E_Q = \sim 0.4 \text{ mm s}^{-1}$; $\delta_{i.s.} = \sim 0.5 \text{ mm s}^{-1}$) compared to corresponding values for complexes of **58** ($\Delta E_Q = \sim 0.7 \text{ mm s}^{-1}$; $\delta_{i.s.} = \sim 0.3 \text{ mm s}^{-1}$), indicate a much reduced contribution from $d_{\pi}-\pi^*$ bonding involving the metal atom and the pyridine ring. The structural flexibility of **60** is believed to give rise to conformational isomerism in [Fe **60c**]₂(ClO₄)₂·CH₃CN. It is suggested that these have *fac* (LS) and *mer* (HS) structures, the *fac* structure being favoured at high temperature. The possible existence of conformational equilibria within the six-membered chelate rings has also been considered. Therefore, for this system, the Mössbauer spectra reveal an increasing fraction of LS species with increasing temperature – the reverse of that observed for a true spin crossover system. The presence of the low spin fraction is difficult to reconcile with the average Fe–N distance measured at room temperature (2.22 Å), which is slightly longer if anything than that usually found for HS Fe(II) [99].

**60****61**

60a: R=R'=H; 60b: R=H; R'=Me; 60c: R=R'=Me

The tris(imidazolyl) system **61** is structurally related to **60**, but in this instance the FeN₆ coordination environment is less distorted and the average Fe–N distance (2.18 Å) is normal for high spin iron(II). In addition, the Fe–N_{central} distance in this system is not significantly different from the Fe–N_{distal} [100]. This system also undergoes a spin transition, the extent and nature of which is dependent on the associated anion [101].

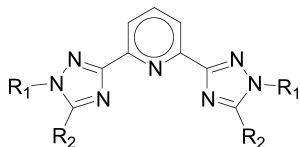
The tris(pyrazolyl)borate and tris(pyrazolyl)methane systems represent an important class of tridentates which lead to spin crossover behaviour in iron(II) but they belong to a totally different structural category and are

considered in detail in chapter 4 by Long. Nevertheless attention is drawn to the destabilisation of the singlet state in these relative to the tris(pyridin-2-yl)methane system, a further manifestation of the effect of five-membered rings [102]. The tris(imidazole) system **61** is the only reported instance of three linked five-membered heterocycles constituting a linear tridentate and leading to spin crossover behaviour in iron(II). It would seem unlikely that a conjugated terimine system containing three five-membered heterocycles would be capable of tridentate coordination to iron(II).

3.4

2,6-Bis(triazolyl)pyridine Systems

2,6-bis(1,2,4-triazol-3-yl)pyridine (btp) **62** ($R_1=R_2=H$) is closely related to bpp and also offers hydrogen bonding sites.



62

It is found for this system that solvate water can again have a decisive, but different, role in controlling the ground state of iron in salts of $[Fe(btp)_2]^{2+}$ [103]. Most of the salts studied are simple high spin paramagnets (average Fe–N distance in $[Fe(btp)_2][NO_3]_2 \cdot 4H_2O$ is 2.18 Å, close to that in the high spin salts of $[Fe(bpp)_2]^{2+}$), but $[Fe(btp)_2]Cl_2 \cdot 3H_2O$ undergoes a partial transition to low spin at low temperatures. This salt readily loses its solvate water and the anhydrous salt is entirely low spin at room temperature and shows no significant change in its magnetic moment up to 373 K. The effect of the lattice water here is the reverse of that observed in salts of $[Fe(bpp)_2]^{2+}$ and in most other systems where solvate water has a strong influence on spin-state. The effect in this instance can be rationalised from structural features of the iso-structural $[Ni(btp)_2]Cl_2 \cdot 3H_2O$. An extensive hydrogen-bonded network involving the uncoordinated >NH groups of the triazole rings, the anions and the water molecules is found. Unlike in salts of $[Fe(bpp)_2]^{2+}$ the hydrogen bonding from the ligands is to the anions (Cl^-) *only*, which are, in turn, hydrogen-bonded to the water. Therefore, loss of water should strengthen the ligand-anion interaction and thereby increase the σ -donor power of the triazole moieties. In the hydrated salts of $[Fe(bpp)_2]^{2+}$, on the other hand, the principal hydrogen bonding from the ligand is to the solvate water and in this instance dehydration would lead to a weakening of the overall hydrogen bonding and so a de-stabilisation of the singlet state. The loss of water from $[Fe(btp)_2]Cl_2 \cdot 3H_2O$ is facile, reversible, and readily de-

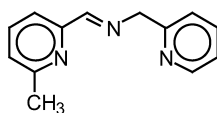
tectable at room temperature by accompanying major changes in, for example, the color, magnetism or Mössbauer spectrum. Hence this species has been proposed as a remote moisture sensor [104].

Methyl-substituents in the triazole rings of btp affect the electronic properties of the $[\text{Fe N}_6]^{2+}$ salts. The most pronounced effect seems to occur with the blocking of the hydrogen-bonding from the N-1 atom with concomitant stabilisation of the quintet state in the systems where for **62** $\text{R}_1=\text{CH}_3$ $\text{R}_2=\text{H}$ and $\text{R}_1=\text{CH}_3$ $\text{R}_2=\text{CH}_3$. In contrast, in salts of the $[\text{Fe N}_6]^{2+}$ derivative of **62** $\text{R}_1=\text{H}$ $\text{R}_2=\text{CH}_3$ the singlet state is more accessible than in the unsubstituted system, both in the solid state and in acetone solution. In this instance the electron-donating power of the 5-methyl group, together with the hydrogen-bonding from N-1, more than offset any barriers to coordination introduced by the 5-methyl group adjacent to the donor atom, though in any case the latter is not expected to be great in five-membered ring systems.

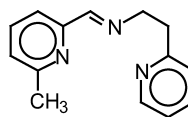
3.5

Schiff Base Terimines

As with the diimine systems, it is readily possible to generate the “terimine chromophore” [105] through Schiff base condensation of suitable amines and aldehydes. Though this does not always lead to the conjugated terimine moiety $-\text{N}=\text{C}-\text{C}=\text{N}-\text{C}=\text{C}-\text{N}=\text{C}$, Krumholz has demonstrated that conjugation over the two chelate rings is not essential to give the typical terimine behaviour [105]. Many such tridentates have been prepared and spin transitions have been reported for the $[\text{Fe N}_6]^{2+}$ derivatives in some instances. Maeda et al. have demonstrated the importance of chelate ring size in these systems [52]. They found that the tridentate **63** yields a low spin $[\text{Fe N}_6]^{2+}$ derivative in which the chelate rings are all five-membered, despite the presence of a substituent adjacent to one of the donor atoms, while the complex of **64** shows a very gradual and incomplete spin transition within the range 14–296 K.

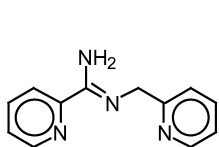


63

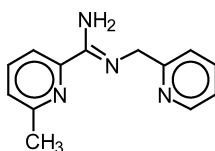


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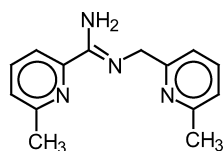
It is surprising that the quintet state for iron(II) is appreciably populated in the derivatives of the amidine system **65** ($\text{Dq}(\text{Ni}^{2+})=1170\text{ cm}^{-1}$), despite the absence, in this instance, of any apparent steric barrier to coordination from substituents and the formation of five-membered chelate rings.



65



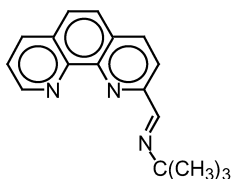
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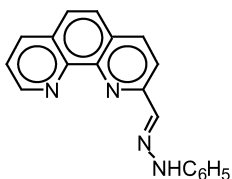
67

With a single methyl substituent **66** ($Dq(Ni^{2+})=1060\text{ cm}^{-1}$) yields a completely high spin species, as does the system with two substituents **67** ($Dq(Ni^{2+})=900\text{ cm}^{-1}$) [106].

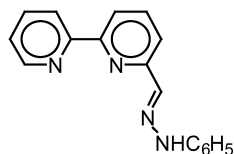
Condensation of 1,0-phenanthroline-2-carbaldehyde with a series of primary amines produces terimine systems in which the field can be varied in relatively small steps, leading to a continuous spin transition in the $[Fe N_6]^{2+}$ complex of the system obtained from the bulky *t*-butylimine **68** [107]. Similarly hydrazones may be obtained, the most important of which, in the present context, is the phenyl-hydrazone **69** (phy) [108].



68



69



70

These systems are very closely related structurally to terpyridine. The spin transitions in both the perchlorate and tetrafluoroborate salts of the $[Fe N_6]^{2+}$ derivative of **69** are discontinuous and centred just below room temperature. For the perchlorate $T_{1/2\downarrow}=239\text{ K}$ and $T_{1/2\uparrow}=247\text{ K}$, and for the tetrafluoroborate the values are $T_{1/2\downarrow}=276\text{ K}$ and $T_{1/2\uparrow}=282\text{ K}$ [109]. There is a crystallographic phase change along with thermal hysteresis accompanying the transitions [110]. The enthalpy and entropy changes at the transition have been determined as $\Delta H=15.8\text{ kJ mol}^{-1}$; $\Delta S=64.6\text{ J K}^{-1}\text{ mol}^{-1}$ for the perchlorate [111] and $\Delta H=24\text{ kJ mol}^{-1}$; $\Delta S=86\text{ J K}^{-1}\text{ mol}^{-1}$ for the tetrafluoroborate [110]. The transitions, occurring close to room temperature, are quite sensitive to the application of pressure, and the unusual effect of pressure in both displacing the transition in $[Fe(phy)_2](BF_4)_2 \cdot H_2O$ to higher temperature and in flattening it out at both extremes has been noted [112]. An interpretation in terms of both short-range and long-range interactions has been given [113].

In contrast to the phenanthroline-based systems, the similar incorporation of an azo-methine linkage into the 6-position of 2,2'-bipyridine is less effective in producing spin crossover behaviour because the higher fields produced stabilise the singlet state for iron(II). The $Dq(Ni^{2+})$ values for the

phenanthroline and bipyridine phenyl-hydrazones are 1110 and 1220 cm^{-1} , respectively and the $[\text{Fe N}_6]^{2+}$ complex of the latter is low spin [114]. This same effect was noted above (Sect. 3.2) in a comparison of the fields produced by systems containing a five-membered heterocycle attached to the 2-position in phenanthroline or to the 6-position of bipyridine.

4

Aryl-Aryl Interactions

In many salts of bis(terpyridine)metal ions the cations are oriented within the crystal structure in what has been termed the “terpyridine embrace”. This results in an interlocked arrangement which allows for offset face-to-face and edge-to-face interactions involving the pyridine rings in a layer-type structure, as illustrated in Fig. 4. [115]. Aryl-aryl interactions of this kind have been proposed as a mechanism for the cooperativity of the transitions in certain systems of the $[\text{Fe}(\text{dimine})_2(\text{NCS})_2]$ type [116] and in the bis(terimine)iron(II) system where the terimine is 57 [117]. This type of interlocking has been found to be fairly general for a wide variety of bis(terimine)systems, including certain salts of $[\text{Fe}(\text{bpp})_2]^{2+}$ [118]. It is present too in the crystal of bis(2,6-bis(pyrazol-1-yl)pyridine)iron(II) tetrafluoroborate [94]. In the latter system the cooperativity associated with the transition is

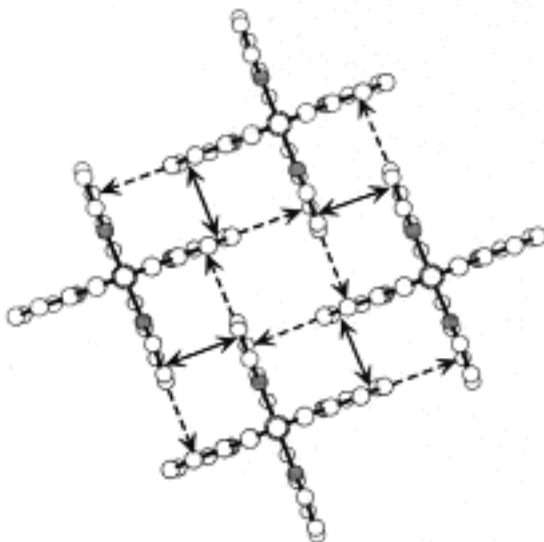


Fig. 4 Representation of the edge-to-face and face-to-face interactions in bis(terimine)metal systems. From [115]. Reproduced with the permission of CSIRO Publishing (www.publish.csiro.au/journals/ajc/)

apparently not associated with a crystallographic phase change and the possible involvement of the change in the anion motion in the region of the transition temperature with the actual spin transition has been raised. In salts of $[\text{Fe}(\text{bpp})_2]^{2+}$ hydrogen bonding from the pyrazole $>\text{NH}$ groups to the anion is considered a likely mechanism for the observed cooperativity, but it is possible that in these systems propagation of the spin change through the crystal is facilitated by these particular forms of aryl-aryl interactions. This is unlikely to be the case for the nitroprusside salt described in Sect. 3.3, however. For this salt the “terpyridine embrace” is not adopted by the lattice and the mechanism of the cooperativity most probably does involve the simple, but highly effective hydrogen-bonding network which links the spin transition centres via the nitroprusside ion bridges.

5

Conclusions

The tris(diimine) and bis(terimine) systems are, along with the $[\text{Fe}(\text{diimine})_2(\text{NCS})_2]$ family, probably the most common models for spin crossover behaviour in six-coordinate iron(II). The important feature of these is that they can be modified readily, in generally subtle ways, in order to fine tune the field strength. Their $[\text{Fe N}_6]^{2+}$ derivatives display virtually all of the features associated with the spin crossover phenomenon and can be adapted to exploit most of the mechanisms available for the cooperative propagation of spin changes throughout a solid. Unlike most examples from the $[\text{Fe}(\text{diimine})_2(\text{NCS})_2]$ family, these systems frequently display transitions in both the solid and solution phases, and so they are amenable to study by a greater variety of techniques, enabling the complementary characterisation of the spin crossover phenomenon both at the macroscopic and the molecular levels.

The incorporation into multinuclear species has so far achieved only limited success, but this is an area which should attract increasing attention in the future. A very interesting strategy to obtaining polymeric systems involving the utilisation of a mixed ligand system has recently been reported [119]. The tris(2-(pyridin-2-yl)imidazole)iron(II) system has been modified by replacing one of the bidentate ligands with the bridging 4,4'-bipyridine. This results in the build-up of a zig-zag chain of directly-linked FeN_6 centres together with effective π -stacking interactions. Despite this, the observed spin transition is gradual. Nevertheless, this approach is promising and offers considerable scope for extension.

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Spin Crossover in Pyrazolylborate and Pyrazolymethane Complexes

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Abstract The electronic spin-state crossover observed upon cooling and at high-pressure in the iron(II) and cobalt(II) complexes formed with the HB(pz)₃ and HC(pz)₃ ligands and their various methyl derivatives span a variety of different behaviors. Specifically [Fe(HB(pz)₃)₂], which is low-spin at 295 K, undergoes a spin state crossover to the high spin state both upon heating to ca. 420 K and at high pressure. [Fe(HB(3,5-(CH₃)₂pz)₃)₂], which is high-spin at 295 K, undergoes a spin state crossover to the low spin state both upon cooling below ca. 195 K and at high pressure. In contrast, [Fe(HB(3,4,5-(CH₃)₃pz)₃)₂] remains high-spin between 1.9 and 295 K but is gradually converted to the low-spin state with increasing pressure. Similarly, [Fe(HC(pz)₃)₂](BF₄)₂, which is low-spin at 295 K, undergoes a spin-state crossover to the high spin state upon heating. In a parallel fashion, [Fe(HC(3,5-(CH₃)₂pz)₃)₂]I₂, which is high-spin at 295 K, is completely converted to the low-spin state upon cooling. In contrast, [Fe(HC(3,5-(CH₃)₂pz)₃)₂](BF₄)₂, which is high-spin at 295 K, exhibits a phase transition upon cooling below 206 K in which only one-half of the iron(II) is converted to the low-spin state; the remaining one-half of the iron(II) remains high-spin even upon cooling to 4.2 K. This chapter presents a detailed discussion of these spin-state changes and those observed in the related cobalt(II) complexes.

Keywords High-pressure studies · Magnetic susceptibility · Mössbauer and Nuclear Magnetic Resonance spectroscopy · Pyrazolylborate complexes · Pyrazolymethane complexes

Abbreviations

acpa[H]	N-(1-acetyl-2-propylidene)(2-pyridylmethyl)amine
HS	high-spin
LS	low-spin
NMR	nuclear magnetic resonance
Ph	phenyl
pz	pyrazolyl
py	pyridyl

1**Introduction**

After their initial preparation by Trofimenko in the 1960's [1, 2], the new pyrazolylborate ligands, and more specifically the tris(1-pyrazolyl)borate anion, $\text{HB}(\text{pz})_3^-$, and the related substituted anions, such as $\text{HB}(3,5-(\text{CH}_3)_2\text{pz})_3^-$, and $\text{HB}(3,4,5-(\text{CH}_3)_3\text{pz})_3^-$, acquired a wide-ranging importance throughout chemistry as a whole, and especially in inorganic and coordination chemistry. By the beginning of the twenty-first century there were a few thousand papers dealing with the chemistry and coordinating ability of these ligands (and their close to 180 related derivatives). Indeed, an excellent starting point for any research in the pyrazolylborate field is the book *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands* by Swiatoslaw Trofimenko, a resource [1] which has 1568 references to the primary literature. Because this chapter is devoted to the study of the electronic spin-state crossover, only a few other recent papers will be cited to illustrate the utility of this family of ligands.

The role of the coordinated ligand $\text{HB}(3,5-(\text{CH}_3)_2\text{pz})_3^-$ in promoting alkane C–H bond activation through oxidative addition at rhodium has been reported by Bromberg et al. [3] and discussed in a recent in-depth review article [4] on C–H bond activation. References to the use of this and related ligands in C–H bond activation are summarized in a recent paper [5] which also reports the structures of several metal complexes with a new ligand, $\text{HB}(3,4,5-\text{Br}_3\text{pz})_3^-$, a strongly electron-withdrawing ligand.

Kirby et al. [6] have used an exchange coupled dinuclear iron(III) complex containing the $\text{HB}(\text{pz})_3^-$ ligand to experimentally observe the quenching of excited-state electron transfer. Because of their bulkiness $\text{HB}(3,5-(\text{CH}_3)_2\text{pz})_3^-$, $\text{HB}(3,4,5-(\text{CH}_3)_3\text{pz})_3^-$, and related ligands often lead to coordinately unsaturated complexes. Shirasawa et al. [7] have utilized this feature to study highly coordinately unsaturated tetrahedral iron, cobalt, and nickel complexes which represent 14, 15, and 16 electron systems, respectively. Ogihara et al. [8] have used the bulky nature of these ligands to induce the extradiol oxygenation of iron-catcholato complexes. Further, three-center

two electron bonds in iron, cobalt, and nickel complexes of dihydrobis(3-*t*-butylpyrazolyl)borate complexes have been studied by Belderrain et al. [9].

Pyrazolylborate ligands and their derivatives have played an important role in enzyme modeling [1], particularly for enzymes containing a metal coordinated to imidazolyl nitrogen derived from histidine ligands. A specific example involves molybdenum which, in its higher oxidation states, is found in several enzymes which catalyze oxygen transfer reactions. As a consequence, molybdenum is an essential nutrient for sustaining life. Specific examples of models are the $[\text{MoO}_2(\text{HB}(3,5-(\text{CH}_3)_2\text{pz})_3)](\text{SP}(\text{S})\text{R}_2)$ complexes which can both catalyze the oxidation of PPh_3 to PPh_3O and the reduction of $(\text{CH}_3)_2\text{SO}$ to $(\text{CH}_3)_2\text{S}$ [10]. Enemark and colleagues have also studied an extensive variety of related enzymatic systems involving pyrazolylborate related ligands [11–14].

Poly(pyrazolyl)borate and tris(pyrazolyl)methane ligands have been used to prepare a series of monomeric cadmium(II) complexes in which the coordination sphere about the cadmium can be carefully controlled [15–18]. These complexes have been studied by solution and solid phase Cd-113 NMR as model systems for the active sites in zinc metalloproteins [19–21]. These studies were important because zinc has relatively few spectroscopic probes. Zinc complexes with pyrazolylborate-like ligands have also been found to be very useful in modeling zinc-based enzymes such as carbonic anhydrase, an enzyme which has three histidine imidazolyl ligands coordinated to zinc [1]. The correlation between the mode of zinc coordination by bicarbonate and the activity of zinc-substituted carbonic anhydrase has been studied through the use of zinc complexes of pyrazolylborate derivatives. Specifically, Parkin and coworkers have studied [22–24] the properties of various complexes, including the structural properties of the carbonate ligated $[\text{Zn}(\text{HB}(3,5-(\textit{iso}\text{-propyl})_2\text{pz})_3)_2]\text{CO}_3$ complex, and have found monodentate coordination for the carbonate ligand.

Recently, Lipton et al. [25] have used zinc-67 NMR to investigate $[\text{Zn}(\text{HB}(3,5-(\text{CH}_3)_2\text{pz})_3)_2]$ complexes which have been doped with traces of paramagnetic $[\text{Fe}(\text{HB}(3,4,5-(\text{CH}_3)_3\text{pz})_3)_2]$. The low-temperature Boltzmann enhanced cross polarization between ^1H and ^{67}Zn has shown that the paramagnetic iron(II) dopant reduces the proton spin-lattice relaxation time, T_1 , of the zinc complexes without changing the proton spin-lattice relaxation time in the $T_{1\rho}$ rotating time frame. This approach and the resulting structural information has proven very useful in the study of various four-coordinate and six-coordinate zinc(II) poly(pyrazolyl)borate complexes that are useful as enzymatic models.

This chapter will concentrate on the electronic spin-state crossover observed in the iron and cobalt complexes formed with the $\text{HB}(\text{pz})_3^-$ and $\text{HC}(\text{pz})_3$ ligands and their various methyl derivatives. In the majority of cases, the spin-state crossover occurs in the solid state and, as a consequence, solid state studies will be covered first, followed by the more limited studies

in solution. A few other related complexes will also be discussed as appropriate.

2

Solid State Studies of Pyrazolylborate Complexes

Since its initial preparation, $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz})_3)_2]$ has become a classic example of an iron(II) complex exhibiting an electronic spin-state crossover from high-spin to low-spin upon cooling below room temperature. In addition, both $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ and $[\text{Fe}(\text{HB}(3,4,5\text{-(CH}_3)_3\text{pz})_3)_2]$ also exhibit important but differing spin-state crossover behaviors. More specifically, the low-spin iron(II) complex, $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$, undergoes a spin-state crossover from the low-spin to the high-spin state either upon heating above ca. 400 K or under the application of an external pressure. In contrast, $[\text{Fe}(\text{HB}(3,4,5\text{-(CH}_3)_3\text{pz})_3)_2]$ is high-spin at all temperatures down to 1.7 K but undergoes a spin-state crossover to the low-spin state at high pressure. Each of these complexes, as well as their cobalt analogues will be discussed in this section.

2.1

$[\text{Fe}(\text{HB}(\text{pz})_3)_2]$

The single crystal x-ray structure [26] of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$, which is essentially identical to that of the cation in the tris(pyrazolyl)methane analog, $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz})_3)_2](\text{BF}_4)_2$, shown and discussed below, indicates that at room temperature this distorted octahedral complex has an iron–nitrogen bond distance of ca. 1.97 Å, a distance which is indicative of a low-spin iron(II) complex with a nominal t_{2g}^6 electronic configuration and a $^1A_{1g}$ ground state. Indeed, Jesson et al. [27, 28] reported that $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ is diamagnetic between 4 and 300 K, whereas subsequent studies [29, 30] of the magnetic properties of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ between 78 and 470 K, see Fig. 1, clearly reveal, beginning at ca. 380 K, a transition to high-spin iron(II) with the nominal $t_{2g}^4e_g^2$ electronic configuration and a $^5T_{2g}$ ground state. A differential scanning calorimetry study [30] indicates that this spin-state crossover is accompanied by a crystallographic phase transition. Therefore $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ represents one of only a few low-spin iron(II) complexes which have been observed to undergo a spin state crossover above room temperature. No doubt there are many more such complexes yet to be discovered.

Several interesting features of the magnetic properties of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ are revealed in Fig. 1. First, between 78 and ca. 295 K the magnetic moment is not zero, as might be expected for a diamagnetic compound, but rather increases slightly from a moment of ca. $0.6 \mu_B$ at 78 K. This non-zero moment is typical of low-spin iron(II) complexes, and is a consequence of sec-

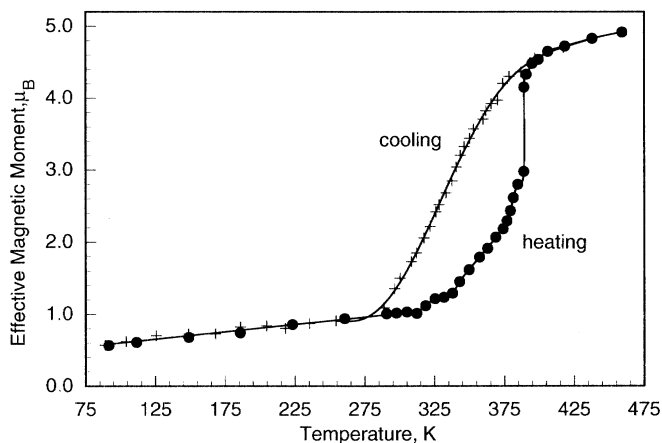


Fig. 1 The temperature dependence of the effective magnetic moment of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ during heating and cooling. Data obtained from Fig. 3 of [30]

and order Zeeman mixing of magnetic excited state wave functions with the non-magnetic ground state wave function – the temperature independent paramagnetic contribution to the magnetic moment. Second, upon initial heating the crossover from the low-spin state to the high-spin state occurs first gradually between ca. 325 and 375 K and then sharply to reach a value of ca. $5 \mu_B$ at 470 K, a value which is close to the value of ca. $5.2 \mu_B$ observed in many high-spin iron(II) complexes; the spin-only magnetic moment would be $4.9 \mu_B$. Third, upon cooling and subsequent reheating the magnetic moment exhibits a different temperature dependence with a substantial hysteresis in the thermal behavior. Finally, for all subsequent reheating and re-cooling cycles the magnetic properties essentially retrace the initial cooling curve and *not* the initial heating curve.

The unusual magnetic properties revealed in Fig. 1 are also apparent in the Mössbauer spectra of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ obtained upon its initial heating and cooling. As expected between 4.2 and 295 K the Mössbauer spectra of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$, obtained with samples that have never been heated above 295 K, are all very similar to that shown in Fig. 2 at 295 K and are typical of low-spin iron(II) complexes with the rather symmetric t_{2g}^6 electronic environment [31]. However, upon the initial heating above 295 K, the spectrum broadens but remains rather similar until ca. 405 K where there is a dramatic change as is illustrated in Fig. 2. All of the spectra obtained as a function of temperature may be found in reference [30]. Between 410 and 430 K the Mössbauer spectrum of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ is essentially that expected of a high-spin iron(II) complex. As expected, there is a dramatic increase in both the isomer shift and the quadrupole splitting, an increase which is a result of the nominal iron(II) high-spin $t_{2g}^4 e_g^2$ electronic configuration – a configura-

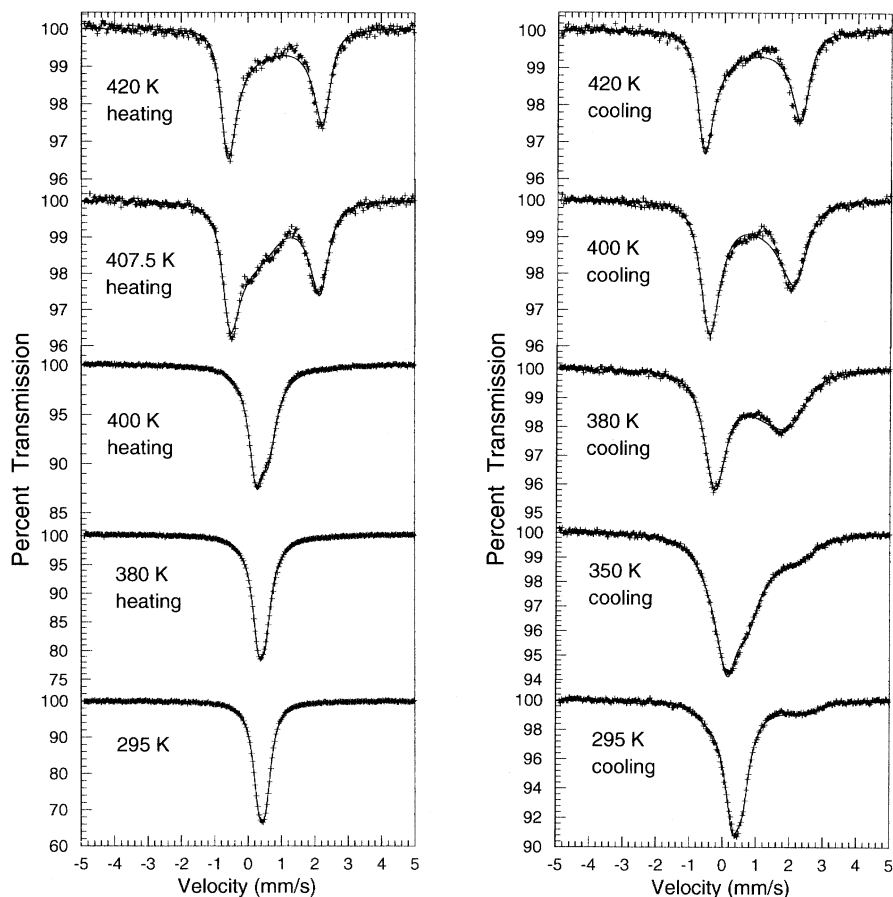


Fig. 2 The Mössbauer spectra obtained during the initial heating, left, and initial cooling, right, of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ and fitted with a relaxation model. Data obtained in part from [30]

tion which can lead to a highly asymmetric electronic environment in the presence of a low-symmetry crystal field.

Upon cooling, see Fig. 2, the observed Mössbauer spectra of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ are very different from those observed upon the initial heating. Indeed, the dramatic difference is immediately apparent through a comparison of the 380 and 400 K spectra shown in Fig. 2 for the initial heating and initial cooling. The spectra shown in this figure are very typical of rapid relaxation on the Mössbauer effect time scale between the high-spin and the low-spin iron(II) states. As a consequence, all of the Mössbauer spectra of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ obtained above 295 K were fitted with a relaxation model de-

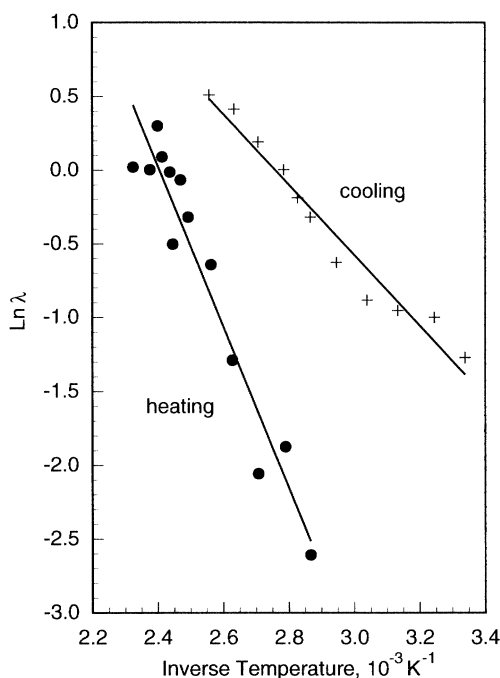


Fig. 3 An Arrhenius plot of the logarithm of the spin-state relaxation rate observed in $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ versus the inverse temperature. Data obtained from Fig. 9 of [30]

veloped by Litterst and Amthauer [32]. These fits are shown in Fig. 2 and more details of the fitting procedure are given in reference [30].

The relaxation fits of the Mössbauer spectra of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ yield [30] the temperature dependence of both the population of the iron(II) high-spin and low-spin states and the relaxation rate between these two states. The resulting population of the high-spin state has a striking resemblance to that of the magnetic moment shown in Fig. 1 and these populations provide clear support both for the spin-state crossover and for the difference in populations upon heating and cooling.

An Arrhenius plot of the natural logarithm of the spin-state relaxation rate observed for $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ is shown in Fig. 3. As might be expected from Fig. 2, the activation energy for the relaxation is higher for the initial heating of the crystals than for their cooling after the phase transition associated with the spin-crossover has shattered them. The linear fits shown in Fig. 3 yield activation energies of 7300 cm^{-1} for the initial heating of the single crystals and 1760 cm^{-1} for the cooling of the much smaller crystals present after they have been shattered by the phase transition.

The long-range cooperative nature of the electronic spin-state crossover in $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ and the accompanying crystallographic phase transition is

indicated by an abrupt increase in the high-spin population upon initial heating, see Fig. 1, and is also confirmed by the large activation energy observed upon initial heating. Although the observation of electronic spin-state relaxation on the Mössbauer-effect time scale is unusual for iron(II) compounds in the solid state, [33] relaxation rates very similar to those found for $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ have been reported for several iron(III) complexes [34, 35]. For instance, in $[\text{Fe}(\text{acpa})_2]\text{PF}_6$ the rapid electronic relaxation is associated with a crystallographic phase transformation [35]. In another study of an iron(II) compound, Adler et al. [36] found that $[\text{Fe}(\text{2-aminomethylpyridine})_3](\text{PF}_6)_2$ undergoes relaxation on the iron-57 Mössbauer effect time scale between ca. 200 and 290 K with an activation energy of 1720 cm^{-1} for the high-spin to low-spin state electronic transition. The activation energy for $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ upon cooling after the phase transition is virtually the same, but the activation energy for the initial heating is substantially larger.

The difference in the relaxation rate and activation energies between the two electronic spin states of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ and hence in the Mössbauer spectra obtained on heating and cooling may be understood on the basis of the physical changes that occur in the crystals during the crystallographic phase change that occurs during the initial heating. A visual microscopic examination of the crystal both before and after the heating indicates that, at the phase transition, the large well-formed deep violet single crystals of sublimed $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ shatter to yield extremely fine white crystals whose largest dimension is approximately one to two percent of that of the initial crystals. Therefore the magnetic measurements and the infrared and Mössbauer spectral studies [30] indicate that the initial spin-state crossover is a cooperative phenomenon which depends upon crystallite size. The activation energy for the electronic spin-state relaxation in the shattered microcrystals is reduced by a factor of three to four, perhaps as a result of a substantial decrease in the elastic energy of the lattice [37], an energy which may be stored in the crystals before their size has been greatly reduced. As a consequence, the electronic environment at a specific iron(II) site in $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ is free to fluctuate on the Mössbauer-effect time scale. On continued cooling, the Boltzmann population of the higher energy, high-spin, $^5\text{T}_{2g}$ electronic state is reduced, and the observed Mössbauer spectra gradually approach that expected for the low-spin iron(II) compound.

Finally it should be noted that, upon subsequent reheating, the Mössbauer spectra are the same as those obtained upon the initial cooling, see Fig. 2, and there is no indication of any abrupt change as is observed upon the initial heating.

As has been noted above, $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ undergoes a color change from deep violet to white upon heating, a change that is clearly revealed in its electronic absorption spectrum, see Fig. 4. The 297 K spectrum is dominated by a very intense charge-transfer band centered in the ultraviolet region and a less intense band centered at $19,000\text{ cm}^{-1}$. These absorptions account for

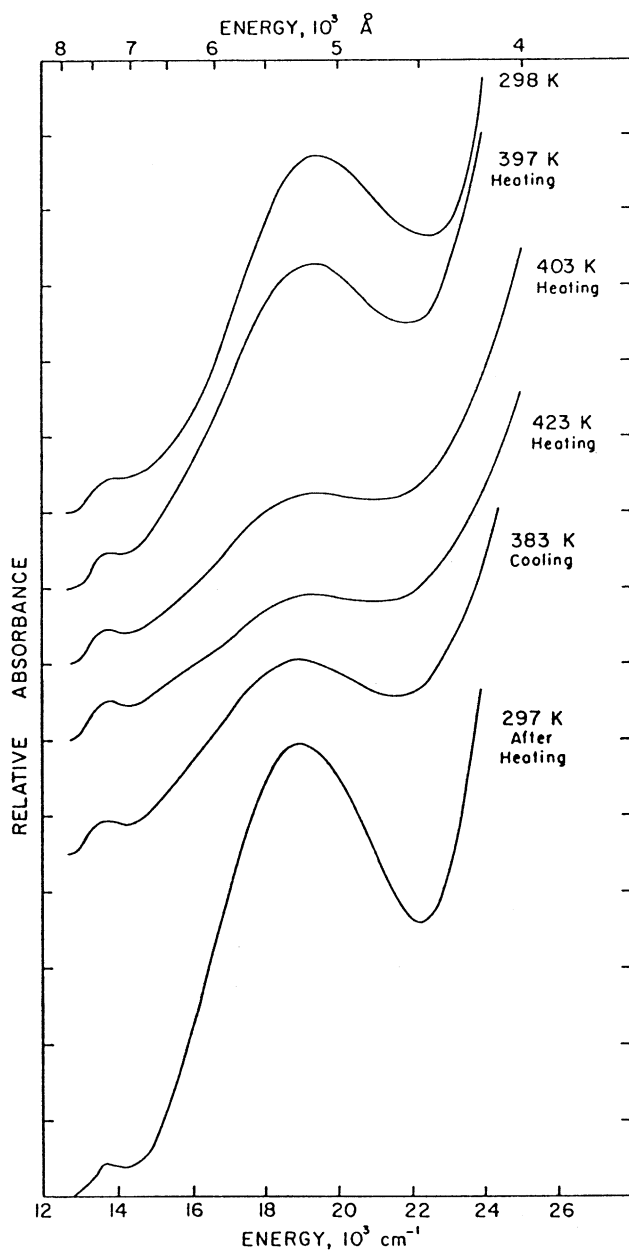


Fig. 4 The electronic absorption spectra of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ obtained upon heating and cooling. Figure obtained from [30]

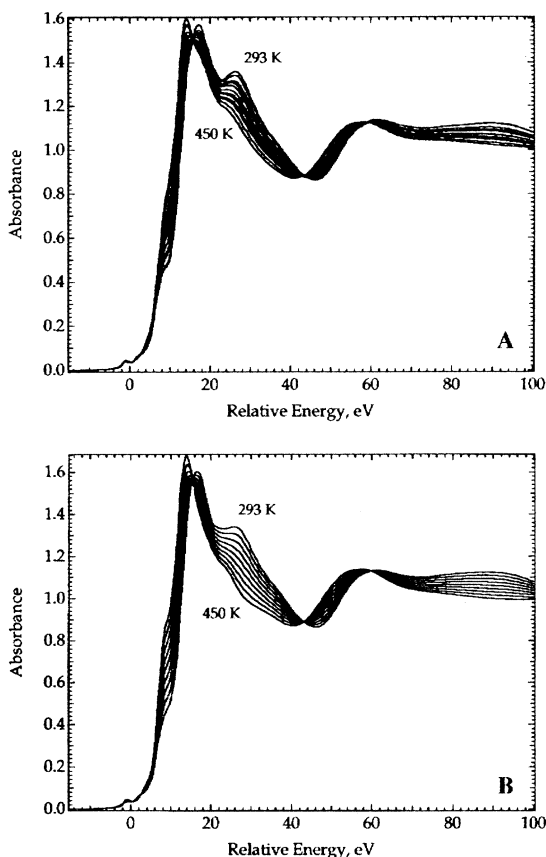


Fig. 5 The x-ray absorption near edge structure of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ obtained at various temperatures between 293 and 450 K, **A**, and its simulation obtained by taking weighted linear combinations of the 293 K low-spin spectrum of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ and the high-spin spectrum of $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz})_3)_2]$, **B**. At 30 eV in each plot the highest curve is for 293 K and the lowest curve is for 450 K

the deep violet color of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ at room temperature. Between 297 K and ca. 390 K the absorbance of the $19,000\text{ cm}^{-1}$ peak remains relatively constant. However, above ca. 390 K its absorbance decreases sharply, a decrease which is no doubt associated with the crystallographic phase transition observed at ca. 400 K. This change is observed visually as the crystals change from deep violet to white between 390 and 410 K. During the subsequent cooling of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ the absorbance at $19,000\text{ cm}^{-1}$ increases gradually until, at the lowest temperatures, it exceeds that of the unheated sample. These results indicate that $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ is slowly converted from the low-spin to the high-spin state upon an initial heating between 325 and 390 K, at which point the phase transition and electronic spin-state crossover occur

with a sharp decrease in the population of the $^1A_{1g}$ state and hence a decrease in the $19,000\text{ cm}^{-1}$ absorption peak. Upon cooling there is a gradual decrease in the population of the high-spin state and an increase in the population of the low-spin state in the admixture making up the electronic ground state. Upon subsequent reheating, the absorbance follows the cooling path. This behavior is completely consistent with the magnetic properties, see Fig. 1.

The electronic spin-state crossover in $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ has also been observed in the fine structure of its *K*-edge x-ray absorption spectrum [38]. The changes in the x-ray absorption spectra of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ are especially apparent between 293 and 450 K at ca. 25 eV, as is shown in Fig. 5. The 293 K x-ray absorption spectral profile observed in Fig. 5 for $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ has been reproduced [39] by a multiple photoelectron scattering calculation, a calculation that indicated that up to 33 atoms at distances of up to 4.19 Å are involved in the scattering. As expected, the extended x-ray absorption fine structure reveals [38] no change in the average low-spin iron(II)–nitrogen bond distance of 1.97 Å in $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ upon cooling from 295 to 77 K.

Rather unexpectedly, a high-pressure Mössbauer spectral study [31] has revealed that $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ undergoes a partial spin-state conversion from the low-spin iron(II) state at ambient pressure to the high-spin state at high pressure. Specifically, the Mössbauer spectra of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ show 15 and 22 percent high-spin iron(II) at 45 and 78 kbar, respectively. This spin-state conversion may seem unlikely as the high pressure should not decrease the crystal field potential and promote the population of the high-spin $^5T_{2g}$ state. Indeed, no such component was found [40], at least up to 50 kbar in $[\text{Fe}(\text{phenanthroline})_2\text{X}_2]$, where X is NCS, NCSe, and N_3 . However, Drickamer and his co-workers [41–43] have reported the formation of the high-spin state in a low-spin complex at high pressure. This occurs because the relative energy of the high-spin state decreases at high pressure due to the extensive changes in the ligand to metal π -bonding. Although extensive changes in the ligand to metal π -bonding are not expected in $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$, high-temperature Mössbauer spectral studies [30] discussed above do indicate the presence of the high-spin state that is populated through relaxation between the low-spin and high-spin states above ca. 400 K.

2.2

$[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz})_3)_2]$

As was mentioned above, the $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz})_3)_2]$ complex represents a “classic” example [27, 28] of an iron(II) spin-state crossover that may be induced in a high-spin complex upon cooling. The room temperature crystal structure of this complex [26] reveals a structure rather similar to that of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$, but with a substantially longer average iron–nitrogen bond

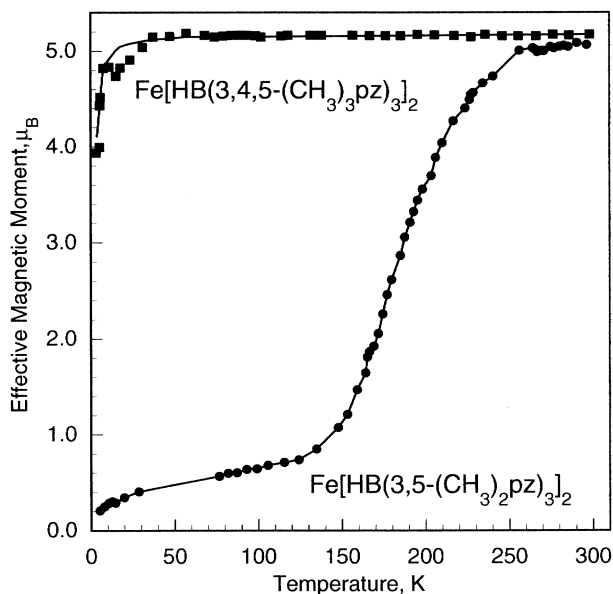


Fig. 6 The temperature dependence of the effective magnetic moment of $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz})_3)_2]$, lower plot, and $[\text{Fe}(\text{HB}(3,4,5\text{-(CH}_3)_3\text{pz})_3)_2]$, upper plot. Data obtained from Figs. 3 and 9 of [31]

length of 2.17 Å, a value typical of high-spin iron(II) in a pseudooctahedral coordination environment. The spin-state crossover upon cooling is immediately apparent in the lower plot of Fig. 6, which indicates that the effective magnetic moment of $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz})_3)_2]$ decreases from ca. 5 μ_B at 295 K, a value typical of high-spin iron(II) to close to 0.2 μ_B at 4.2 K, a value typical of low-spin iron(II) [28].

The spin-state crossover upon cooling of $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz})_3)_2]$ is also apparent in its Mössbauer spectrum as has been reported by Jesson et al. [28] and is shown [44] in part in Fig. 7. Indeed, the temperature dependence of the Mössbauer spectra of $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz})_3)_2]$ indicates that it is completely transformed from the high-spin state at 295 K to the low-spin state at 150 K and below. This figure indicates the importance of Mössbauer spectroscopy in the study of the spin-state crossover in iron(II) complexes. As is apparent in Fig. 7, the highly symmetric electronic environment produced by the nominal t_{2g}^6 electronic configuration yields a spectrum with at most a small quadrupole splitting, see the 78 K spectrum in Fig. 7. In contrast, the highly asymmetric electronic environment associated with the nominal high-spin iron(II) $t_{2g}^4 e_g^2$ electronic configuration, in the presence of a low-symmetry component of the crystal field, yields a large quadrupole splitting, see the 295 K spectrum of Fig. 7. Because the hyperfine parameters of the high-spin and low-spin doublets are so different they are well resolved

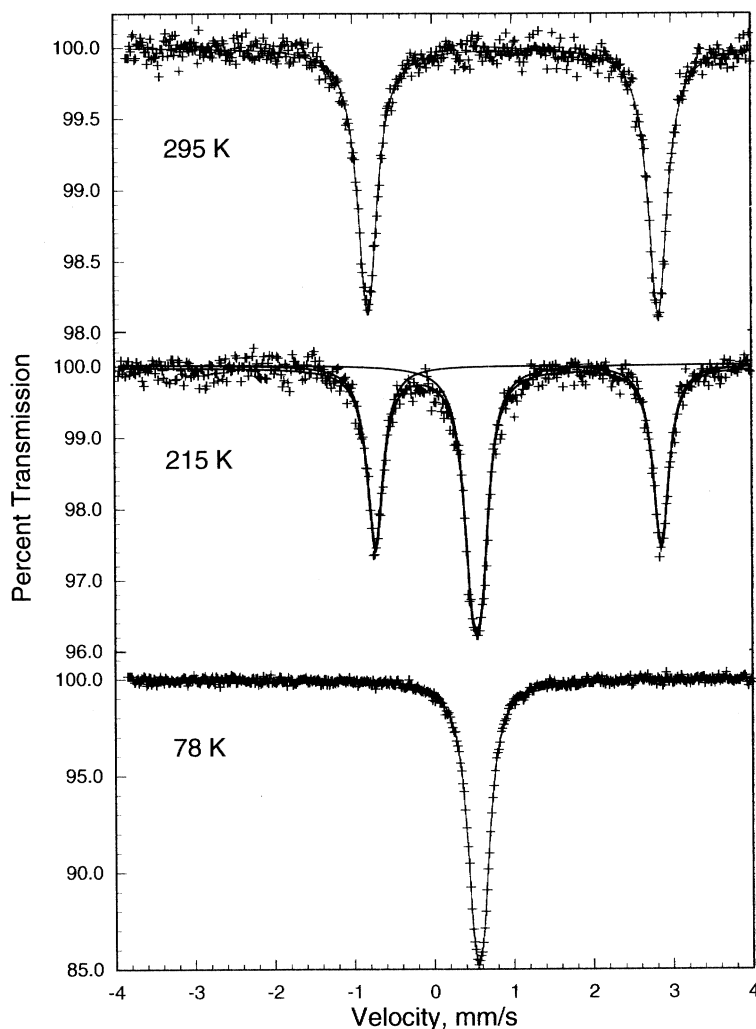


Fig. 7 The Mössbauer spectra of $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]$ obtained at the indicated temperatures and fitted with symmetric quadrupole doublets

in the Mössbauer spectrum, see the 215 K spectrum of Fig. 7, as long as the relaxation between the two sites is slow on the Mössbauer effect time scale.

The separation of the high-spin and low-spin components in the Mössbauer spectra of an iron(II) complex is especially useful in the study of the spin crossover at high pressure. Indeed, as is seen in Fig. 8, the application of as little as 2 kbar of pressure to $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]$ results in the generation of the low-spin state. At 4 kbar over 50 percent of the iron(II) in $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]$ has been converted to the low-spin state. The pres-

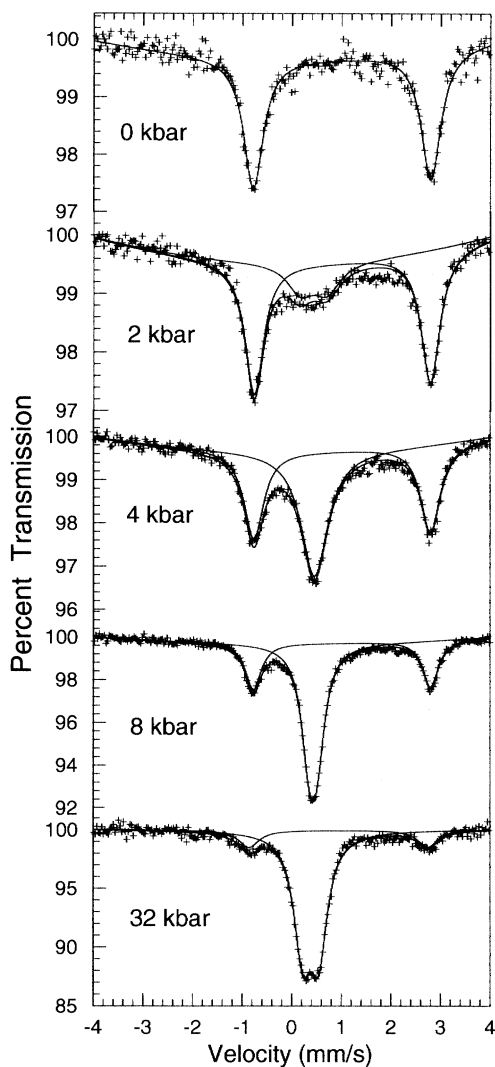


Fig. 8 The Mössbauer spectra of $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]$ obtained at 295 K and the indicated pressures. Plot obtained from [31]

sure dependence of the high-spin fraction of the Mössbauer spectral area observed for $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]$ is shown in Fig. 9. It has already been noted earlier [26] that $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]$ has one of the longest iron–nitrogen bond distances for the high-spin iron(II) state as compared to those of the low-spin state. Apparently, the application of pressure slowly decreases the iron–nitrogen bond distances in $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]$, a decrease which lowers the relative energy of the low-spin state and increases

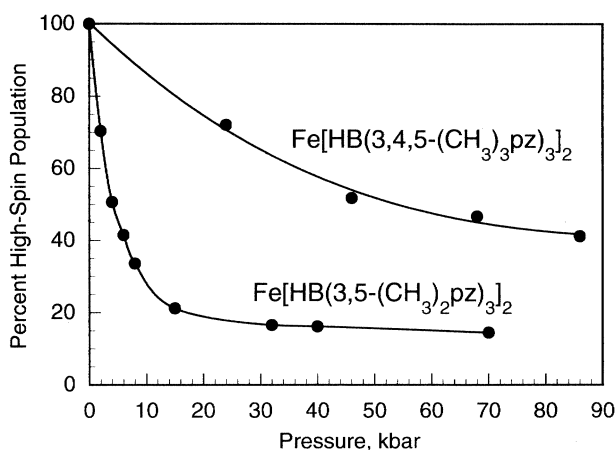


Fig. 9 The percentage of high-spin iron(II) observed in the Mössbauer spectra of $[\text{Fe}(\text{HB}(3,5-(\text{CH}_3)_2\text{pz})_3)_2]$ and $[\text{Fe}(\text{HB}(3,4,5-(\text{CH}_3)_3\text{pz})_3)_2]$ as a function of the applied pressure. Data obtained from [31]

its relative population. It appears that this bond compression reaches saturation at ca. 30 kbar and that both states are populated at 30 kbar and above, see Fig. 9.

Clearly the ambient pressure 295 K spectra of $[\text{Fe}(\text{HB}(3,5-(\text{CH}_3)_2\text{pz})_3)_2]$ shown in Figs. 7 and 8 show no sign of low-spin iron(II). Therefore at ambient pressure the sample can contain at most only a few percent of low-spin iron(II), the estimated detection limit, and probably much less. So, by assuming a Boltzmann distribution between the high-spin and low-spin state separated in energy by Δ , it is possible to calculate the changes in the energy between the two states with increasing pressure. The absence of the low-spin state at ambient pressure indicated that this state is at least 600 cm^{-1} above the high-spin ground state. At 2 kbar this separation has decreased to ca. 175 cm^{-1} and at 4 kbar the two states are approximately equivalent in energy. At 6, 8, 15, 40, and 70 kbar the low-spin state is the ground state and the high-spin state is, respectively, at 85, 140, 270, 340, and 360 cm^{-1} above the ground state. Hence, as might be expected for a compound with a long iron-nitrogen bond [26], there is a gradual shift in the relative energy of the two spin states with increasing pressure. This behavior is quite different from the sudden change in spin state with pressure that is observed [40] in $[\text{Fe}(\text{phenanthroline})_2(\text{NCS})_2]$.

The Mössbauer spectral isomer shifts of both spin states in $[\text{Fe}(\text{HB}(3,5-(\text{CH}_3)_2\text{pz})_3)_2]$ show the expected decrease with increasing pressure as the *s*-electron density at the iron-57 nucleus increases. In contrast, the quadrupole splitting for the high-spin state is almost independent of pressure whereas that of the low-spin state, which is dominated by the lattice contribution to

the electric field gradient tensor, increases by a factor of at least three between 3 and 70 kbar. Apparently the applied pressure has a significant influence upon the symmetry and packing of the ligands about the iron(II) in $[\text{Fe}(\text{HB}(3,5-(\text{CH}_3)_2\text{pz})_3)_2]$. In the high-spin state a difference in sign for the pressure dependence of the valence and lattice contribution to the electric field gradient tensor may account for the small change in the quadrupole splitting with pressure.

2.3

$[\text{Fe}(\text{HB}(3,4,5-(\text{CH}_3)_3\text{pz})_3)_2]$

The electronic spin-state crossover properties of $[\text{Fe}(\text{HB}(3,4,5-(\text{CH}_3)_3\text{pz})_3)_2]$ are quite different from those of either $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ or $[\text{Fe}(\text{HB}(3,5-(\text{CH}_3)_2\text{pz})_3)_2]$. Indeed, as may be seen in Fig. 6, the magnetic moment of $[\text{Fe}(\text{HB}(3,4,5-(\text{CH}_3)_3\text{pz})_3)_2]$ is essentially constant at ca. $5.2 \mu_B$ between 40 and 295 K; the small decrease in the moment below 40 K is a consequence of electron delocalization and the reduced symmetry crystal field in a distorted high-spin iron(II) complex with the nominal $^5T_{2g}$ ground state. Therefore, $[\text{Fe}(\text{HB}(3,4,5-(\text{CH}_3)_3\text{pz})_3)_2]$ remains high-spin upon cooling, a conclusion which is supported by Mössbauer spectral work [31] down to 1.7 K. It seems that the added bulk of the third methyl group in $[\text{Fe}(\text{HB}(3,4,5-(\text{CH}_3)_3\text{pz})_3)_2]$ effectively prevents the contraction of the lattice upon cooling to the extent needed to yield conversion to the low-spin state. In other words, the thermal contraction upon cooling is not significant enough to increase the crystal field and promote the population of the low-spin state.

A study of the pressure dependence of the spin state in $[\text{Fe}(\text{HB}(3,4,5-(\text{CH}_3)_3\text{pz})_3)_2]$ provides a nice contrast to the temperature dependence work. The Mössbauer spectra of $[\text{Fe}(\text{HB}(3,4,5-(\text{CH}_3)_3\text{pz})_3)_2]$, obtained at various pressures, see Fig. 10, indicate that a much higher pressure is required to produce the low-spin state than was required for $[\text{Fe}(\text{HB}(3,5-(\text{CH}_3)_2\text{pz})_3)_2]$, see Fig. 8. An increase in the pressure by a factor of twelve times is required to produce the same low-spin state population in $[\text{Fe}(\text{HB}(3,4,5-(\text{CH}_3)_3\text{pz})_3)_2]$ as in $[\text{Fe}(\text{HB}(3,5-(\text{CH}_3)_2\text{pz})_3)_2]$.

As was the case for $[\text{Fe}(\text{HB}(3,5-(\text{CH}_3)_2\text{pz})_3)_2]$, the conversion to the low-spin state in $[\text{Fe}(\text{HB}(3,4,5-(\text{CH}_3)_3\text{pz})_3)_2]$ is gradual, and the results indicate that at 24 kbar the low-spin state is ca. 200 cm^{-1} above the high-spin ground state. The two spin states are equivalent in energy at ca. 55 kbar and the low-spin state is 75 cm^{-1} below the high-spin state at 86 kbar. These results are an indication that the application of high pressure is sufficient to produce a spin-state change in iron(II) even when no such change is indicated at low temperature.

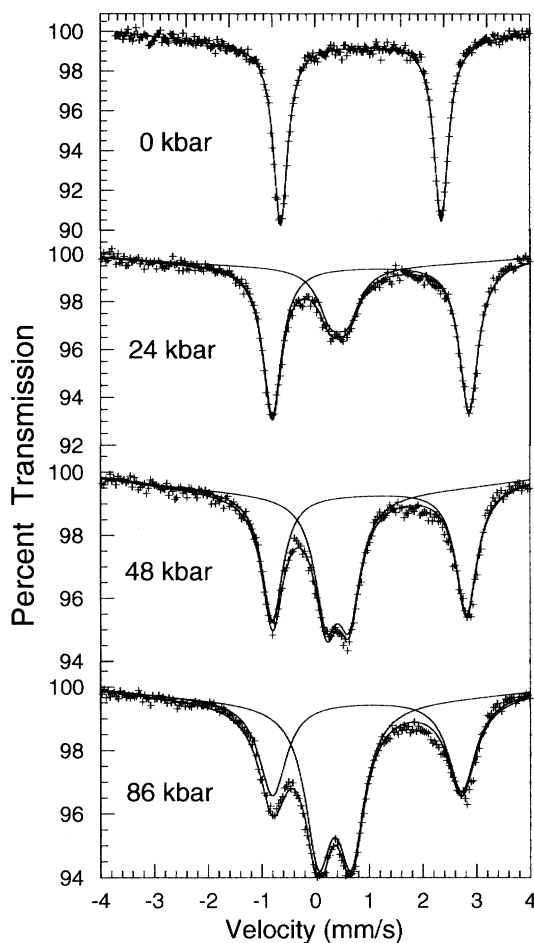


Fig. 10 The Mössbauer spectra of $[\text{Fe}(\text{HB}(3,4,5\text{-(CH}_3)_3\text{pz)}_3)_2]$ obtained at 295 K and the indicated pressures. Plot obtained from [31]

2.4

$[\text{Co}(\text{HB}(\text{pz})_3)_2]$, $[\text{Co}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]$, and $[\text{Co}(\text{HB}(3,4,5\text{-(CH}_3)_3\text{pz)}_3)_2]$

The electronic properties of the cobalt(II) complexes, $[\text{Co}(\text{HB}(\text{pz})_3)_2]$, $[\text{Co}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]$, and $[\text{Co}(\text{HB}(3,4,5\text{-(CH}_3)_3\text{pz)}_3)_2]$ are less well studied, but a recent x-ray absorption study [38] has revealed changes, with increasing pressure, in their electronic spin states from the high-spin $t_{2g}^5 e_g^2$ electronic configuration with the nominal $^4T_{1g}$ electronic ground state at ambient pressure to the low-spin $t_{2g}^6 e_g^1$ electronic configuration with the nominal ^2E_g ground state at high pressure. This study was made possible because the cobalt(II) complexes are isostructural with their analogous iron(II) com-

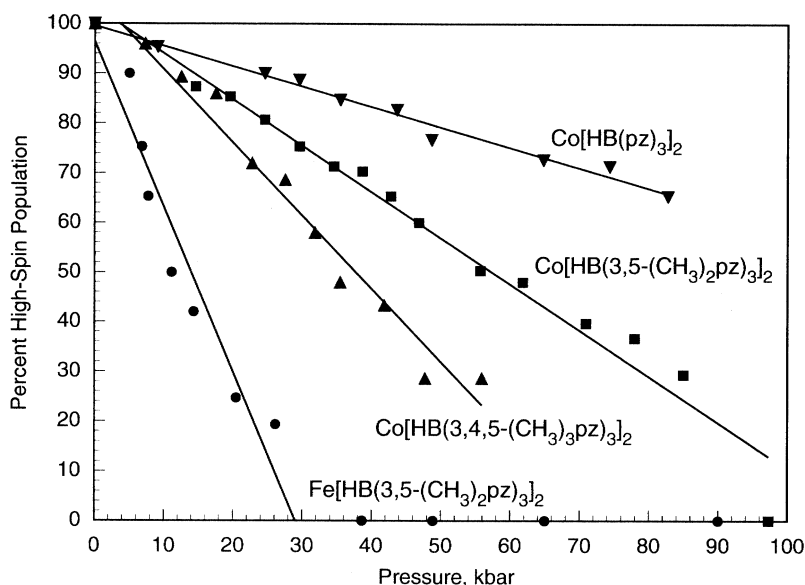


Fig. 11 The pressure dependence at 295 K of the percentage of high-spin state in [Fe(HB(3,5-(CH₃)₂pz)₃)₂], [Co(HB(pz)₃)₂], [Co(HB(3,5-(CH₃)₂pz)₃)₂], and [Co(HB(3,4,5-(CH₃)₃pz)₃)₂]. Data obtained from [38]

plexes whose properties are well known. The x-ray absorption near-edge structure, measured as a function of applied pressure, reveals, see Fig. 11, an essentially linear decrease in the cobalt(II) high-spin population with increasing pressure, a change that is most pronounced for [Co(HB(3,4,5-(CH₃)₃pz)₃)₂] and least pronounced for [Co(HB(pz)₃)₂].

The x-ray absorption near-edge structure of both the iron and cobalt complexes reveals that the energies of the metal 4*p* virtual orbitals are very sensitive to pressure and to the electronic spin state of the metal. A subsequent full photoelectron multiple scattering calculation [39] of the *K*-edge x-ray absorption spectra of both the iron and cobalt tris(pyrazolyl)borate and tris(pyrazolyl)methane complexes has revealed the importance of considering a large cluster of metal near neighbors in determining the absorption spectra and their associated changes upon spin-state crossover.

An extended x-ray absorption fine structure analysis [38] of the photoelectron scattering in the three cobalt complexes indicates both that they are all structurally very similar and that they exhibit the expected high-spin cobalt to nitrogen bond distance of 2.12 Å at 295 K and ambient pressure. Further, although all three of the cobalt complexes undergo a spin state change at high-pressure, they remain high-spin upon cooling from 295 to 77 K.

3

Solid State Studies of Pyrazolylmethane Complexes

Although the poly(pyrazolyl)borate complexes of iron(II) have been well known for many years, [1] it is only recently that the complexes with the tris(1-pyrazolyl)methane ligand, $\text{HC}(\text{pz})_3$, [45–48] have been studied in detail. It should be noted that poly(pyrazolyl)methane ligands, such as the tris(1-pyrazolyl)methane ligand, are neutral, whereas the poly(pyrazolyl)borate ligands, such as the tris(1-pyrazolyl)borate ligand, $\text{HB}(\text{pz})_3^-$, are monoanions. As a consequence, the metal(II) poly(pyrazolyl)methane complexes are dications and often have quite different properties from those of the analogous metal(II) poly(pyrazolyl)borate molecular complexes. But, in spite of these differences there are often very close structural similarities between the dicationic complexes and the neutral complexes. Therefore the study of the pyrazolylmethane complexes will parallel that of the borate complexes discussed above.

3.1

$[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$

The single crystal x-ray structure of the dication of $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$, see Fig. 12, has been found [46] to be essentially identical to the structure [26] of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$. Indeed, in both complexes the room temperature

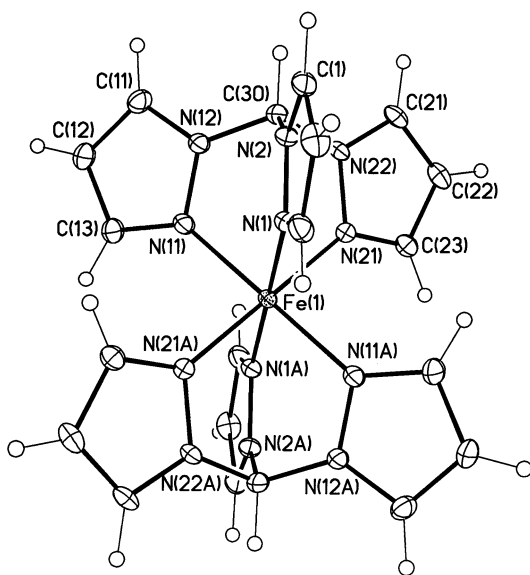


Fig. 12 The room temperature single crystal x-ray structure of the dication in $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$. Data obtained from [46]

iron–nitrogen bond distance is 1.97 Å, a distance which is indicative of low-spin iron(II) complexes. In a fashion similar to that of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$, it has been found that the magnetic moment of $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$ also increases at higher temperatures.

The increase in the magnetic moment observed for $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$ above ca. 300 K is very indicative of a spin-state crossover to the high-spin state at high temperature, a change that is supported by the Mössbauer spectra observed above 300 K, see Fig. 13. As may be observed in this figure, between 4.2 and 295 K the Mössbauer spectrum of $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$ is that expected of a low-spin iron(II) complex. In contrast, between 327 and 400 K the spectra clearly indicate that relaxation is occurring between the low-spin and high-spin states on the Mössbauer effect time scale of 10^{-8} s. Finally, at 472 K the spectrum is that expected of high-spin $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$.

An Arrhenius plot of the high-spin to low-spin relaxation rate, λ , obtained from the Mössbauer spectra of $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$, is shown in Fig. 14. The slope of this plot yields an activation energy for the relaxation of 2820 cm^{-1} , an energy which is intermediate between the 7300 and 1760 cm^{-1} values observed, respectively, for the initial heating and the subsequent cooling and reheating [30] of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$. In order to avoid extensive sublimation, the study of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ involved the use of rather large crystallites for the initial heating, crystallites which shattered at the spin crossover to yield much smaller crystallites and consequently a lower activation energy, see Fig. 5. For $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$ sublimation is not a problem and the relatively small crystallites used do not shatter at the spin crossover but do require a somewhat higher activation energy for relaxation than do the shattered $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ crystallites.

The 472 K hyperfine parameters [46] of $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$ are quite similar to those observed [30] at 430 K for $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$, the highest temperature at which it could be studied. However, in the relaxation model the signs for the electric field gradient of the two spin states are the same in $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ and opposite in $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$. This is immediately apparent from the narrower nature of the spectrum observed at 327 K than at 295 K, see Fig. 13. The reason for this difference between $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ and $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$ is not clear but may be related to the disposition of the BF_4^- anions about the cation in $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$. This disposition may also explain why the 472 K quadrupole splitting of 2.98 mm/s observed for the high-spin state of $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$ is smaller than the 430 K quadrupole splitting of 3.15 mm/s observed for the high-spin state of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$.

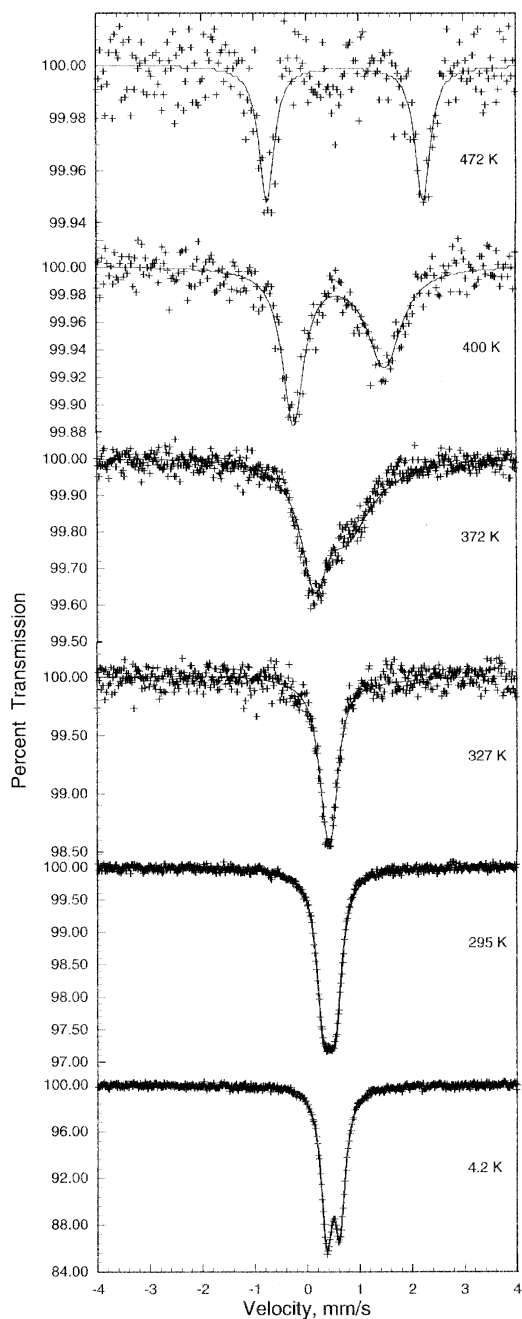


Fig. 13 The Mössbauer spectra of $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$ obtained at the indicated temperatures and fitted with a model for relaxation between the high-spin and low-spin electronic states. Data obtained from [46]

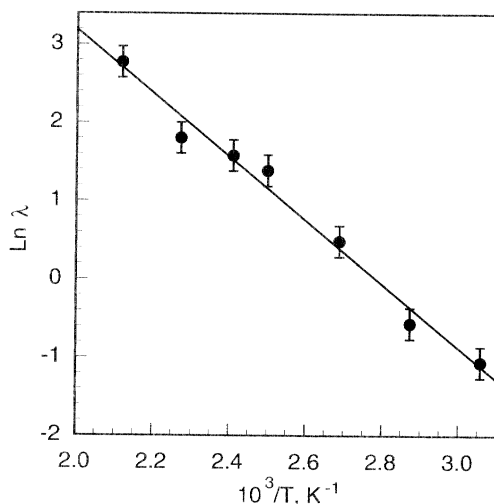


Fig. 14 An Arrhenius plot of the high-spin to low-spin relaxation rate obtained from the fits of the Mössbauer spectra of $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$ shown in Fig. 13. Data obtained from [46]

3.2

$[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz})_3)_2](\text{BF}_4)_2$

The room temperature single crystal x-ray structure of the dication of $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz})_3)_2](\text{BF}_4)_2$, see Fig. 15, has been found [46] to be essentially identical [26] to the structure of $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz})_3)_2]$. In both complexes the room temperature iron–nitrogen bond distance is 2.17 Å, a distance which is indicative of high-spin iron(II).

The inverse magnetic susceptibility and the effective magnetic moment, μ_{eff} of $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz})_3)_2](\text{BF}_4)_2$ are shown in Fig. 16 where it is immediately obvious that the magnetic properties of this complex are quite unusual [46]. Above ca. 210 K the μ_{eff} of ca. $5.0 \mu_{\text{B}}$ is clearly that expected of a high-spin iron(II) complex. But below ca. 190 K the moment decreases to a substantially lower value of ca. $3.7 \mu_{\text{B}}$. Further, at ca. 90 K there is a small irreversible change in susceptibility and moment, a change that is associated with crystal reorientation in the applied field. The reason for the abrupt decrease in the moment at ca. 200 K to ca. $3.7 \mu_{\text{B}}$ becomes apparent from a study of the Mössbauer spectra of $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz})_3)_2](\text{BF}_4)_2$.

The Mössbauer spectra of $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz})_3)_2](\text{BF}_4)_2$, obtained at the indicated temperatures are shown in Fig. 17. These spectra indicate that, unlike $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz})_3)_2]$ in which 100 percent of the iron(II) is low-spin at low temperature, see Fig. 7, the spin-state crossover in $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz})_3)_2](\text{BF}_4)_2$ involves only 50 percent of the iron(II) sites; in other words, below about 200 K one-half of the iron(II) cations have changed to

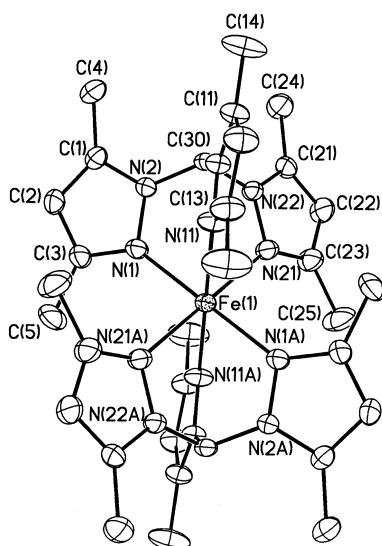


Fig. 15 The room temperature single crystal x-ray structure of the dication in $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$. Data obtained from [46]

the low-spin state whereas the other one-half of the cations have remained high spin. The partial spin-state crossover in $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$ is accompanied by a crystallographic phase transition, a transition which is also observed [47, 48] in $[\text{M}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$, where M is Co, Ni, and Cu.

The temperature dependence of the isomer shift and quadrupole splitting for the high-spin and low-spin iron(II) states in $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$ and details of the fits and their temperature dependence may be found elsewhere [46]. The extent of the spin-state crossover is shown in Fig. 18, a figure which clearly indicates that the spin-state crossover in $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$ stops at 50 percent. In contrast it should be noted that, in the structurally very similar $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]\text{I}_2$ complex, [49] the spin-state crossover is 100 percent complete at 4.2 K.

The reason for the partial spin-state crossover in $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$ is best understood through a study of the temperature dependence of the structural properties of the $[\text{M}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$ complexes, where M is Co, Ni, and Cu, [47] and a comparison with the analogous results [48] for $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$. In the case of the Co, Ni, and Cu complexes there is a crystallographic phase transition at some temperature between 220 and 125 K. In the high-temperature phase all metal(II) sites are equivalent but two distinct metal(II) sites are observed at low temperature. An analogous crystallographic phase transition also occurs in $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$ between 220 and 173 K [47].

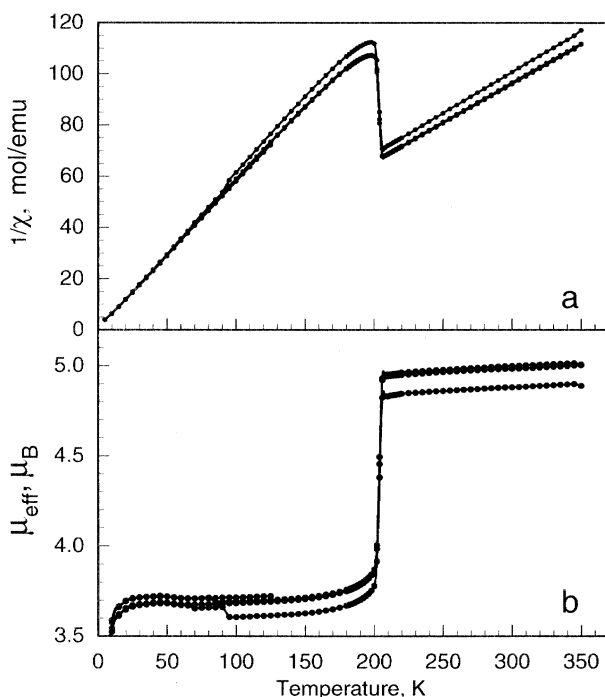


Fig. 16 The temperature dependence of the inverse molar magnetic susceptibility, **a**, and the corresponding effective magnetic moment, **b**, of $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$. Data obtained from [46]

In each case, at the lower temperatures, the two crystallographically different metal(II) sites have rather different coordination environments, the first remaining quite similar to that observed above the transition and the second becoming much more symmetric. Magnetic studies indicate that all of the cobalt(II) in $[\text{Co}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$ is fully high spin both above and below the crystallographic phase transition. In contrast, in $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$ at 173 K and below, the iron(II) site with the lower symmetry environment remains high spin whereas the iron(II) site with the higher symmetry becomes low spin. Therefore the unusual partial spin-state crossover observed in $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$ is apparently driven by the symmetry changes at the iron(II) site induced by the lattice energy driven crystallographic phase transition. Specifically, during the phase change, one-half of the cations distort in a way that favors their remaining high spin, whereas the other half distort in a way that favors their changeover to the low-spin state. The same change takes place in the other three metal complexes, but it appears that the strength of the crystal field present at the highly symmetric cobalt(II) site in $[\text{Co}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$ is not sufficient to yield low-spin cobalt(II) at the lower temperatures.

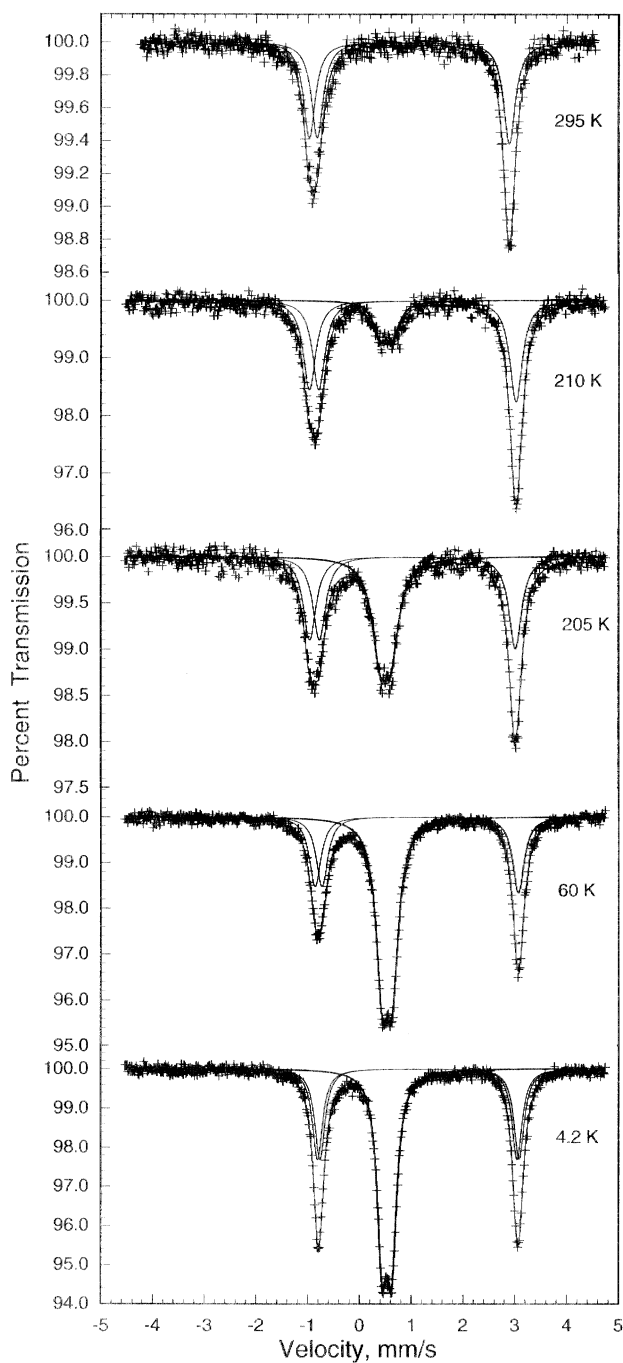


Fig. 17 The Mössbauer spectra of $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$ obtained at the indicated temperatures. Data obtained from [46]

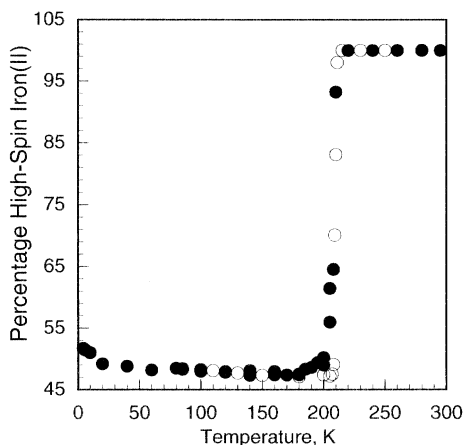


Fig. 18 The temperature dependence of the percentage of high-spin iron(II) found in $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$. The data obtained upon initial cooling from 295 to 85 K and warming from 4.2 K are indicated by filled circles and data obtained upon initial warming from 85 to 280 K are indicated by unfilled circles. Data obtained from [46]

It is interesting to recall that $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]\text{I}_2$, which at 295 K is structurally very similar to $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$, is fully converted to the low-spin state at low temperature. Although the structural environments of the iodide and BF_4 anions in both complexes are very similar [46, 47, 49] it would seem that upon cooling there is a lattice driven crystallographic phase transition in $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$ that is not present in $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]\text{I}_2$, such that in the latter case, the normal lattice contraction upon cooling converts all of the high-spin iron(II) to the low-spin state. In contrast, in the former case, the phase transition favors one-half of the iron sites retaining their longer iron–nitrogen bond distances and, hence, the high-spin state. Indeed, a recent high-pressure x-ray absorption spectral study has revealed [50] that the iron(II) in $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]\text{I}_2$ undergoes the expected gradual spin-state crossover from the high-spin to the low-spin state with increasing pressure, whereas the iron(II) in $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2](\text{BF}_4)_2$ remains high spin between ambient pressure and 78 kbar and is only transformed to the low-spin state at an applied pressure of between 78 and 94 kbar.

4

Solution Studies of Poly(pyrazolyl)borate Complexes

As outlined above, in the solid state $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ is low spin at ambient temperature changing to the high-spin state at higher temperatures, whereas $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]$ is high-spin at ambient temperature changing to

the low-spin state at lower temperatures. In contrast, in solution [27] $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]$ remains high spin between 200 and 295 K and the same is true for $[\text{Fe}(\text{HB}(3,4,5\text{-(CH}_3)_3\text{pz)}_3)_2]$. For the latter complex, the magnetic moment is $5.22 \mu_{\text{B}}$ at ambient temperature and remains essentially constant down to 210 K. The slight reduction in the moment to $5.0 \mu_{\text{B}}$ at the lower temperatures was interpreted as due to “varying populations of the sub-levels in the E state” arising from the axially distorted $^5\text{T}_{22}$ state. NMR spectra show large chemical shifts, especially for the 3-position methyl group in both complexes and the 4-position hydrogen in $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]$, as expected for paramagnetic complexes. The temperature dependence of the resonance absorption shows Curie-law behavior. The absorption spectra, measured in cyclohexane, show one $d\text{-}d$ band that may be assigned to the $^5\text{T}_{2g}$ to $^5\text{E}_g$ transition as expected for high-spin iron(II) complexes. The electronic transition, whose energy is equal to 10Dq , is observed at ca. $12,500 \text{ cm}^{-1}$. The location of this band in the near-infrared explains the lack of color for the high-spin complexes.

The $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ complex shows interesting spin-state changes in solution and has been extensively studied by a variety of physical techniques. At ambient temperature in CH_2Cl_2 the magnetic moment of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ is $2.71 \mu_{\text{B}}$, a value that is representative of the presence of a mixture of the high-spin and low-spin states [27]. As the temperature is lowered, the magnetic moment decreases as the equilibrium between the high-spin and low-spin states shifts toward the low-spin state. Analysis of the susceptibility data measured as a function of temperature yields thermodynamic parameters for the high-spin/low-spin equilibrium of $\Delta H = 16.1 \text{ kJ/mol}$ and $\Delta S = 47.7 \text{ J/(Kmol)}$. In a separate study [51], the magnetic moment was measured in aqueous solution and found to increase from ca. $2.1 \mu_{\text{B}}$ at 293 K to $3.8 \mu_{\text{B}}$ at 350 K.

The NMR spectra [27] of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ exhibit shifted resonances as would be expected for a paramagnetic complex, but the shifts are intermediate between those observed for fully diamagnetic complexes and the comparable resonances in the fully high-spin $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]$ complex. In contrast to the increasing chemical shifts, either in the positive or negative direction, that follow the Curie law, observed at lower temperatures for $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz)}_3)_2]$ and $[\text{Fe}(\text{HB}(3,4,5\text{-(CH}_3)_3\text{pz)}_3)_2]$, the chemical shifts of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ decrease as the temperature is decreased, as would be expected for an increase in the percentage of the low-spin complex.

The observation of a single set of resonances in the NMR spectra of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$, spectra that are clearly obtained for a mixture of the high-spin and low-spin forms of the complex, indicates that the equilibrium between the two states is rapid on the NMR time scale [27]. Subsequent solution studies by Beattie et al. [52, 53] using both a laser temperature-jump technique and an ultrasonic relaxation technique have established that the spin-state lifetime for $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ is $3.2 \times 10^{-8} \text{ s}$. These studies also established

that the volume difference between the low-spin and high-spin states in solution is $23.6 \text{ cm}^3/\text{mol}$. Subsequent studies [54] that measured the partial molar volume of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ in tetrahydrofuran established that the volume of the low-spin state is very close to that found in the solid state by x-ray crystallography [26].

Both the solution magnetic moments and optical spectra of $[\text{Fe}(\text{HB}(\text{pz})(3,5\text{-(CH}_3)_3\text{pz})_2)_2]$ and $[\text{Fe}(\text{HB}(\text{pz})_2(3,5\text{-(CH}_3)_2\text{pz}))_2]$ have been measured and found to be temperature dependent [55]. As observed for $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$, the magnetic moments decrease with decreasing temperature, although the rate of decrease is less than is observed for $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$. At a given temperature the magnetic moment for each complex decreases in the order, $[\text{Fe}(\text{HB}(3,5\text{-(CH}_3)_2\text{pz})_3)_2] > [\text{Fe}(\text{HB}(\text{pz})(3,5\text{-(CH}_3)_2\text{pz}))_2] > [\text{Fe}(\text{HB}(\text{pz})_2(3,5\text{-(CH}_3)_2\text{pz}))_2] > [\text{Fe}(\text{HB}(\text{pz})_3)_2]$, indicating that the high-spin state is stabilized by “increasing the number of methyl substituents on the pyrazolyl rings”.

In addition to the impact of substituents at the 3-position of the pyrazolyl rings, substitution of the remaining hydrogen on the central boron with either a phenyl group or a fourth pyrazolyl ring, to form $[\text{Fe}(\text{PhB}(\text{pz})_3)_2]$ or $[\text{Fe}(\text{B}(\text{pz})_4)_2]$, yields complexes that are low spin in solution at all temperatures studied [27]. Sohrin has argued, by using a combination of crystallographic and molecular mechanics calculations, that the intraligand steric effects introduced by the fourth boron substituent favors the smaller bite angle of the low-spin state of iron(II) [56]. It has also been noted [27] that $[\text{Fe}(\text{iso-propylB}(\text{pz})_3)_2]$ shows a spin-state behavior that is similar to that of $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$. Presumably in this complex the *iso*-propyl group does not result in the steric problems introduced by the planar pyrazolyl or phenyl group because the methyl groups can arrange themselves in a staggered fashion with respect to the pyrazolyl rings.

Gas phase photoelectron studies [57] have shown that $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ is in the high-spin state at 400 K as is also the case [58] for $[\text{Fe}(\text{B}(\text{pz})_4)_2]$ between 480 and 560 K. Although both complexes are in the high-spin state, the steric effects mentioned above for $[\text{Fe}(\text{B}(\text{pz})_4)_2]$ are revealed as a more pronounced trigonal distortion for this complex as compared to $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$.

5

Solution Studies of Tris(pyrazolyl)methane Complexes

As was the case for $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$, in solution the tris(pyrazolyl)methane complexes of the parent $\text{HC}(\text{pz})_3$ ligand have proved most interesting. The initial studies [59] were carried out using variable temperature absorption spectroscopy on $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{ClO}_4)_2$. Of interest was the observation that the ligand field strength of $\text{HC}(\text{pz})_3$ in $[\text{Fe}(\text{HC}(\text{pz})_3)_2]^{2+}$ was very similar to that observed for the anionic tris(pyrazolyl)borate analog in $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$. As would be expected from this observation, $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{ClO}_4)_2$ shows

absorptions between 233 and 295 K for both the high-spin and low-spin forms of the complex with the high-spin population increasing from 6 percent at 233 K to almost 30 percent at 295 K.

A subsequent paper reported [46] the variable temperature proton NMR spectra of $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$ in dimethylformamide, see Fig. 19. As is shown in Fig. 19a, at 223 K the normal spectrum expected for the diamagnetic low-spin form of $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$ in the 6 to 11 ppm range is observed. In addition, at 223 K small resonances shifted from 74.8 to -60.9 ppm are observed and can be attributed to the presence of a small amount of $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$ that is in the high-spin state. These resonances are shown in Fig. 19b in which the vertical scale has been increased so as to show the paramagnetic portion of the spectra at the expense of pushing the diamagnetic resonances off scale. The highly shielded resonance is assigned to the methine hydrogen on the basis of its relative integration. As the temperature increases, see Fig. 19b, the relative intensities of the paramagnetic resonances increase such that they represent ca. 22 percent of the signal at 293 K. In addition, the paramagnetic resonances move to lower absolute chemical shift values, shifts that are expected for Curie law behavior. Although the resonances observed for the paramagnetic form of the complex are somewhat broad at low temperatures, as expected, they broaden considerably at 303 K and by 353 K all resonances have collapsed into the baseline. The complex is not stable in dimethylformamide above this temperature, but subsequent cooling of the sample reproduced the spectra recorded as the sample was heated, indicating that the process is reversible. As the temperature is increased, the resonances of the diamagnetic form shift toward their associated resonances in the paramagnetic complex; the methine hydrogen absorption shifts to higher shielding and the remaining resonances shift to lower shielding. Therefore, two changes take place as $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$ is warmed in solution. First, as is observed by absorption spectroscopy, the percentage of the paramagnetic form increases as the temperature increases and, second, although the two forms equilibrate slowly on the NMR time scale at 223 K, they start to equilibrate at a rate comparable to the NMR time scale above 283 K.

Observation by NMR of both the high-spin and low-spin forms of a complex in solution is unusual. As outlined above [27], $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ shows only averaged spectra upon cooling to 243 K. Given that the two spin states differ in their solid state Fe-N bond distances by ca. 0.2 Å, slow exchange is expected.

The equilibrium constant, $K=[\text{HS}]/[\text{LS}]$, has been measured between 223 and 293 K and the resulting thermodynamic parameters, derived from a plot of $\ln K$ vs. $1/T$, are $\Delta H^\circ=20$ kJ/mol and $\Delta S^\circ=58$ J/(Kmol). Similar parameters of $\Delta H^\circ=18$ kJ/mol and $\Delta S^\circ=53$ J/(K mol) were obtained earlier [59] for $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{ClO}_4)_2$ from visible electronic absorption spectra.

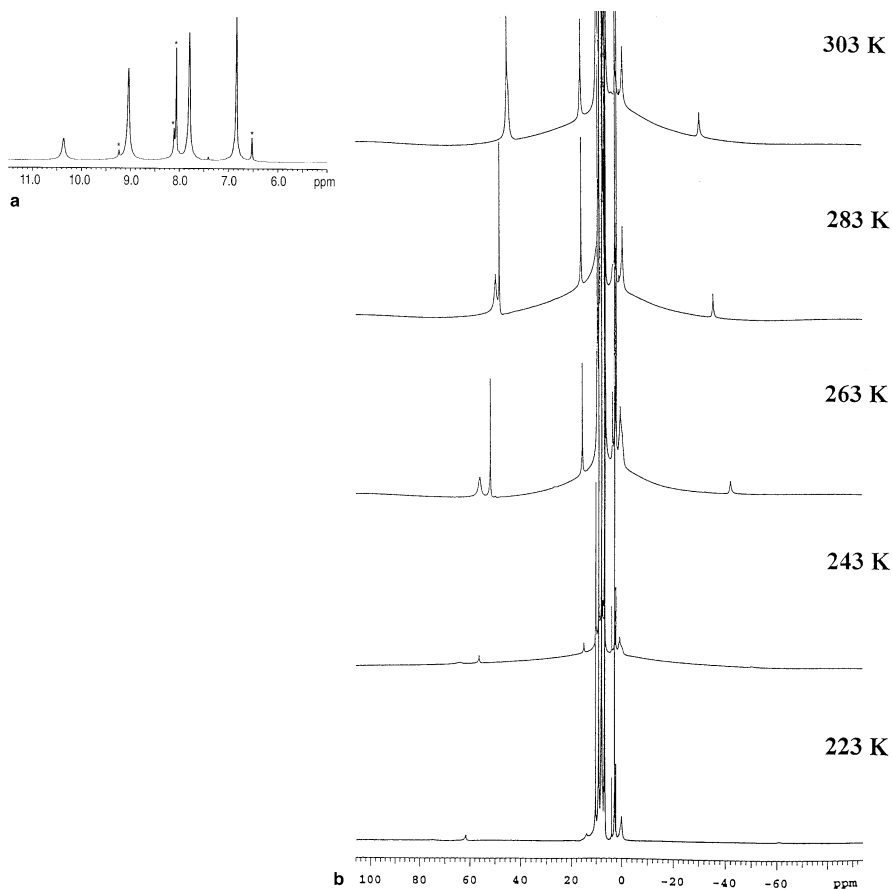


Fig. 19 The proton NMR spectrum of $[\text{Fe}(\text{HC}(\text{pz})_3)_2](\text{BF}_4)_2$ obtained at 223 K, **a**, where the stars indicate solvent impurities, and at various temperatures, **b**. In **b** the vertical scales of the spectra have been expanded driving the diamagnetic resonances off scale. Plots obtained from [46]

Solution ^1H NMR spectra [46] obtained for $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz})_3)_2](\text{BF}_4)_2$ at 293 K are broad with chemical shifts ranging from 52 to -42 ppm, a range that is indicative of a paramagnetic high-spin iron(II) complex. Decreasing the temperature leads to large changes in the positions of the resonance absorptions, changes that are consistent with the Curie law behavior expected of a paramagnetic complex. There is no indication of the formation of any of the low-spin diamagnetic complex as is observed in the solid state at lower temperatures. As expected, the same ^1H NMR spectral behavior is observed [49] for $[\text{Fe}(\text{HC}(3,5\text{-(CH}_3)_2\text{pz})_3)_2]\text{I}_2$. $[\text{Fe}(\text{HC}(3,4,5\text{-(CH}_3)_3\text{pz})_3)_2](\text{BF}_4)_2$ is also fully high-spin in solution at ambient temperature [60]. NMR spectral studies have also shown that $[\text{Fe}(\text{PhC}(\text{pz})_2(\text{py}))_2](\text{BF}_4)_2$, where py

is the pyridyl ring, and $[\text{Fe}(\text{HC}(3,4,5\text{-(CH}_3)_3\text{pz})_3)(\text{H}_2\text{O})_3](\text{BF}_4)_2$ are low spin in solution [46, 61].

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Special Classes of Iron(II) Azole Spin Crossover Compounds

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Abstract In this chapter, selected results obtained so far on Fe(II) spin crossover compounds of 1,2,4-triazole, isoxazole and tetrazole derivatives are summarized and analysed. These materials include the only compounds known to have Fe(II)N₆ spin crossover chromophores consisting of six chemically identical heterocyclic ligands. Particular attention is paid to the coordination modes for substituted 1,2,4-triazole derivatives towards Fe(II) resulting in polynuclear and mononuclear compounds exhibiting Fe(II) spin transitions. Furthermore, the physical properties of mononuclear Fe(II) isoxazole and 1-alkyl-tetrazole compounds are discussed in relation to their structures. It will also be shown that the use of α,β - and α,ω -bis(tetrazol-1-yl)alkane type ligands allowed a novel strategy towards obtaining polynuclear Fe(II) spin crossover materials.

Keywords Spin crossover · Fe(II) · 1,2,4-Triazole · Isoxazole · Tetrazole

Abbreviations

4-R-trz	4-substituted-1,2,4-triazole
Htrz	1,2,4-4H-triazole
trz	1,2,4-triazolato
hyetrz	4-(2'-hydroxy-ethyl)-1,2,4-triazole
NH ₂ trz	4-amino-1,2,4-triazole

Hpt	3-(pyridin-2-yl)-1,2,4-triazole
H3mpt	3-methyl-5-(pyridin-2-yl)-1,2,4-triazole
abpt	4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole
TCNQ	7,7',8,8'-tetracyanoquinodimethane
phen	1,10-phenanthroline
mbpt	4- <i>p</i> -methylphenyl-3,5-bis(pyridin-2-yl)-1,2,4-triazole
mmbpt	4- <i>m</i> -methylphenyl-3,5-bis(pyridin-2-yl)-1,2,4-triazole
btzp	1,2-bis(tetrazol-1-yl)propane
btze	1,2-bis(tetrazol-1-yl)ethane
btzb	1,4-bis(tetrazol-1-yl)butane
LIESST	light-induced excited spin-state trapping

1

Introduction

Over the past few decades, a large variety of ligand systems have been tested with the aim of obtaining novel iron(II) spin crossover systems which could possibly be utilised in electronic devices [1]. In most cases an Fe(II)N₆ chromophore is required in order to generate the spin crossover phenomenon [2]. A large majority of the ligands used are represented by heterocyclic systems, in which the lone electron pair on the nitrogen atom coordinates to the Fe(II) ion.

Only for 4-R-substituted 1,2,4-triazoles, isoxazoles and 1-alkyl-tetrazoles (Fig. 1), has the Fe(II)N₆ spin crossover chromophore been found to consist of six chemically identical heterocyclic ligands. These spin transition materials are of particular interest. Since only a single N-donor ligand is involved in the synthetic procedure, the formation of mixed ligand species is avoided, and hence rather high yields are usually obtained. In addition, the choice of such relatively small heterocyclic ligands favours almost regular O_h symmetry about the Fe(II) ion. This is especially so for low-spin Fe(II).

In this chapter, selected results obtained so far on Fe(II) spin crossover compounds of these ligand systems are compiled and analysed.

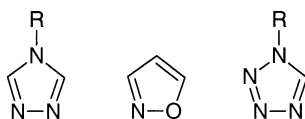


Fig. 1 4-R-1,2,4-Triazole, isoxazole and 1-alkyl-tetrazole

2 Fe(II) Spin Crossover Compounds of 1,2,4-Triazoles

2.1 Coordination Properties of 1,2,4-Triazole Derivatives

The 1,2,4-triazole system has been found to be particularly suited towards generating spin crossover behaviour in Fe(II)N₆ derivatives of the simple molecule and in bidentate and tridentate systems containing at least one 1,2,4-triazole ring. The ambidentate nature of the 1,2,4-triazole ring is closely associated with tautomerism of the 1,2,4-triazole nucleus, as shown in Fig. 2.

The N-1 coordination mode has been found in bidimensional- [3] and in tridimensional materials [4] derived from 4,4'-bis-1,2,4-triazole, as well as in mononuclear compounds of bidentate 1,2,4-triazole ligands in which the N-4 atom is protected from coordination by a non-coordinating substituent, as in 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole [5–8], 4-*p*-methylphenyl-3,5-bis(pyridin-2-yl)-1,2,4-triazole [9] and 4-*m*-methylphenyl-3,5-bis(pyridin-2-yl)-1,2,4-triazole [9].

The N-4 coordination towards Fe(II) has been found in mononuclear Fe(II) spin crossover compounds containing bidentate 1,2,4-triazole ligands [10–13], as well as tridentate ligands bearing no substituent at N-4 of the 1,2,4-triazole ring [14–16]. The only exception known is the mononuclear Fe(II) spin crossover compound of the tridentate hydrotris(1,2,4-triazol-1-yl)borate [17–21], where coordination is through N-1 rather than N-4. This probably occurs because of the resulting favourable geometry of the chelate rings.

The N-2, N-4 bridging coordination mode has not (yet) been observed in Fe(II) spin crossover compounds, whereas the N-1, N-2 bridging mode has been confirmed by X-ray structure determinations of oligomeric and polymeric Fe(II) spin crossover materials. Depending on the nature of the substituted 1,2,4-triazole ligand and the presence of potentially coordinating an-

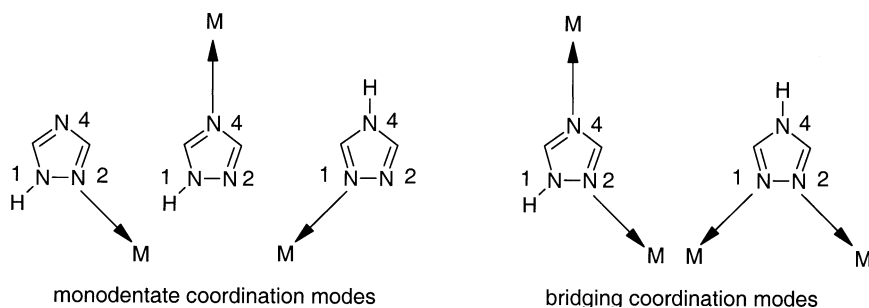


Fig. 2 Possible coordination modes of 1H(4H)-1,2,4-triazole

ions and/or solvent molecules, the spin crossover materials may be dinuclear [22], linear trinuclear [23] or linear polynuclear [24–54]. Only in the linear trinuclear [23] and linear polynuclear [24–54] materials does the 1,2,4-triazole molecule form FeN_6 spin crossover chromophores.

In the following section, attention is directed towards these linear polynuclear Fe(II) spin crossover systems, whereas subsequent sections focus on mononuclear Fe(II) spin transition compounds containing chelating 1,2,4-triazole derivatives.

2.2

Linear Polynuclear Fe(II) Spin Crossover Compounds

Among all Fe(II) spin crossover compounds known to date, the extensively studied polymeric $[\text{Fe}(4\text{-R-1,2,4-triazole})_3](\text{anion})_2$ systems (R=amino, alkyl, hydroxyalkyl) appear to have the greatest potential for technological applications, for example in molecular electronics [1, 24, 25] or as temperature sensors [24, 26]. This arises because of their near-ideal spin crossover characteristics: pronounced thermochromism, transition temperatures near room temperature, and large thermal hysteresis [1, 24, 27].

Typically, Fe(II) compounds of 4-R-1,2,4-triazole appear as fine microcrystalline powders. Therefore, EXAFS has been the only method available to directly probe the local structure around the metal ion. In addition, the detailed analysis of the multiple scattering EXAFS signal displayed at the double metal-metal distance has confirmed metal alignment in these compounds [28, 29]. In fact, for $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ and $[\text{Fe}(\text{Htrz})_3](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ (Htrz=1,2,4-4H-triazole; trz=1,2,4-triazolato) EXAFS studies pointed out that the compounds consist of linear chains with typical Fe–Fe separations of 3.65 Å in the low-spin state [28]. Later, the EXAFS data for these Fe(II) derivatives were compared with those of the structurally characterised Cu(II) derivative $[\text{Cu}(\text{hyetrz})_3](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (hyetrz=4-(2'-hydroxy-ethyl)-1,2,4-triazole), confirming that both metal ions form one-dimensional polymeric systems [30]. The structure of $[\text{Cu}(\text{hyetrz})_3](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (Fig. 3) shows Cu(II) ions linked by triple N-1,N-2 1,2,4-triazole bridges yielding a chain with alternating Cu1–Cu2 and Cu2–Cu3 distances of 3.853(2) Å and 3.829(2) Å, respectively. It is important to note that even though the Cu(II) coordination sphere is Jahn-Teller distorted, the chain shows only a relatively small deviation from linearity.

The spin crossover characteristics of the corresponding Fe(II) compounds may be fine tuned by the systematic variation of the substituent at N-4 of the 1,2,4-triazole ring, as well as by changing the non-coordinated anionic groups. In this way, thermochromic Fe(II) materials showing a spin transition close to room temperature and accompanied by hysteresis have been obtained. As an example, the optical reflectivity measurements record-

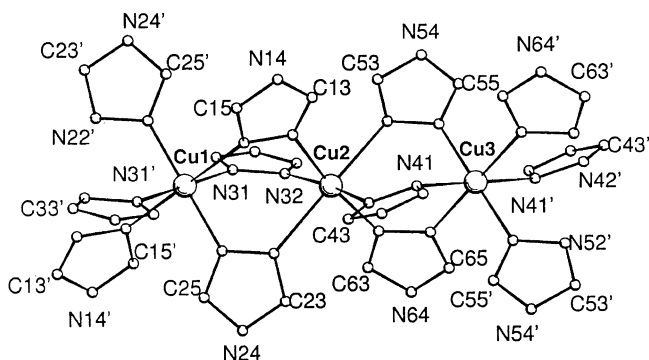


Fig. 3 Projection showing the structure of $[\text{Cu}(4-(2'\text{-hydroxy-ethyl})\text{-}1,2,4\text{-triazole})_3](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ at 298 K (reprinted with permission from [30]. Copyright (1997) American Chemical Society)

ed for $[\text{Fe}(\text{NH}_2\text{trz})_3](2\text{-naphthalene sulfonate})_2 \cdot x\text{H}_2\text{O}$ ($x=0, 2$; $\text{NH}_2\text{trz}=4\text{-amino-}1,2,4\text{-triazole}$) are shown in Fig. 4 [31].

At room temperature, the thermodynamically stable state for $[\text{Fe}(\text{NH}_2\text{trz})_3](2\text{-naphthalene sulfonate})_2 \cdot 2\text{H}_2\text{O}$ is low-spin. This stabilisation of the low-spin state by interactions with lattice water molecules has frequently been observed for mononuclear Fe(II) spin crossover compounds [15, 55–57]. Upon heating, the compound loses its lattice water with an accompanying abrupt change from low-spin to high-spin. When the dehydrated material is cooled, an abrupt high-spin to low-spin transition occurs at $T_{1/2\downarrow}=283\text{ K}$. Subsequent reheating reveals a hysteresis loop of 14 K centred close to room temperature (290 K).

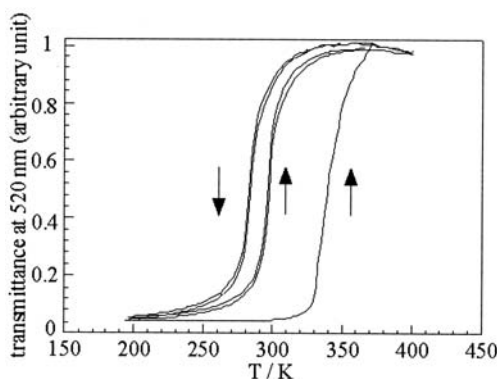


Fig. 4 Optical reflectivity measurement (intensity vs temperature; recorded at 1 K min^{-1}) for $[\text{Fe}(4\text{-amino-}1,2,4\text{-triazole})_3](2\text{-naphthalene sulfonate})_2 \cdot x\text{H}_2\text{O}$ ($x=0, 2$) ([31] (reproduced with permission of the Royal Society of Chemistry))

Non-solvated $[\text{Fe}(\text{NH}_2\text{trz})_3](2\text{-naphthalene sulfonate})_2$ [31] represents one of the very few Fe(II) spin crossover materials showing a spin transition with hysteresis and an associated thermochromic effect near room temperature. A further example is $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{tosylate})_2$, which has been reported to have a hysteresis loop of width 17 K around 290 K [32]. Moreover, by forming the mixed-ligand species $[\text{Fe}(\text{Htrz})_{3-3x}(\text{NH}_2\text{trz})_{3x}](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ thermal hysteresis ($\Delta T_{1/2} = 17$ K) centred around 304 K has also been obtained [33]. The examples do not seem to be restricted to 4-amino-1,2,4-triazole; in addition, the spin transition in $[\text{Fe}(\text{hyetrz})_3]\text{I}_2$ (hyetrz = 4-(2'-hydroxy-ethyl)-1,2,4-triazole) is associated with thermal hysteresis ($\Delta T_{1/2} = 12$ K) centred around 291 K [34].

2.3

Mononuclear Fe(II) Spin Crossover Compounds of Tridentate Chelating 1,2,4-Triazole Derivatives

Spin transitions occurring above room temperature have also been observed for mononuclear compounds. The bis[hydrotris(pyrazol-1-yl)borate]iron(II) system [58] has been known for more than thirty years and this also displays a spin transition above room temperature (G.J. Long, F. Grandjean, D.L. Reger, this volume). The related system bis[hydrotris(1,2,4-triazol-1-yl)borate]iron(II), $[\text{Fe}\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3\}_2]$, has been studied more recently [17–21]. This is the only mononuclear Fe(II) spin transition compound containing six N-1-donating 1,2,4-triazole nuclei. The anionic tridentate ligand is shown in Fig. 5.

$[\text{Fe}\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3\}_2]$ has been obtained by dehydration under heating of the low-spin hexahydrate. The crystal structure for this hexahydrate has been determined at room temperature [17]. It clearly contains Fe(II) ions in the low-spin state (average Fe–N distance = 1.99 Å). The dehydrated derivative $[\text{Fe}\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3\}_2]$ has been reported to exhibit a very abrupt spin transition between 334–345 K via variable temperature UV-vis and ^{57}Fe Mössbauer spectroscopy studies [19]. After the publication of a preliminary magnetic study in 1994 [19], a more detailed report appeared in 1998 [20].

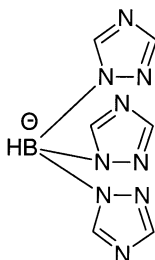


Fig. 5 The hydrotris(1,2,4-triazol-1-yl)borate anion

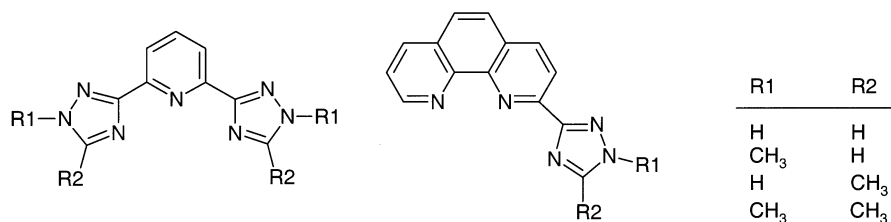


Fig. 6 2,6-Bis(triazol-3-yl)pyridine, 2-triazolyl-1,10-phenanthroline, and their methyl-substituted derivatives

The coordination properties of two other classes of tridentate chelating 1,2,4-triazole-containing-ligands have been studied by Goodwin et al. [14–16]. These are represented by 2,6-bis(triazol-3-yl)pyridine [14] and 2-triazolyl-1,10-phenanthroline [15, 16] and their methyl-substituted derivatives (H. A. Goodwin, this volume) (Fig. 6).

The crystal structures of $[\text{Fe}(\text{2,6-bis(triazol-3-yl)pyridine})_2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $[\text{Ni}(\text{2,6-bis(triazol-3-yl)pyridine})_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ revealed that the tridentate ligand coordinates to the metal(II) ion using both N-4 atoms of the two 1,2,4-triazole moieties together with the pyridyl nitrogen atom [14]. The N-1 of the 1,2,4-triazole ring that is not coordinated sets up an important hydrogen-bonding network involving the anions and the non-coordinated water molecules. It was found that the water content had a strong influence on the spin state of Fe(II). $[\text{Fe}(\text{2,6-bis(triazol-3-yl)pyridine})_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ is high-spin at room temperature and exhibits a partial transition to low-spin upon cooling. Upon heating the material above 100 °C, the water is lost and the anhydrous species is low-spin. It is worth noting that the removal of solvent molecules leads in this case to the exact opposite effect to that observed in the linear chain compounds of formula $[\text{Fe}(\text{4-R-1,2,4-triazole})_3](\text{anion})_2 \cdot x\text{H}_2\text{O}$ [27, 31, 34, 36], where the dehydration upon heating is accompanied by an Fe(II) spin transition from the low-spin to the high-spin state. On the other hand, Fe(II) compounds of 2,6-bis(triazol-3-yl)pyridine ligands bearing N-methyl substituents yielded Fe(II) systems, which could only be obtained as non-hydrated materials, in which the $[\text{FeN}_6]^{2+}$ derivative is high-spin.

Structure determinations of several Fe(II) compounds of 2-triazolyl-1,10-phenanthroline and its methyl-substituted derivatives proved that in addition to the two nitrogen donor atoms of the 1,10-phenanthroline entity, the N-4 of the 1,2,4-triazole ring participates in coordination, even when a methyl substituent occupies the position adjacent to this donor atom [15, 16]. All compounds obtained exhibit Fe(II) spin crossover behaviour, its extent depending on the nature of the anionic groups and the solvent content.

2.4

Mononuclear Fe(II) Spin Crossover Compounds of Bidentate Chelating 1,2,4-Triazole Derivatives

Using bidentate chelating 1,2,4-triazole-based ligands, various families of Fe(II) spin crossover systems have been obtained. Among these, the mononuclear Fe(II) spin crossover compounds of 3-(pyridin-2-yl)-1,2,4-triazole derivatives have been known for several years [10–12]. Early studies on $[\text{Fe}(\text{Hpt})_3](\text{anion})_2(\text{solvent})_x$ (Hpt=3-(pyridin-2-yl)-1,2,4-triazole (Fig. 7); anion= Cl^- , ClO_4^- , PF_6^- , BF_4^- ; solvent= $\text{C}_2\text{H}_5\text{OH}$, H_2O) and $[\text{Fe}(\text{H3mpt})_3](\text{anion})_2(\text{H}_2\text{O})_x$ (H3mpt=3-methyl-5-(pyridin-2-yl)-1,2,4-triazole; anion= ClO_4^- , PF_6^-) have been reported by Stupik et al. [10, 11] and Sugiyarto et al. [12].

In the absence of any x-ray crystallographic data, the early results could not be explained satisfactorily. It has been assumed that the Fe(II) ion is in a six-nitrogen environment of three bidentate 3-(pyridin-2-yl)-1,2,4-triazole ligands coordinating via the 1,2,4-triazole-N-4 and the pyridine-N atoms. The asymmetry encountered in the bidentate ligand may lead to the formation of FeL_3 units of *facial* or *meridional* geometry. Moreover, the spin transition characteristics appeared to be dependent on the amount and nature of the incorporated solvent molecules [10–12]. In addition, two different iron(II) high-spin sites have been detected in the hydrated BF_4^- and ClO_4^- Fe(II) tris(3-(pyridin-2-yl)-1,2,4-triazole) compounds [10–12]. More recent work, including the x-ray crystal structure of $[\text{Fe}(\text{Hpt})_3](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$ [13], has clarified some of these points.

$[\text{Fe}(\text{Hpt})_3](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$ shows gradual and incomplete spin crossover behaviour with $T_{1/2}=135$ K [13]. The crystal structure determination carried out at 95 and 250 K revealed only one crystallographically independent $[\text{Fe}(\text{Hpt})_3]^{2+}$ cation with the *mer* configuration, despite the observation of two high-spin Fe(II) doublets in the ^{57}Fe Mössbauer spectra. The Fe(II) is octahedrally surrounded by three bidentate Hpt ligands coordinating through the N of the pyridine ring and N-4 of the 1,2,4-triazole moiety. The average Fe–N bond length is reduced by about 0.15 Å at 95 K. As expected, the N–Fe–N4 bite angles increase with decreasing temperature, ranging from 75.53–77.13° at 250 K to 80.17–80.86° at 95 K. Therefore, the octahedron about the Fe(II) ion becomes more regular upon the transition from the high-spin to the low-spin state. However, a large deviation from the ideal value of 90° remains, which is due to the expected restriction of the Hpt bite angle within

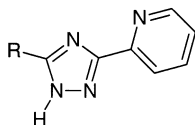


Fig. 7 3-(Pyridin-2-yl)-1,2,4-triazole (Hpt)

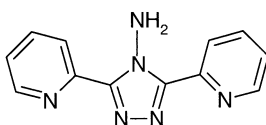


Fig. 8 4-Amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (abpt)

the five-membered chelate ring, as well as the fact that at 95 K about 35% of the Fe(II) ions remain high-spin.

It has been postulated that the origin of the two different high-spin Fe(II) doublets observed in the ^{57}Fe Mössbauer spectra may be that a small fraction (about 6%) of the Fe(II) ions experience a different local environment, most likely in the distribution of the non-coordinating solvent and anion molecules, from that of the majority of the high-spin Fe(II) ions.

In the second family of spin crossover compounds containing bidentate 1,2,4-triazole-based ligands, additional N-donating co-anions occupy *trans* positions about the Fe(II) ion. The first representative of this family is $[\text{Fe}(\text{abpt})_2(\text{TCNQ})_2]$ (abpt=4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (Fig. 8), TCNQ=7,7',8,8'-tetracyanoquinodimethane), which is the only Fe(II) complex containing coordinated radical anions. It undergoes a complete, gradual spin crossover ($T_{1/2}=280$ K) [5]. This compound represents one of the few cases in which the Fe(II) spin crossover centre contains two monodentate substituents in *trans* positions. This geometry has now been found for several bis(thiocyanato)iron(II) spin crossover compounds [3b, 7, 9, 59, 60]. The first was observed more than a decade ago for $[\text{Fe}(4,4'\text{-bis-1,2,4-triazole})_2(\text{NCX})_2]$ ($\text{X}=\text{S}$ [3a, 3b], or Se [3c]), which consists of layers of six-coordinated Fe(II) ions linked in the equatorial plane by single bridges of the 4,4'-bis-1,2,4-triazole ligand via the N-1 atoms. Recently, the dicyanamide anion has also been shown to lead to *trans* $[\text{Fe}(\text{abpt})_2(\text{N}(\text{CN})_2)_2]$ entities, which is also a spin crossover system [8].

The structure of $[\text{Fe}(\text{abpt})_2(\text{TCNQ})_2]$ was determined at 298 and 100 K. The molecular structure is depicted in Fig. 9.

The unit-cell contains one $[\text{Fe}(\text{abpt})_2(\text{TCNQ})_2]$ unit with Fe(II) at the inversion centre. The coordination sphere in the equatorial plane is formed by two bidentate abpt ligands coordinating via N(pyridyl) and N-1(1,2,4-triazole). The high-spin to low-spin change is accompanied by a non-uniform shortening of the Fe–N bond lengths. The Fe–N(pyridyl) distance is 2.12(1) Å at 298 K and 2.02(1) Å at 100 K, whereas the Fe–N-1(1,2,4-triazole) distance is 2.08(1) Å at 298 K and 2.00(2) Å at 100 K. More significant changes in the Fe–N(TCNQ) bond lengths are observed: 2.16(1) Å at 298 K and 1.93(1) Å at 100 K, the latter distance being particularly short. This change of 0.23 Å is among the largest that has been observed for Fe(II) spin crossover compounds. It can probably be related to the extended π -system of TCNQ and the increased $d_{\pi} \rightarrow \pi^*$ backbonding when Fe(II) is in the low-

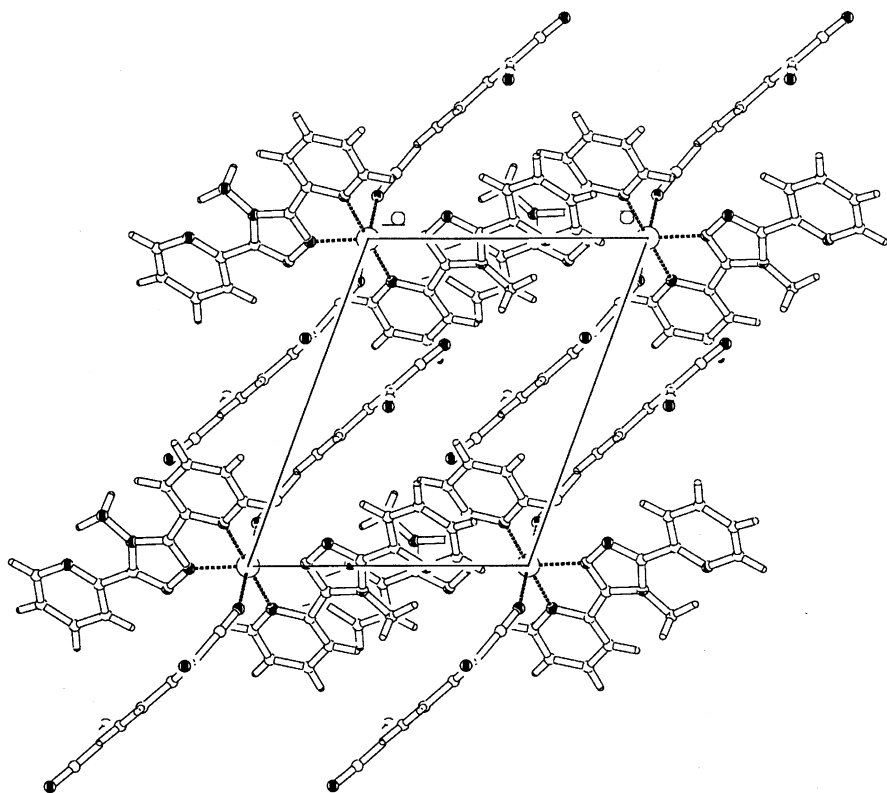


Fig. 10 Projection showing the crystal packing of $[\text{Fe}(\text{abpt})_2(\text{TCNQ})_2]$

dination to monovalent metal ions has in several cases been observed, however, binding to divalent metal ions very rarely occurs. Besides of its strong electron accepting properties, the poor coordinating power of TCNQ can also be related to crystal packing efficiency considerations – in other words TCNQ entities favour the formation of stacks, and coordination has been found to occur only if the molecules can form at least stacked dimers at the same time.

These structural features observed for $[\text{Fe}(\text{abpt})_2(\text{TCNQ})_2]$ involving pronounced and extended π - π stacking interactions lead to a duality with respect to its gradual spin crossover behaviour. It has generally been accepted that extended π - π interactions may lead to the occurrence of thermal hysteresis in mononuclear Fe(II) spin crossover compounds [62–65]. Clearly, the requirements responsible for cooperative Fe(II) spin crossover behaviour are not easy to define, since obviously $[\text{Fe}(\text{abpt})_2(\text{TCNQ})_2]$ represents an exception to this rule: in spite of the pronounced TCNQ π - π stacking interactions, the Fe(II) spin crossover displays at best weak cooperativity.

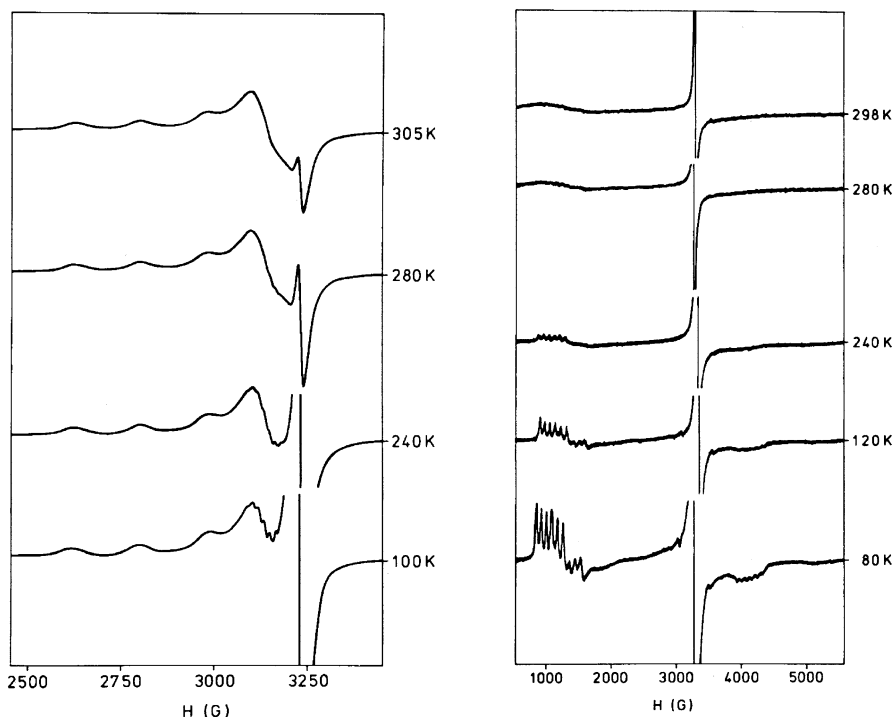


Fig. 11 Selected X-band powder ESR spectra of Cu(II)- (left) and Mn(II)-doped (right) $[\text{Fe}(\text{abpt})_2(\text{TCNQ})_2]$ (reprinted with permission from [5]. Copyright (1996) American Chemical Society)

The spin transition in $[\text{Fe}(\text{abpt})_2(\text{TCNQ})_2]$ can be monitored by focusing on the changes in the ν_{CN} stretching vibrations in the variable temperature FT-IR spectra [5]. The various cyano absorptions show characteristic frequencies and changing intensities upon the Fe(II) spin crossover, which also allows the direct observation of the coexistence of low-spin and high-spin Fe(II) species within the Fe(II) spin crossover temperature range. Related investigations have been carried out for other spin transition systems. In these cases, changes in far infrared Fe-N(ligand) vibrations [66, 67], or M-NCX (X=S, Se) ν_{CN} stretching vibrations [68–70] have generally been studied as a function of the temperature.

The spin transition could be monitored by ESR in Mn(II) or Cu(II)-doped materials. The related pure compounds of the dopants are strictly isomorphous with $[\text{Fe}(\text{abpt})_2(\text{TCNQ})_2]$. The inclusion of a small percentage of the paramagnetic Mn(II) or Cu(II) ions provides ESR probes for monitoring the Fe(II) spin transition from within the crystal lattice. The results are displayed in Fig. 11.

Although the TCNQ radical anions form diamagnetic diads, the narrow signal at $g=2.00$, indicative of $\text{TCNQ}^{\cdot-}$ impurities, remains visible in all spectra. The Fe(II) host lattice is paramagnetic above the transition temperature and essentially diamagnetic below this temperature. Above $T_{1/2}$, the ESR spectra are poorly resolved due to exchange broadening, but this changes dramatically after the spin transition, and spectra with sharp and distinct features typical for the dopant in a tetragonal environment are observed. The Cu(II)-doped Fe(II) species shows a broad signal with $g_{\perp}=2.09$ and $g_{\parallel}=2.25$, together with hyperfine structure ($A_{\parallel}=180$ Gauss) above $T_{1/2}$, whereas at $T_{1/2}$ and below, superhyperfine structure ($A_{\text{NH}}=16$ Gauss) appears. The superhyperfine structure splits each line into nine components, due to the coupling of the unpaired electron situated on the Cu(II) ion with the four abpt nitrogen atoms located in the equatorial coordination sphere. For the Mn(II)-doped material, a very broad signal at $g=2.00$ is visible above $T_{1/2}$, which sharpens at $T_{1/2}$ to reveal zero-field splitting yielding signals at $g=1.6$ and $g=5.5$. Six hyperfine lines ($A_{\parallel}=80$ Gauss) are clearly visible on both signals.

Further studies have shown that instead of $\text{TCNQ}^{\cdot-}$, NCS^- or NCSe^- [6,7] can also occupy the *trans*-located axial positions, resulting in spin crossover compounds with structures comparable to those of $[\text{Fe}(\text{abpt})_2(\text{TCNQ})_2]$ [5]. The Fe(II) spin transition is also gradual for these derivatives, however, with considerably lower transition temperatures: 224 K for the NCSe^- derivative and 180 K for the NCS^- analogue.

Recently, the crystal structure of the related $[\text{Fe}(\text{abpt})_2(\text{N}(\text{CN})_2)_2]$ has been determined [8]. The species undergoes an incomplete transition ($T_{1/2}$ = approximately 86 K) with an indication of two steps, the origin of which is unclear. Below 60 K, about 37% of the Fe(II) ions remain high-spin.

$[\text{FeL}_2(\text{NCS})_2]$ compounds have also been recently reported with 4-*p*-methylphenyl-3,5-bis(pyridin-2-yl)-1,2,4-triazole (mbpt) and 4-*m*-methylphenyl-3,5-bis(pyridin-2-yl)-1,2,4-triazole (mmbpt) (Fig. 12) [9]. For both compounds the structure has been determined at 293 K.

The ligand mbpt coordinates to Fe(II) through the N of the pyridyl substituent ($\text{Fe}-\text{N}=2.213(3)$ Å) and N-1 of the 1,2,4-triazole ring ($\text{Fe}-\text{N}1=2.192(2)$ Å). Two N-donating thiocyanate anions occupy *trans* positions at significantly shorter distances ($\text{Fe}-\text{N}=2.114(3)$ Å). These distances are consistent with high-spin Fe(II). The spin transition ($T_{1/2}=231$ K) in this instance is more abrupt than in $[\text{Fe}(\text{abpt})_2(\text{anion})_2]$ (anion= $\text{TCNQ}^{\cdot-}$ [5], NCS^- [6, 7], NCSe^- [6, 7], $[\text{N}(\text{CN})_2]^{\cdot-}$ [8]). This may be related to the replacement of the 4-amino substituent in abpt by the 4-*p*-methylphenyl substituent in mbpt, resulting in more pronounced π - π stacking interactions, which may enhance the cooperativity of the spin crossover.

In contrast, in $[\text{Fe}(\text{mmbpt})_2(\text{NCS})_2]$, the two thiocyanate anions are coordinated in *cis* positions at relatively short distances ($\text{Fe}-\text{N}=2.051(3)$ Å). The bidentate ligands coordinate at much longer distances ($\text{Fe}-$

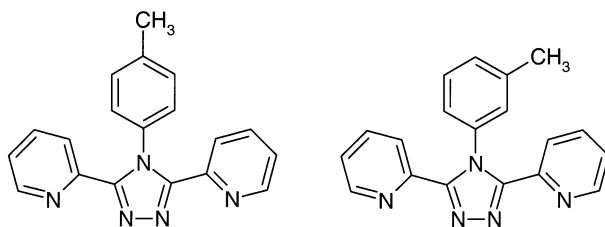


Fig. 12 4-*p*-Methylphenyl-3,5-bis(pyridin-2-yl)-1,2,4-triazole (mbpt) and 4-*m*-methylphenyl-3,5-bis(pyridin-2-yl)-1,2,4-triazole (mmbpt)

$N(\text{pyridyl})=2.217(2)$ Å and $\text{Fe}-N(1,2,4\text{-triazole})=2.248(3)$ Å. $[\text{Fe}(\text{mmbpt})_2(\text{NCS})_2]$ is high-spin down to 77 K.

3 Fe(II) Spin Crossover Compounds of Isoxazoles

In 1977 Driessen and van der Voort identified an extremely abrupt spin crossover with $T_{1/2}$ of 213 K for $[\text{Fe}(\text{isoxazole})_6](\text{ClO}_4)_2$ [71]. Although various spectroscopic techniques have been employed to study this spin transition, the structural features of this compound at the time could not be determined, due to its extreme sensitivity to decomposition [71]. The same applies to the tetrafluoroborate salt that also displays a spin crossover, but in this instance a two-step transition was observed [71].

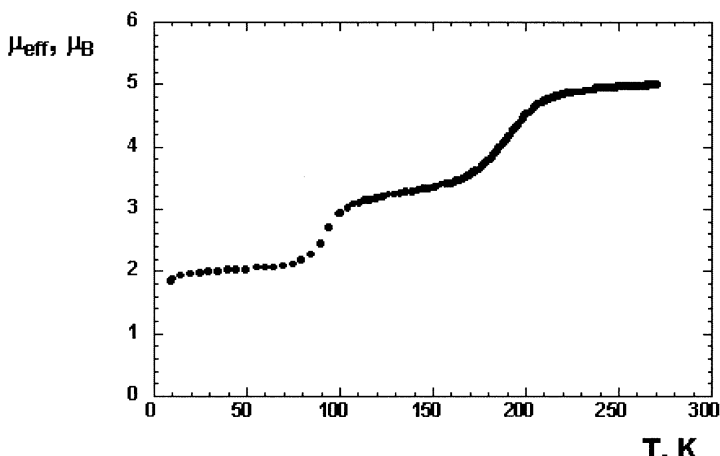


Fig. 13 Temperature dependence of μ_{eff} both in the cooling and warming modes for $[\text{Fe}(\text{isoxazole})_6](\text{BF}_4)_2$ ([72] – reproduced with permission of the Royal Society of Chemistry)

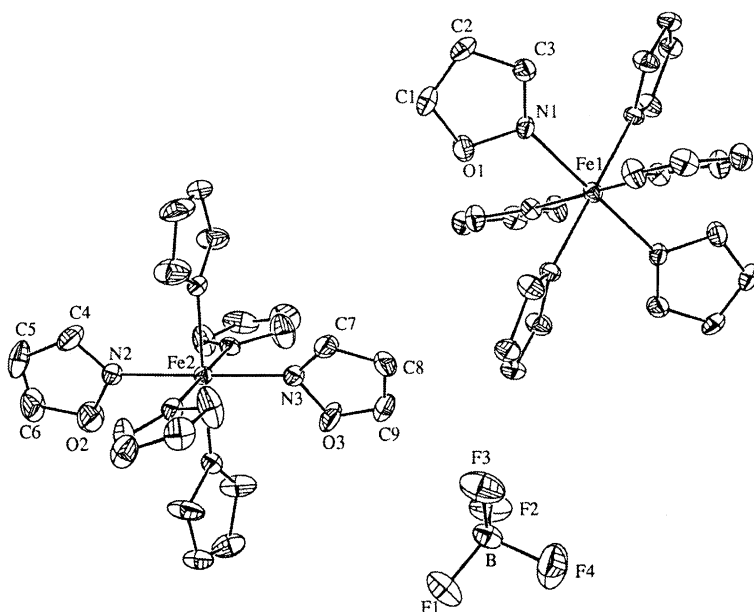


Fig. 14 Projection showing the structure of $[\text{Fe}(\text{isoxazole})_6](\text{BF}_4)_2$ ([72] – reproduced with permission of the Royal Society of Chemistry)

Recently, this family of isoxazole compounds has been re-examined with particular emphasis on the tetrafluoroborate salt. These studies included the first extended magnetic and structural characterisation of $[\text{Fe}(\text{isoxazole})_6](\text{BF}_4)_2$ [72]. In addition, the double salt $[\text{Fe}(\text{isoxazole})_6][\text{Fe}(\text{isoxazole})_4(\text{H}_2\text{O})_2](\text{BF}_4)_4$ was isolated [73].

The initially reported magnetism for $[\text{Fe}(\text{isoxazole})_6](\text{BF}_4)_2$ was reproduced (Fig. 13) and the two-step nature of the spin transition was found to arise from two crystallographically independent $[\text{Fe}(\text{isoxazole})_6]^{2+}$ sites [72]. These sites, designated Fe1 and Fe2, are present in the ratio 1:2 in the high-spin structure determined at 230 K (See Fig. 14). The distinct spin crossover behaviour of each Fe(II) site could be related to the inequality of the Fe1 and Fe2 chromophores, such as the slight differences in bond lengths and bond angles, as well as in the geometrical disposition (in other words the dihedral angles between neighbouring isoxazole ligands). Analysis of the magnetic data revealed that the transition occurring at 91 K could be attributed to Fe1, whereas the transition taking place at 192 K was due to Fe2.

A further report dealt with the synthesis, variable temperature magnetic susceptibility measurements, and crystal structure determination at various temperatures (115, 136, 140, 150 and 231 K; space group *P*-1) of $[\text{Fe}(\text{isoxazole})_6][\text{Fe}(\text{isoxazole})_4(\text{H}_2\text{O})_2](\text{BF}_4)_4$ [73]. The molecular structure of this well-defined double salt consists of two mononuclear Fe(II) dications,

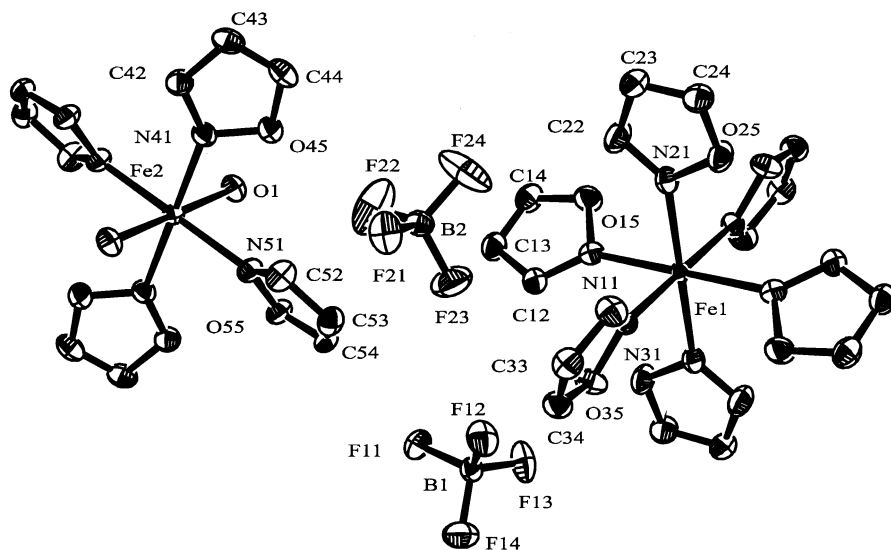


Fig. 15 Projection showing the structure of $[\text{Fe}(\text{isoxazole})_6][\text{Fe}(\text{isoxazole})_4(\text{H}_2\text{O})_2](\text{BF}_4)_4$ at 140 K [73]

$[\text{Fe}(\text{isoxazole})_6]^{2+}$ and $[\text{Fe}(\text{isoxazole})_4(\text{H}_2\text{O})_2]^{2+}$, together with four non-coordinated tetrafluoroborate anions (Fig. 15). The structural details for the low-field *trans* $[\text{Fe}(\text{isoxazole})_4(\text{H}_2\text{O})_2]^{2+}$ are consistent with a high-spin Fe(II) chromophore (average Fe–O=2.09 Å and Fe–N=2.19 Å), whereas those for $[\text{Fe}(\text{isoxazole})_6]^{2+}$ show a marked temperature dependence (average Fe–N=1.98 Å at 115 K and 2.17 Å at 231 K) related to the reversible low-spin to high-spin transition. From magnetic susceptibility measurements, the transition temperature has been found to be $T_{1/2}=137$ K.

4 Fe(II) Spin Crossover Compounds of Tetrazoles

4.1 Mononuclear Fe(II) Spin Crossover Compounds

The mononuclear hexakis(1-alkyl-tetrazole)iron(II) compounds with various anions have been extensively studied. It appears that the spin crossover characteristics of compounds with different alkyl substituents attached to N-1 of the tetrazole heavily depend on the crystal structure features. The transitions may be abrupt or rather gradual, complete or only involving a fraction of the Fe(II) ions, and the $T_{1/2}$ values lie in the range 63–204 K [2c, 2f, 2g, 74–81]. Interest in these systems has focused on their suitability for detailed studies of the LIESST effect (A. Hauser, this volume).

Recently, tetrazole ligands with halogen containing substituents have been added to this family. The first member is $[\text{Fe}(\text{1-(2-chloroethyl)tetrazole})_6](\text{BF}_4)_2$ [82], whose crystal structure shows two symmetry-equivalent Fe(II) ions in the high-spin state at room temperature. On the other hand, the magnetic susceptibility data indicate that two spin transitions in the ratio 1:1 take place at 190 K and 107.5 K. This seems to be inconsistent with the structural data, but they may have their origin in a phase transition taking place at lower temperatures leading to the existence of different Fe(II) sites, or may be the result of additional thermodynamic stability of the mixture of close to 50% of high-spin and 50% of low-spin Fe(II) ions at temperatures between the two steps of the spin crossover.

Among the mononuclear hexakis(1-alkyl-tetrazole)iron(II) compounds, the extensively-studied $[\text{Fe}(\text{1-propyl-tetrazole})_6](\text{BF}_4)_2$ [2c, 2f, 2g, 74–78] shows an abrupt spin transition in both cooling and heating mode, a feature which may very well be described by the model of elastic interactions [83]. In addition, an associated hysteresis loop, which is due to a first order crystallographic phase transition, is observed [84]. Since for the envisaged use of Fe(II) spin crossover materials in most feasible technical applications molecular bistability is a necessary criterion, the occurrence of thermal hysteresis is a pre-requisite. Therefore, it is important to acquire a detailed understanding of the factors likely to be responsible for this feature. It appears that the occurrence of thermal hysteresis in mononuclear Fe(II) spin crossover compounds may also be brought about by strong intermolecular interactions resulting from the presence of an important hydrogen-bonding network [85, 86] or extended π - π interactions [62–65].

4.2

Polynuclear Fe(II) Spin Crossover Compounds

The observation of thermal hysteresis associated with the spin transition in particular mononuclear systems described above suggested that a useful strategy for the enhancement of this cooperativity would be the coordination of bi-functional ligand systems leading to polymeric derivatives. This use of ligands capable of linking the active spin-switching metal centres has been motivated by the proposal that efficient propagation of the molecular distortions originating from the Fe(II) spin transition through the crystal lattice would be enhanced by the covalent bonds linking the spin crossover centres.

α,β - and α,ω -bis(tetrazol-1-yl)alkane type ligands were used to obtain polynuclear Fe(II) spin crossover materials. In this section, the compounds that have been reported with the ligands 1,2-bis(tetrazol-1-yl)propane (abbreviated as btzp), 1,2-bis(tetrazol-1-yl)ethane (abbreviated as btze) and 1,4-bis(tetrazol-1-yl)butane (abbreviated as btzb) (Fig. 16) will be discussed.

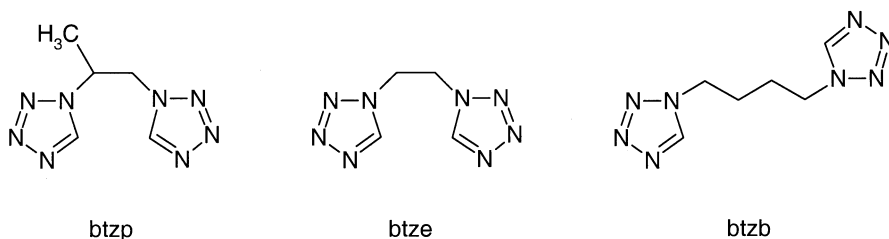


Fig. 16 1,2-Bis(tetrazol-1-yl)propane (btzp), 1,2-bis(tetrazol-1-yl)ethane (btze) and 1,4-bis(tetrazol-1-yl)butane (btzb)

Interest in $[\text{Fe}(\text{btzp})_3](\text{ClO}_4)_2$ [87] and $[\text{Fe}(\text{btze})_3](\text{BF}_4)_2$ [88] arises because they represent the first structurally characterised Fe(II) linear chain compounds exhibiting spin crossover. The incomplete transitions are gradual with $T_{1/2}$ of 148 K and 140 K, respectively.

Both compounds crystallise in the trigonal space group $P\bar{3}c1$, and this space group remains unchanged upon the Fe(II) spin crossover. The structure of $[\text{Fe}(\text{btzp})_3](\text{ClO}_4)_2$ [87] has been solved at 200 K and 100 K, whereas the structure of $[\text{Fe}(\text{btze})_3](\text{BF}_4)_2$ [88] has been determined at 296, 200, 150 and 100 K. A projection of the linear chain structure of $[\text{Fe}(\text{btzp})_3](\text{ClO}_4)_2$ [87] is displayed in Fig. 17.

Because of symmetry considerations, in both compounds the Fe(II) ion lies on the threefold axis and has an inversion centre. It is in an octahedral environment formed by six crystallographically related N-4 coordinating 1-tetrazole moieties. The almost perfect O_h symmetry for the FeN_6 core is therefore present in the high-spin and low-spin state. Three bis(tetrazole)alkane ligands, in a bent *syn* conformation, link the Fe(II) centres to form reg-

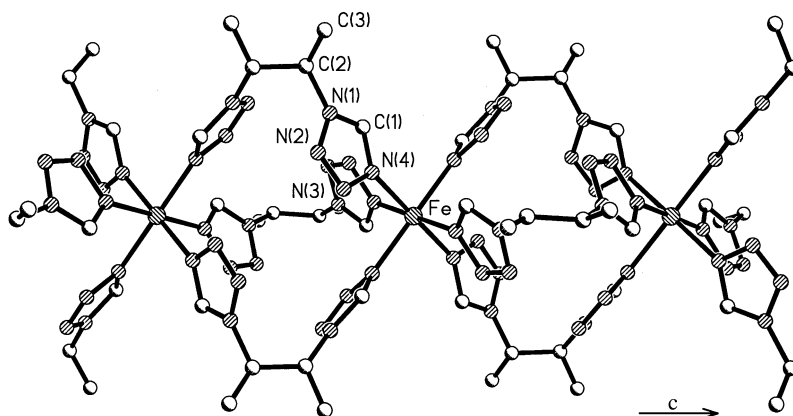


Fig. 17 Projection showing the structure of $[\text{Fe}(\text{btzp})_3](\text{ClO}_4)_2$ perpendicular to the *c*-axis at 100 K (adapted from [87])

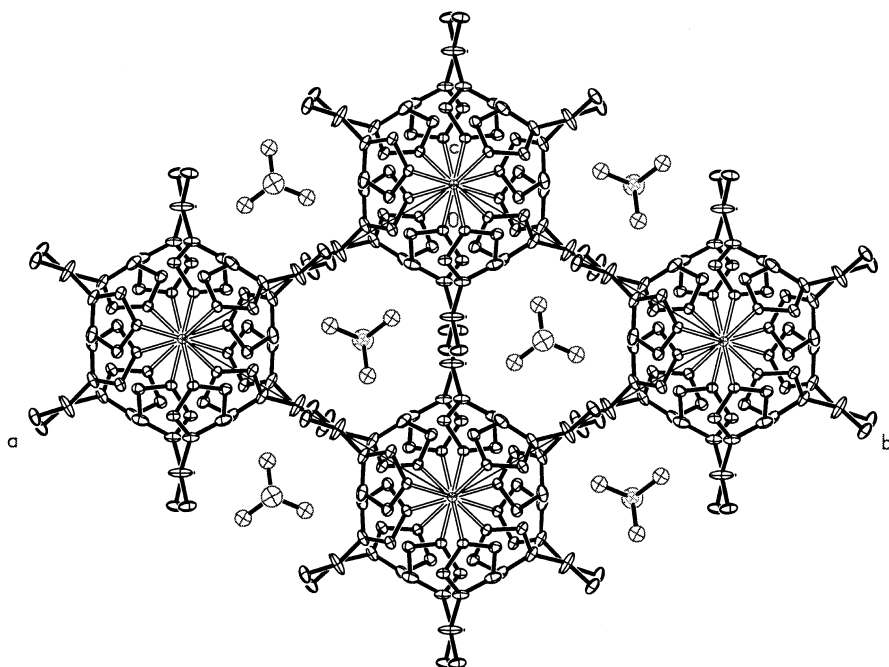


Fig. 18 Projection showing the structure of $[\text{Fe}(\text{btzp})_3](\text{ClO}_4)_2$ down the c -axis at 100 K (adapted from [87])

ular cationic chains running parallel to the crystallographic c -axis. The spin crossover is associated with the typical marked temperature dependence of the Fe–N distances, and is also reflected by the Fe–Fe separations over the bis(tetrazole)alkane ligands. The Fe–Fe separations for the btzp ligand are 7.422(1) Å at 200 K and 7.273(1) Å at 100 K, whereas these are 7.477, 7.461, 7.376 and 7.293 Å at 296, 200, 150 and 100 K, respectively, for the btze analogue. In the ab plane the linear chains are arranged in a hexagonal close-packed fashion, creating channel-like hexagonal cavities between them, in which the non-coordinated anionic groups are located (Fig. 18).

The gradual spin transition observed for these compounds may be directly related to their structures. It is generally believed that the direct connectivity of the Fe(II) sites in polynuclear Fe(II) spin transition compounds may have a favourable effect on the strength of the elastic interactions between the active Fe(II) spin crossover centres, thereby increasing the cooperativity of the spin transition, leading to very abrupt spin crossover behaviour or even thermal hysteresis. This is illustrated by the properties of the linear chain derivatives of 1,2,4-triazole discussed in Sect. 2.2. When the ligand spacer linking the Fe(II) ions becomes more flexible, as is the case for $[\text{Fe}(1,2\text{-bis}(\text{tetrazol-1-yl})\text{propane})_3](\text{ClO}_4)_2$ [87] and $[\text{Fe}(1,2\text{-bis}(\text{tetrazol-1-yl})\text{ethane})_3](\text{ClO}_4)_2$ [88], the spin crossover behaviour becomes more gradu-

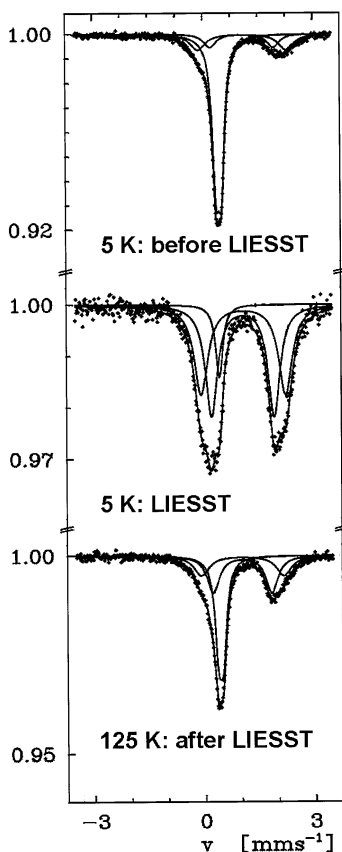


Fig. 19 LIESST effect observed by ^{57}Fe Mössbauer spectroscopy for $[\text{Fe}(\text{btzp})_3](\text{ClO}_4)_2$: at 5 K, without light irradiation (top); at 5 K, after light irradiation (middle); at 125 K, after light irradiation (bottom). (Reprinted with permission from [87]. Copyright (2000) American Chemical Society)

al indicating only weak elastic interactions, most probably due to the 1,2-propane or 1,2-ethylene unit acting as some kind of shock absorber and thereby disrupting the communication of the structural changes at the metal centres.

Most interestingly, $[\text{Fe}(\text{btzp})_3](\text{ClO}_4)_2$ is the first one-dimensional Fe(II) spin crossover compound, which shows the LIESST effect, detected in this instance by ^{57}Fe Mössbauer spectroscopy (Fig. 19).

At 5 K, the spectrum is dominated (area fraction of 80%) by a singlet, typical for one of the rare cases of cubic local symmetry for low-spin Fe(II). In addition, two distinct high-spin Fe(II) doublets are observed, contributing 16 and 4%, respectively. The presence of two high-spin Fe(II) doublets together with the fact that the Mössbauer resonance lines arising from the

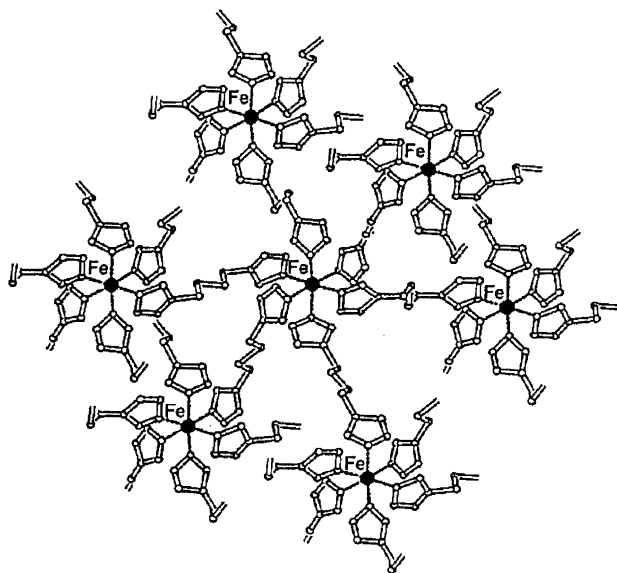


Fig. 20 Projection showing the tentative 3-D model for $[\text{Fe}(\text{btzb})_3](\text{ClO}_4)_2$ at 150 K ([89] – reproduced with permission of the Royal Society of Chemistry)

high-spin states as well as those from the low-spin state all are broadened, may be related to the disorder encountered in the 1,2-propane linkage, leading to a statistical distribution of different Fe(II) sites. The second spectrum was recorded after the sample had been irradiated at 5 K with green light using an Argon-ion laser (514 nm, 25 mW cm⁻²) for 20 minutes. This spectrum shows that the spectral contribution for low-spin Fe(II) has been reduced to 9%, whereas both high-spin fractions have considerably increased to 44% and 47%, respectively. Upon warming the sample up to 20 K, 60% of the high-spin sites were found to have relaxed to the low-spin state. Above 50 K, the relaxation is complete. The ⁵⁷Fe Mössbauer spectrum recorded at 125 K after LIESST (Fig. 19) is exactly identical to the spectrum recorded upon thermal treatment at the same temperature.

Increasing the length of the alkyl spacer in such a way as to yield 1,4-bis(tetrazol-1-yl)butane (abbreviated as btzb) (Fig. 16), changes the dimensionality of the Fe(II) spin crossover material [89]. In fact, $[\text{Fe}(\text{btzb})_3](\text{ClO}_4)_2$ is the first highly thermochromic Fe(II) spin crossover material with a supramolecular catenane structure consisting of three interlocked 3-D networks [89]. Unfortunately, only a tentative model of the 3-D structure of $[\text{Fe}(\text{btzb})_3](\text{ClO}_4)_2$ could be determined based on the x-ray data collected at 150 K (Fig. 20).

Since each of the btzb ligands is located on an inversion centre, all central C–C linkages are in the *anti* conformation. Of the six independent N–C–C–C

torsions in the ligands, four are also in the *anti* conformation, but two fit the electron density best when brought into a *gauche* conformation. A detailed re-analysis of the crystallographic data has been carried out recently [90]. This revealed a structure showing three symmetry related, interpenetrating, 3-D Fe-btzb networks. The shortest Fe–Fe separations of 8.3 and 9.1 Å occur between Fe(II) ions of two unconnected networks. The crystal structure of the Cu(II) analogue confirmed this threefold interpenetrating 3-D catenane structure [91]. Interestingly, the crystal structure determination did not reveal any well-defined specific intra- or intermolecular interactions, which could be responsible for the stabilisation of this unusual supramolecular structure. It may well be that the driving force for the formation of these remarkable supramolecular 3-D catenane materials lies in the conformation adopted by the alkyl spacer used to link the tetrazole moieties. Upon increasing the spacer length, the *anti* conformation, as has been found for the free btzb and for the Fe(II) catenane of btzb [89], is favoured over the bent *syn* conformation as found in the linear chains of ligands with smaller spacers [87, 88, 92].

The system is strongly thermochromic, so variable temperature optical reflectivity measurements could be used to determine the spin crossover characteristics along with the usual magnetic susceptibility measurements. These revealed that only ca. 16% of the Fe(II) ions participate in the spin transition, characterised by $T_{1/2\downarrow}=150$ K and $T_{1/2\uparrow}=170$ K. This hysteresis loop of width 20 K is reversible over several thermal cycles. It is worth noting that this is the largest thermal hysteresis observed up to now for iron(II) tetrazole derivatives. Apparently, the rigidity originating from the interweaving within this threefold 3-D interlocked supramolecular lattice, is responsible for the efficient propagation of the elastic interactions leading to this type of cooperative spin crossover behaviour. However, the same factors may also be invoked for explaining the small fraction of Fe(II) ions undergoing the spin transition. Most probably, the structural changes accompanying the Fe(II) spin transition modify the structure in such a way that further spin crossover of the high-spin Fe(II) ions upon cooling is severely disfavoured. The small low-spin fraction present at low temperatures can be converted to a metastable high-spin state by irradiation with green light (by the LIESST effect).

5 Conclusions

All the hexakis(ligand) Fe(II) materials derived from isoxazole, 1-alkyl-tetrazole and 4-R-1,2,4-triazole exhibit very favourable Fe(II) spin crossover response functions, which make them the likely compounds of choice for various applications in molecular electronics. The interconversion from low-spin

($S=0$) and high-spin ($S=2$) represents the magnetic response, and moreover, it is associated with a pronounced thermochromic effect. Interestingly, these are among the very few ligand systems known for which the absorption spectrum of the Fe(II) spin transition materials is not obscured by ligand- or charge-transfer bands, conferring the colour arising from the $d-d$ transitions of the Fe(II) ion to the compound (purple to pink in the low-spin state and colourless in the high-spin state).

The Fe(II) spin crossover chromophores in compounds of isoxazole and tetrazole all consist of an FeN_6 octahedron comprising six chemically identical heterocyclic ligands. Although the isoxazole nucleus has been found to be able to coordinate in a monodentate, as well as in a bidentate bridging fashion through the N and/or O atoms, the predominant coordination mode towards transition metal ions appears to be the monodentate-N mode [93]. It is this which occurs in $[\text{Fe}(\text{isoxazole})_6](\text{BF}_4)_2$ [72] and $[\text{Fe}(\text{isoxazole})_6][\text{Fe}(\text{isoxazole})_4(\text{H}_2\text{O})_2](\text{BF}_4)_4$ [73]. Therefore, these Fe(II) isoxazole materials show some structural similarity with the mononuclear hexakis(1-alkyl-tetrazole)iron(II) compounds [2c, 2f, 2g, 74–81]. In contrast to this, the $[\text{Fe}(4\text{-R-1,2,4-triazole})_6]^{2+}$ spin crossover chromophore has almost exclusively been found in polynuclear compounds. Depending on the nature of the substituted 1,2,4-triazole ligand and the presence of potentially coordinating water molecules, the spin crossover materials may be linear trinuclear [23], linear polynuclear [24–54] or even tridimensional [4]. The only mononuclear Fe(II) compound containing a hexakis(N1-1,2,4-triazole)iron(II) chromophore is bis[hydrotris(1,2,4-triazol-1-yl)borate]iron(II) [17–21].

Although 1,2,4-triazole frequently tends to establish a direct bridge between Fe(II) ions, currently this has not yet been structurally identified for isoxazole and tetrazole. However, the formation of polynuclear Fe(II) spin crossover materials containing tetrazole ligands has been achieved with bi-functional systems in which the coordinating moieties are sufficiently separated to preclude chelate ring formation. In this respect it is interesting to note that results indicative of the formation of polynuclear Fe(II) spin crossover materials containing tetrazolate bridges have been available since 1966. At that time, Holm and Donnelly reported their experiments involving 1H-tetrazole and Fe(II) salts [94]. Both cream-yellow and pink products were described suggesting that different spin states were involved. In addition, analytical data indicated the likely presence of bridging tetrazole. Therefore, these systems may resemble the rigid 1,2,4-triazole-bridged species and warrant further study. Nevertheless, the further exploration of this family of compounds may find its place in a research field focusing on new types of explosives – the materials explode upon heating above 110 °C – rather than in investigations aimed at the development of new Fe(II) spin crossover materials for “safe” applications in molecular electronics.

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Iron(II) Spin Crossover Systems with Multidentate Ligands

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Abstract This chapter focuses on the synthesis and characterization of iron(II) spin crossover compounds in which one of the ligands is multidentate. Here we have chosen to deal only with multidentate ligands having more than three donor atoms. The ligands are either linear or branched chelates or macrocycles. The present chapter only covers mononuclear systems (multidentate ligands which bridge two or more metal ions are discussed in the chapter by Murray and Kepert). The chapter is organized according to the nature of the ligands (N,P,S donor atoms), the denticity and the topology. The following aspects are covered for each type: synthesis, x-ray structure, magnetism and spectroscopy. The nature of the spin crossover in the solid phase or in solution is discussed in the cases where thermodynamic data are available.

Keywords Iron(II) spin crossover complexes · Multidentate ligands · Ligand design · Synthesis · Magnetic properties

1 Introduction

Most known iron(II) spin crossover systems based on multidentate ligands show a gradual, thermal spin-transition and the behavior in the solid and in solution is not markedly different. This behavior indicates that the spin states of these systems are primarily determined by the first ligand coordination sphere. It is therefore expected that the value of the transition temperature $T_{1/2}$ is correlated with the magnitude of the ligand field strength. The thermodynamic parameters for a series of iron(II) complexes for which the $^1A_{1g} \rightleftharpoons ^5T_{2g}$ equilibrium has been studied in solution are listed in Table 1. The data are typically obtained from UV/Vis, magnetic susceptibility, or NMR data. The thermodynamic parameters have, in most cases, been evaluated from $\ln K_{eq}$ vs. $1/T$ plots. In contrast to the solid-state behavior, solvent and counterion effects are rather modest in diluted solutions. Since no cooperativity is present in solutions, all reported transition curves exhibit gradual Boltzmann profiles.

The rationale behind much of the ligand design is based on simple ligand field arguments. Although aliphatic amines are known to be stronger bases, and therefore better σ -donors than heterocyclic amines, they will typically form high-spin complexes, whereas the heterocyclic systems often give low-spin or crossover systems. This tendency is a simple result of the π -acceptor properties of the heteroaromatic systems. Pyridine is the favored group in many ligands used in this area. It will be seen that nearly 90% of the systems discussed in the present chapter contain at least two pyridine functions. There are many other groups which could be considered, but the existence of convenient synthetic routes for pyridine-containing ligands certainly has an important influence on the choice. It is well-known that other factors in

Table 1 Thermodynamic parameters for some Fe(II) spin crossover systems in solution

Complex	Solvent	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S/J \text{ mol}^{-1} \text{ K}^{-1}$	Reference
[Fe 11 NCS] ²⁺	MeCN	–	–	20
[Fe 21] ²⁺	EtCN	19.4	85	26
[Fe 23''] ²⁺	(CH ₃) ₂ CO	15	50	27
[Fe 18] ²⁺	DMF	26.4	72.8	28
[Fe 19] ²⁺	DMF	45.1	49.0	28
[Fe 27] ²⁺	MeOH	17.1	59	33
[Fe 26] ²⁺	EtCN	23.6	84	32
[Fe 28] ²⁺	–	12	30	34
[Fe 29] ²⁺	MeOH	27.6	89	35

addition to the ligand field strength may influence the magnetic behavior of a given compound (for instance: method of preparation, crystallization solvent and isomorphous metal dilution [1-2]).

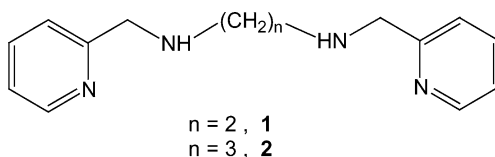
2

Tetradentate N4 Ligands

2.1

Linear Chelates

The aliphatic N4 ligand “triethylenetetramine”=1,4,7,10-triazadecane (trien) is strongly basic and forms only high-spin complexes with iron(II). If the two terminal amino groups are replaced by imine functions such as pyridine (1) the ligand field strength is increased sufficiently that low-spin or spin crossover iron(II) complexes can be made.



If the two remaining coordination groups in an octahedral iron(II) complex of **1** are chosen to be cyanides, a low-spin complex is formed. However, if the two terminal groups are isothiocyanates a spin crossover system is formed: *cis*-[Fe **1**(NCS)₂]. In the solid state, this complex shows a typical abrupt transition at 70 K with a thermal hysteresis of 4 K [5]. If the sample is rapidly cooled from room temperature to 4 K, a metastable high-spin state can be formed. During a subsequent increase in temperature the magnetic moment first increases to about 4.5 BM, then from 50 K it drops to a minimum of 3 BM at 60 K, and finally it follows the regular variation. Increase of the size of the chelate rings from five-membered to six-membered is usually expected to decrease the ligand field. However, for the present type of systems the opposite trend is observed. Expanding the middle chelate with one CH₂ (**2**) results in another spin crossover system *cis*-[Fe **2**(NCS)₂]. Compared with **1**, system **2** shows a 100 K higher critical temperature in the magnetic moment vs temperature curve, but the transition in the latter case is gradual [3].

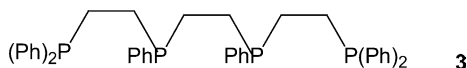
The choice of isothiocyanate as the anionic ligand is to some extent historical, but it seems to be a very appropriate ligand with an intermediate ligand field strength. The variation in ligand field strengths for a list of “cyanide” ligands is:



2.2

Linear Tetradentate Ligands with Phosphorus Donors

Thirty years ago Bacci and Sacconi [15] reported on five coordinate metal complexes of the tetradentate ligand 1,4,7,10-tetraphenyl-1,4,7,10-tetraphosphadecane (pppp) (**3**).



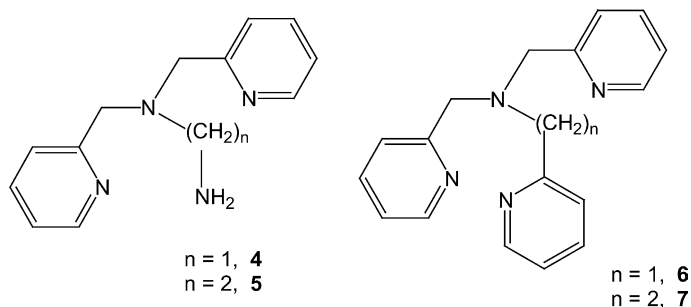
The iron(II) complexes [Fe(pppp)X]BPh₄ (X=Br[−], I[−]) showed unusual magnetic behavior, which was interpreted as being due to a singlet↔triplet spin transition [16].

2.3

Branched Chelates

The branched tetradentate ligand tris(2-aminoethyl)amine (tren) forms rather stable metal complexes with most transition metal ions. It is a very *hard* and basic ligand and consequently its iron(II) complexes are all high-spin. Later we will discuss hexadentate derivatives of this ligand which form crossover complexes (see Sect. 3.2).

The combination of pyridine and aliphatic nitrogen donors creates an intermediate ligand field which has yielded a long list of spin crossover systems [2]. Recently, Kahn et al. obtained two new tetradentate ligands in which two 2-pyridylmethyl groups replace two hydrogen atoms on the same amine function in 1,2-diaminoethane and 1,3-diaminopropane (**4**, **5**) [5–6].



The iron(II) complexes [Fe L(NCS)₂] are new spin crossover systems. Both complexes form several polymorphs, as does the related tpa complex (see below). The ligand **4** coordinates with the bis(2-pyridylmethyl)amine group in a meridional geometry, whereas this group adopts the facial geometry in the complex with ligand **5**. The complex [Fe **5**(NCS)₂] shows a rather abrupt transition at 138 K but without hysteresis. One of the three polymorphs of [Fe **4**(NCS)₂] has its transition at 176 K, again with no hysteresis, whereas another polymorph shows an 8 K hysteresis between $T_{1/2\downarrow}=112$ K and $T_{1/2\uparrow}=120$ K. Hydrogen-bonding involving the N-H groups seems to be

important in fine-tuning the ligand field for these systems. It is therefore interesting to note that the *N*-dimethylated version of ligand **4** forms an iron(II) diisothiocyanato complex which is high-spin [7].

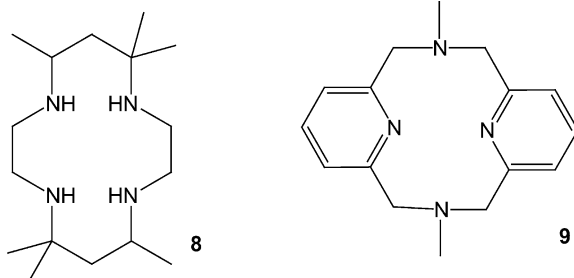
About twenty years ago we reported on the di-isothiocyanato iron(II) complex of the tetradentate ligand tpa (tris(2-pyridylmethyl)amine) [7] (**6**). It was shown that this complex exhibits the spin crossover phenomenon with a critical temperature $T_{1/2}$ of about 170 K. Several different solvated phases of the same system have since been characterized by Chansou et al. [8]. The unsolvated phase which can be isolated from an aqueous solution has been investigated by nuclear forward scattering (NFS), nuclear inelastic scattering (NIS) [9], extended x-ray absorption fine structure (EXAFS) spectroscopy, conventional Mössbauer spectroscopy, and by measurements of the magnetic susceptibility (SQUID) [10–13]. The various measurements consistently show that the transition is complete and abrupt and it exhibits a hysteresis loop between 102 and 110 K.

It is expected that ligands providing a weaker ligand field than tpa will be obtained if one or more of the 2-pyridylmethyl arms are replaced by 2-pyridylethyl arms. However, the first ligand of such a series of expanded tripodal ligands (**7**) still forms an iron(II) spin crossover system. However, if more than one of the chelate rings are six-membered, only high-spin complexes are formed [14].

2.4

Macrocyclic Ligands

Tetraza-macrocycles of the right ring size are expected to give very high in-plane ligand field strengths. Fe(II) complexes based on such ligands are therefore expected to be either low-spin or spin-crossover. Busch and his coworkers [17] have synthesized six coordinate iron(II) complexes [Fe(tet-a) X_2], where tet-a is one of the isomers of hexamethyl cyclam, a 14-membered tetraza-macrocycle (**8**).



The complexes were found to be predominantly low-spin when the axial ligands X (CN^- , NO_2^-) are relatively strong. The complex with NCS^- shows $S=0 \rightleftharpoons S=2$, spin crossover at elevated temperature. These compounds are the

only known examples where low-spin Fe(II) has been stabilized by a purely aliphatic tetraza-macrocyclic.

Whereas a 14-membered tetraza-macrocyclic fits ideally to a first row divalent transition metal ion, a 12-membered ring is too small to bind a metal in a planar configuration. However, in this case the macrocyclic ring folds and then binds the metal in a *cis*-configuration. No purely aliphatic versions of such Fe(II) spin crossover complexes have yet been reported. Recently Krüger and coworkers [18] have created Fe(II) spin-crossover complexes of this type using a 12-membered macrocyclic ligand (**9**) where two of the aliphatic nitrogen functions have been replaced by pyridine groups.

Increasing the number of imine functions in a given macrocyclic ring will further increase the in-plane ligand field strength. A well-known class of ligands of this type are the porphyrins and phthalocyanins, which are most commonly derived from fully conjugated tetraza-hexadecanes, where the nitrogen donors are provided by pyrroles. The magnetic behavior of the iron complexes of these systems has been well-investigated; however, there are very few examples, if any, of genuine Fe(II) spin-crossover systems among them. They show intermediate-spin ground states ($S=1$) with spin-admixed effects, rather than spin-crossover [19].

3

Pentadentate N5 Ligands

3.1

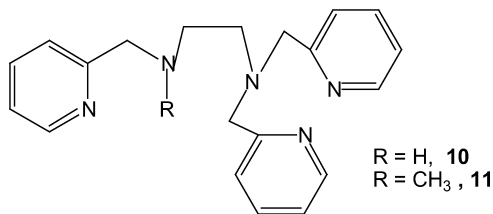
Linear Chelates

To the best of our knowledge no Fe(II) spin crossover complexes have been created with these type of ligands.

3.2

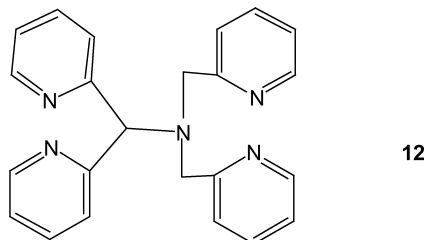
Branched Chelates

Some pyridine-containing ligands of this type have been used to mimic the protein environment in non-heme iron metal proteins. The ligands **L** (**10** and **11**) tend to bind strongly to five positions of the coordination sphere leaving the sixth position available to bind unidentate ligands X: $[\text{FeLX}]^{n+}$.



These complexes are either high-spin or low-spin depending on the nature of the ligand X. It has been possible to create spin-crossover complexes [20] in a few cases, such as $X=NCS^-$.

A more compact ligand with four pyridine groups and one aliphatic nitrogen group has been used by Lubben et al. [21] (12).

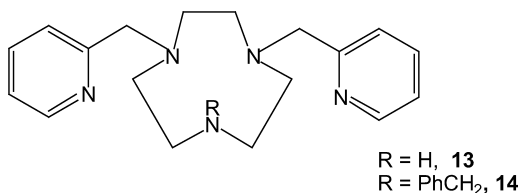


These authors noted that if the last group in the Fe(II) coordination sphere is acetonitrile a low-spin complex is obtained [22]. We found [23] that the aqua complex is high-spin (Mössbauer spectral parameters for the sulfate: $\delta=1.15 \text{ mm s}^{-1}$, $\Delta E_Q=3.23 \text{ mm s}^{-1}$), whereas the corresponding isothiocyanate complex is a crossover complex [23].

3.3

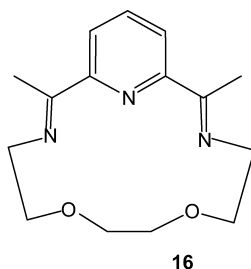
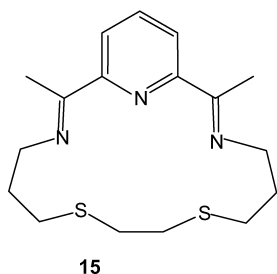
Macrocyclic Ligands

Pentadentate ligands have been prepared by attaching two pendant 2-pyridylmethyl arms to 1,4,7-triazacyclononane. The systems with $R=H$ were investigated by Spiccia et al. [24] (13).



They found that an iron(II) complex with $X=NCS^-$ was low-spin, whereas a similar complex made by Koikawa et al. having $R=benzyl$, (14) turned out to be a crossover complex [25]. Clearly the ligand field is fine-tuned in a subtle way via the substituents of the aliphatic nitrogen groups. The fact that the unsubstituted ligand 13 provides the highest ligand field is probably the result of hydrogen-bonding ($2.28 \text{ \AA}$) from the counterion (PF_6^-) to the N-H function, which increases the basicity of the nitrogen atom.

Earlier Nelson prepared a few pentadentate macrocyclic ligands which form iron(II) complexes with unusual magnetic properties. With the N_3S_2 ligand (15) he obtained a series of hexacoordinated iron(II) complexes of the type: $[Fe 15 X]^+$.

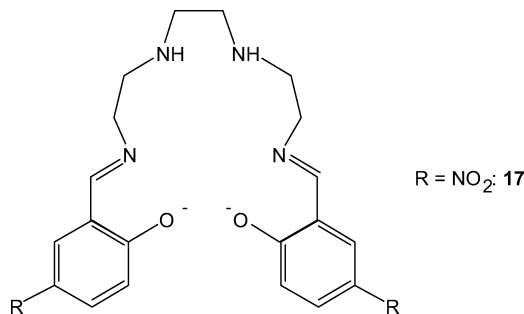


With $X=\text{Cl}^-$ or Br^- high-spin complexes are obtained, whereas low-spin complexes are obtained if $X=\text{I}^-$ or NCS^- [38]. The N_3O_2 ligand (16) gave an apparent seven-coordinated complex with cyanide: $[\text{Fe}(\text{CN})_2 \text{ 16}]\cdot\text{H}_2\text{O}$. This complex exhibits a complex variation of the magnetic moment with temperature [39]. On rapid cooling a metastable high-spin species can be formed and a two-step transition from low-spin to high-spin is observed upon heating. On slow cooling and heating a thermal hysteresis with $T_{1/2\downarrow}=207\text{ K}$ and $T_{1/2\uparrow}=222\text{ K}$ is observed [40]. It is assumed that the low-spin complex is six-coordinated whereas the high-spin complex is seven-coordinated. As cyanide is unlikely to dissociate, the authors suggest that one of the ether functions is dissociated in the low-spin form.

4 Hexadentate N402 Ligands

4.1 Linear Chelates

Salicylaldimine ligands often give stable $\text{Fe}(\text{III})$ complexes, so it is uncommon to meet $\text{Fe}(\text{II})$ complexes with such ligands. The dark blue-green complex $[\text{Fe } 17] \text{ (17)}$ shows an unusual thermally-induced, two-step spin-state conversion where two sharp transitions are separated by a plateau extending over 35 K in which 50% high-spin and 50% low-spin molecules coexist [41].



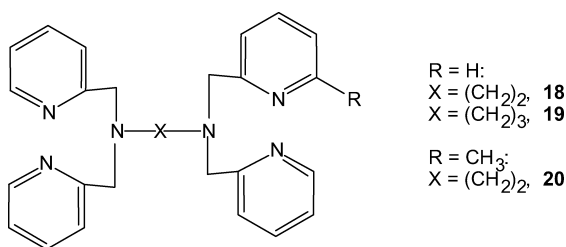
5 Hexadentate N6 Ligands

5.1 Linear Chelates

Even though many ligands of this type have been prepared in recent years, none of their Fe(II) complexes is a spin-crossover system.

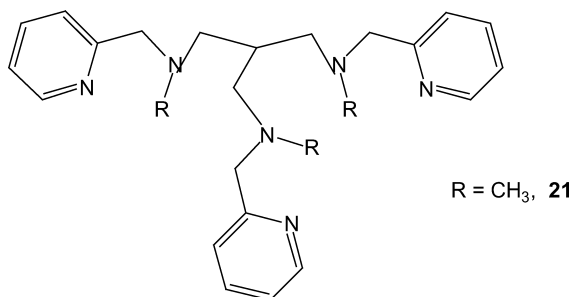
5.2 Branched Chelates

Several pyridine containing ligands of this type have been reported by Toftlund [2]. A combination of two aliphatic and four imine nitrogen functions seems to provide a ligand field at the crossover point. A versatile class of ligands of this type is based on aliphatic diamines substituted with four alkylpyridine groups. The simplest compound of this type is tetrakis(2-pyridylmethyl)-1,2-ethanediamine (tpen) (**18**).



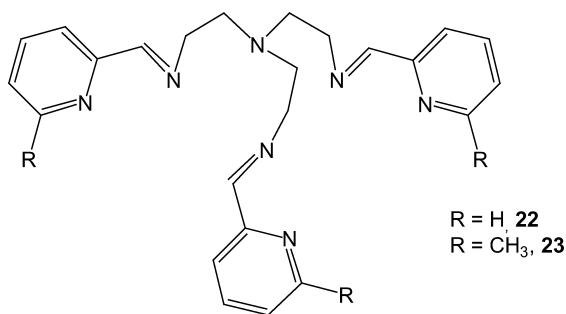
The iron(II) complex of this ligand, [Fe **18**] X_2 is a crossover complex both in the solid and in solution [28]. The single crystal x-ray diffraction analysis of the perchlorate salt was reported at 298 and 358 K. At the lower temperature this complex is entirely low-spin, whereas at 358 K it is 40% high-spin [28]. At both temperatures the coordination geometry has the expected distorted octahedral structure [29]. Some of the strain in the tpen system is released when the alkane strap between the two aliphatic nitrogen atoms is increased. The Fe(II) complex of the trimethylene strapped system is a purely low-spin complex [2, 28] (**19**). Finally, when the diamine chelate is expanded further to a seven-membered chelate ring, the resulting iron(II) complex salts are high-spin [23]. Substitution of a methyl group for hydrogen in the 6-positions of just one of the pyridylmethyl arms creates enough steric hindrance to make the Fe(II) complex purely high-spin (**20**). The single crystal x-ray structure of the perchlorate salt of this complex has been reported [30]. The average Fe-N distance is 2.17 Å. The methyl group shows positional disorder and the geometry is even more distorted than in the case of [Fe **19**](ClO₄)₂. The most remarkable feature is the trigonal twist angle ϕ between the two opposite trigonal faces of the octahedron ($\phi=37^\circ$).

A tripodal ligand (tpmetame) based on 1,1,1-tris(aminomethyl)-ethane substituted by three pyridine functions has recently been prepared [26] (21).



The Fe(II) complex of this ligand shows crossover behavior both in solution and in the solid state. The complex has a distinct green color derived from the ligand field transition ${}^1T_1 \leftarrow {}^1A_1$ ($\lambda = 620$ nm) of the low-spin form of the complex. For most Fe(II) spin-crossover systems this transition is found around 540–580 nm, so in this case Δ_o is unusually small and the critical ligand field strength $\Sigma = \Delta_o/B$ must have been obtained by a reduction in the interelectronic repulsion parameter B . The variable temperature magnetic susceptibility data for [Fe **21**](ClO₄)₂ show a gradual spin transition centered at 196 K. Even in the solid, a straightforward analysis of this transition gives well-defined thermodynamic parameters: $\Delta H^\circ = 18$ kJ mol⁻¹ and $\Delta S^\circ = 95$ J mol⁻¹ K⁻¹.

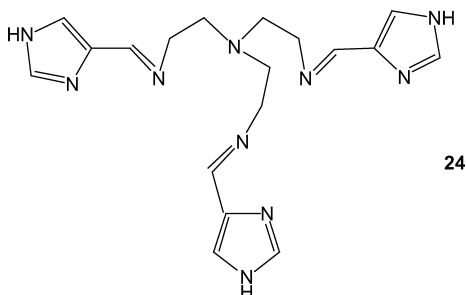
Iron(II) systems based on hexadentate ligands where all the donor functions are imines will generally be low-spin. One well-known example is the Schiff base ligand obtained by condensing tren with 2-pyridinecarbaldehyde (22).



Wilson et al. [27] showed that the introduction of steric hindrance in the 6-position of one or two of the pyridine groups was sufficient to fine-tune the ligand field and obtain crossover compounds. These systems have been investigated using a number of different techniques, both in the solid and solution phases. Thermodynamic parameters have been derived from variable temperature magnetic susceptibility data for the single methyl-substituted (23') ($\Delta H^\circ = 19.7$ kJ mol⁻¹, $\Delta S^\circ = 39.8$ J mol⁻¹ K⁻¹), the double methylsubstitut-

ed (23'') ($\Delta H^\circ=12.7$ kJ/mol, $\Delta S^\circ=39.8$ J/mol K) and the fully methylsubstituted (23) ($\Delta H^\circ=19.7$ kJ mol $^{-1}$, $\Delta S^\circ=85.7$ J mol $^{-1}$ K $^{-1}$) systems. The fully methyl-substituted system 23 is high-spin in solution. A typical set of solution values for the dimethylsubstituted derivative (23'') is shown in Table 1.

Very recently Tuchagues et al. [42] have reported on the analogous imidazolyl ligand (24) and its Fe(II) and Fe(III) complexes.

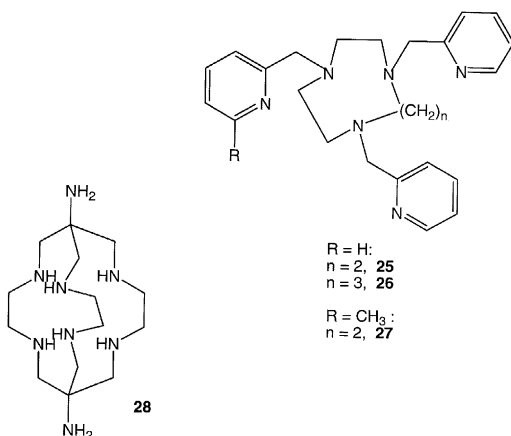


The complex [Fe 24](ClO $_4$) $_2$.xH $_2$ O (0<x<3) is high-spin at room temperature with an average Fe-N distance of 2.25 Å. All the Fe-N distances are very similar. The complex exhibits spin crossover in the temperature range 150–250 K. Above 300 K the water solvate is lost, forming a purely high-spin complex.

5.3

Macrocyclic Ligands

Compared to the linear triamine ligands, the macrocycle 1,4,7-triazacyclononane (tacn) provides a surprisingly strong ligand field. This system can be extended to a hexadentate ligand by introducing 2-pyridylmethyl groups on all of the three nitrogen atoms. The resulting ligand (tptacn) (25) forms a very stable low-spin complex with iron(II) [31].



R = H:
n = 2, **25**
n = 3, **26**

R = CH $_3$:
n = 2, **27**

A simple strategy to reduce the ligand field strength of such a system is to expand the size of the macrocyclic ring. Expansion with just one CH_2 group results in a system based on the 10-membered tri-aza macrocycle: 1,4,7-triazacyclodecane ($\text{tp}[10]\text{ane N}_3$) (**26**). The iron(II) complex of this ligand turns out to be a crossover system [32] with a $T_{1/2}$ of 282 K in a propionitrile solution. Ligand **26** forms six fused chelate rings on coordination to the iron(II) center. Molecular mechanics calculations show that the flexibility of the complex is quite restricted. Four different conformations might exist in an equilibrium, but the rate of interconversion of the conformations might very well be considerably lower than the rate of the spin-state change. The different structural isomers are geometry optimized with different Fe-N distances, so the two spin states are expected to have different conformations [20]. It is, therefore, not too surprising that a flash photolysis study revealed biphasic kinetics for this system [32]. (Refer to the chapter by J. J. McGarvey et al.).

Another strategy for fine-tuning the ligand field strength in this type of system is to introduce steric bulk in the pendant arm part of the ligand. The introduction of a methyl group in the 6-position of the pyridyle group of just one of the three pendant arms turns out to be sufficient to transform the parent low-spin system into a spin crossover system [25] (**27**). The structures of the perchlorate and the hexafluorophosphate salts have been analyzed by single crystal x-ray diffraction. The coordination geometries are close to octahedral in both cases [32]. At 100 K, where the low-spin forms are dominant, the average Fe-N distance is 2.00 Å. As expected, only the distance to the nitrogen atom of the methyl-substituted pyridyl groups is significantly longer: 2.12 Å. An unusual feature of this complex are the very different transition temperatures observed for the solid and for a methanol solution. The perchlorate salt has a $T_{1/2}$ of 380 K, whereas the $T_{1/2}$ of the salt in methanol solution is 283 K. Spectroscopic investigations of the solutions indicate that the ligand environment has changed from an intact FeN_6 species to an $\text{FeN}_5(\text{solv})$ species on dissolution, so the observed spin change in solution is probably due to a more radical chemical reaction rather than a normal spin transition.

5.4

Cage Ligands

Martin et al. have developed a unique series of capped tris(1,2-diaminoethane) cages which can encapsulate divalent transition metal ions in a near octahedral geometry (**28**). The iron(II) complex with the ligand $(\text{NH}_2)_2\text{sar}$ turns out to be a crossover system in solution [34], but the solid triflate salt is low-spin [43]. This is the only Fe(II) crossover system having 6 identical aliphatic nitrogen donors.

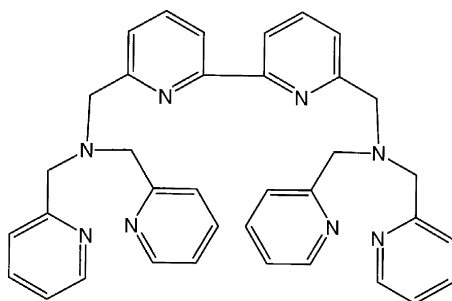
The complex shifts to high-spin on protonation of the apical amino groups. The structure of $[\text{Fe}(\text{NH}_3)_2\text{sar}](\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ is a trigonally distorted octahedral ($\phi=29^\circ$). Unfortunately, because of the easy oxidation of the $\text{NH}-\text{CH}_2$ functions to imines, this compound is very air-sensitive, making the spectroscopic characterization rather difficult.

6 Heptadentate N7 Ligands

If the coordination number of a given complex of a first row transition metal ion exceeds six there seems to be a general stabilization of the high-spin configuration. To our knowledge, there are no examples of Fe(II) crossover complexes with such high coordination numbers.

7 Octadentate N8 Ligands

A potentially octadentate N8 ligand, derived from 6,6'-bis(aminomethyl)-2,2'-bipyridine by attaching four 2-pyridylmethyl groups, has been prepared by Toftlund et al. (29).



29

The Fe(II) complex of this ligand is a crossover system in solution but not in the solid state [35]. From the single crystal x-ray structural analysis of the PF_6 salt it is known that the Fe(II) complex cation occupies two non-equivalent lattice sites. One site has an almost octahedral low-spin $[\text{FeN}_6]$ coordination sphere, whereas the other site consists of a highly distorted high-spin $[\text{FeN}_6]$ coordination sphere. In both cases two 2-pyridylmethyl groups are non-coordinating but, in the case of the high-spin site, one of the non-coordinating pyridyl containing arms is pointing towards the Fe center with an Fe-N distance of only 3.16 Å. It is believed that the approach of this seventh ligand is the factor which triggers the spin change for this compound [23].

8 Comparison of Solution Data

Most spin crossover systems based on multidentate ligands are so stable that ligand dissociation does not interfere with the spin equilibrium even in polar solvents. Thermodynamic data, as listed in Table 1, are obtained from studies of the temperature variation of the equilibrium constants. Linear van't Hoff plots are usually obtained. The quality of the data might be expected to be reflected in good linear isokinetic plots (ΔH° vs ΔS°) [44]. Such a plot based on the data points in Table 1 shows quite a large scatter. However, if the systems are arranged according to the nature of the ligands, much better correlations are obtained. Systems with bidentate and tridentate ligands show large reaction enthalpy values (not shown here) and they define a line with a slope of 385 K. Systems based on hexadentate ligands generally show small reaction enthalpies and the slope of this plot is 223 K [36]. It is suggested that the relative rigidity of the systems based on multidentate ligands prevents major ligand reorganization during the spin change, which is then the origin of the relatively small observed ΔH° values. It is remarkable that the cage system $[\text{Fe } 28]^{2+}$ fits into the plot even though both the enthalpy and the entropy changes are small [34]. In this system all of the donor atoms are secondary nitrogen functions, whereas in the tpmetame (21) system they are all tertiary nitrogen functions [26], suggesting quite different solvation contributions for the two systems.

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Bipyrimidine-Bridged Dinuclear Iron(II) Spin Crossover Compounds

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Abstract This review reports on the study of the interplay between magnetic coupling and spin transition in 2,2'-bipyrimidine (bpym)-bridged iron(II) dinuclear compounds. The coexistence of both phenomena has been observed in {[Fe(bpym)(NCS)₂]₂(bpym)}, {[Fe(bpym)(NCSe)₂]₂(bpym)} and {[Fe(bt)(NCS)₂]₂(bpym)} (bpym = 2,2'-bipyrimidine, bt = 2,2'-bithiazoline) by the action of external physical perturbations such as heat, pressure or electromagnetic radiation. The competition between magnetic exchange and spin crossover has been studied in {[Fe(bpym)(NCS)₂]₂(bpym)} at 0.63 GPa. LIESST experiments carried out on {[Fe(bpym)(NCSe)₂]₂(bpym)} and {[Fe(bt)(NCS)₂]₂(bpym)} at 4.2 K have shown that it is possible to generate dinuclear molecules with different spin states in this class of compounds. A special feature of the spin crossover process in the dinuclear compounds studied so far is the plateau in the spin transition curve. Up to now, it has not been possible to explore with a microscopic physical method the nature of the species

which constitute such a plateau, due to the relatively high temperatures at which the transition takes place. A two-step spin transition has been observed for {[Fe(ph-dia)₂(NCS)₂](phdia)} (phdia: 4,7-phenanthroline-5,6-diamine) with $T_{1/2}(1)$ and $T_{1/2}(2)$ located at 108 and 80 K, respectively. Due to this low temperature transition we were able to thermally trap, at liquid helium temperatures, the species present in the plateau of the spin transition curve. The results have revealed that the plateau consists mainly of [HS–LS] pairs, and they confirmed the hypothesis formulated earlier that the spin conversion in dinuclear entities proceeds via [HS–HS] $\leftrightarrow$ [HS–LS] $\leftrightarrow$ [LS–LS] pairs.

Keywords Spin crossover · Dinuclear complexes · Two-step transition · Plateau · Magnetic field Mössbauer spectroscopy

Abbreviations

ST	Spin transition
SCO	Spin crossover
HS	High spin
LS	Low spin
χ_M	Molar magnetic susceptibility
T	Temperature
$T_{1/2}$	Temperature at which 50 per cent of the “SCO-active” molecules have changed the spin state
T_p	Temperature at which the plateau of a two-step spin transition is centred
P	Pressure
$P_{1/2}$	Pressure at which 50 per cent of the “SCO-active” molecules have changed the spin state
γ_{HS}	HS molar fraction
$\gamma_{HS}(T)$	HS molar fraction as a function of temperature
M	Magnetisation
H	Magnetic field
J	Magnetic coupling parameter
D	Zero field splitting parameter
g	Landé factor
H_{ext}	External magnetic field
H_{eff}	Effective magnetic field
S	Spin quantum number
$\langle S \rangle$	Average spin value
δ_{HS}	Isomeric shift value for the HS state
δ_{LS}	Isomeric shift value for the LS state
$\Delta E_{Q(HS)}$	Quadrupole splitting for the HS state
$\Delta E_{Q(LS)}$	Quadrupole splitting for the LS state
λ	Light wavelength
ΔH	Enthalpy difference between the HS and LS states
W	Energetic stabilization of the [HS–LS] pair relative to the enthalpy average of the [HS–HS] and [LS–LS] states ($\Delta H/2$)
Γ	Parameter that accounts for the intermolecular interactions

bpym	2,2'-bipyrimidine
bt	2,2'-bithiazoline
phen	1,10-phenanthroline
bpy	2,2'-bipyridine
phdia	4,7-phenanthroline-5,6-diamine
pic	2-picolylamine
ptz	1-propyltetrazole
py	pyridine

1

Introduction

In the last fifteen years, activities in the design, synthesis and characterisation of new iron(II) spin crossover (SCO) compounds have increased considerably. In particular, the structural characterisation of a large number of mononuclear complexes displaying different cooperative spin crossover behaviours has been reported. This has provided a base to analyse the cooperative mechanism from a microscopic viewpoint, and in some cases qualitatively rationalise the character of the spin transition (ST) through careful investigation of the intermolecular interactions. The SCO phenomenon involves a transfer of electrons between the t_{2g} and e_g orbitals, with a concomitant variation in the molecular volume of ca. 10–20 Å³. This change is transmitted through space via intermolecular interactions to the whole crystal. An important conclusion can be drawn from such studies: the stronger the interactions, the more cooperative the ST.

Partial or complete filling of the intermolecular empty space by suitable bridging moieties connecting the SCO centres is an interesting synthetic alternative approach developed to obtain more cooperative ST regimes. This strategy has afforded a number of oligonuclear and polymeric SCO compounds with interesting magnetic behaviours. Further, closely related to this polynuclear/polymeric strategy is the idea of combining different electronic properties to obtain multiproperty materials. For instance, a combination of magnetic exchange and ST phenomena in the same molecule or polymeric network could eventually afford new switching materials with considerable amplification of the response signal. In this respect, 2,2'-bipyrimidine (bpym)-bridged iron(II) dinuclear compounds represent a first step along this line.

2

Synthetic Strategy

Bpym is a bis(α -diimine) ligand, and its similarity to the well-known 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) ligands has attracted the

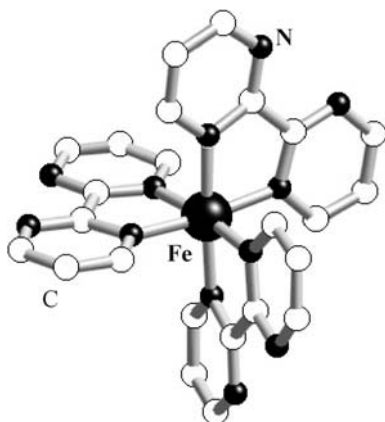


Fig. 1 Molecular structure of the diamagnetic cation $[\text{Fe}(\text{bpy})_3]^{2+}$

attention of chemists in the last twenty years. Like bpy and phen, bpm is a middle-strong field ligand that can induce spin pairing in iron(II) complexes. The crystal structure of the tris-chelate compound $[\text{Fe}(\text{bpm})_3](\text{ClO}_4)_2/4\text{H}_2\text{O}$ (Fig. 1) shows an average Fe–N bond length of 1.970(6) Å [1], which is in full agreement with the diamagnetic LS ground state observed for this compound.

However, the replacement of two bpm molecules by weaker ligands such as pyridine (py) and particularly NCS^- affords the compound $[\text{Fe}(\text{bpm})(\text{py})_2(\text{NCS})_2]1/4\text{py}$ (Fig. 2). The average Fe–N bond length, 2.186(8) Å, at room temperature, is consistent with an iron(II) ion in the HS state. The thermal dependence of $\chi_M T$ (χ_M =molar magnetic susceptibility, T =tempera-

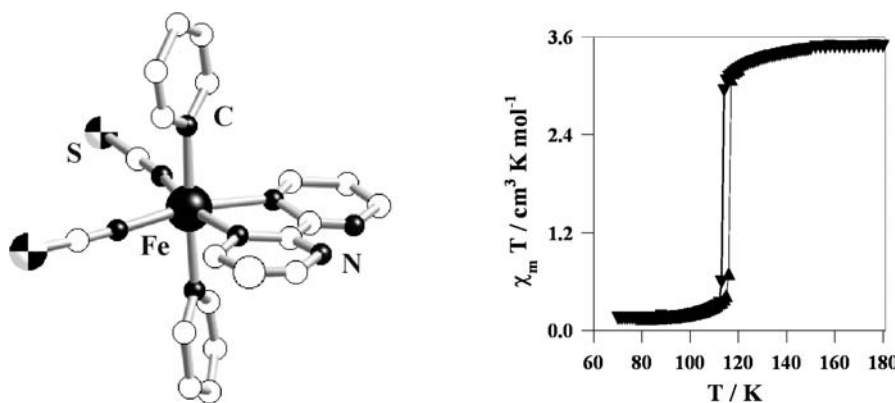


Fig. 2 Molecular structure and magnetic properties of the $[\text{Fe}(\text{bpm})(\text{py})_2(\text{NCS})_2]1/4\text{py}$ compound (adapted from [2])

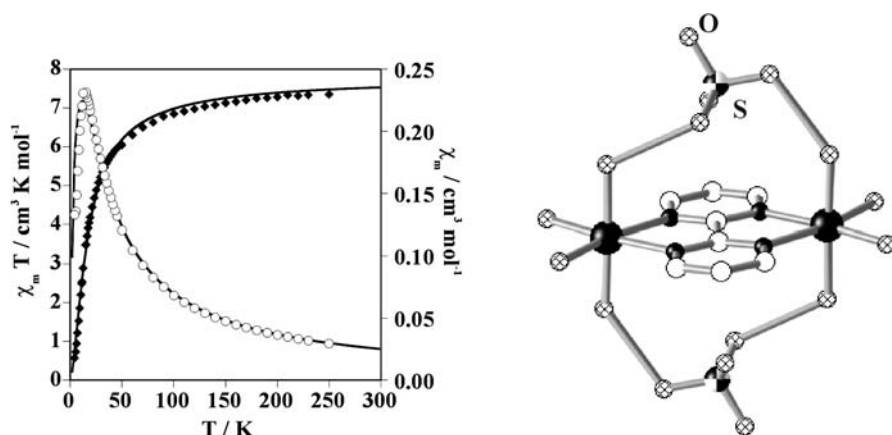


Fig. 3 Magnetic properties and molecular structure of the dimeric species $\{[\text{Fe}(\text{H}_2\text{O})_4]_2(\text{bpym})\}(\text{SO}_4)_2$ (adapted from [3])

ture) shows an abrupt ST close to 115 K for this compound (Fig. 2). This result illustrates the suitability of the bpym ligand in the field of SCO [2].

The most significant difference between bpym and bpy or phen is that the former can act as a bis-chelating ligand and mediate electronic effects between metal centres in the resulting polymetallic species. This fact is illustrated by the dinuclear compound $\{[\text{Fe}(\text{H}_2\text{O})_4]_2(\text{bpym})\}(\text{SO}_4)_2$ [3]. In this centrosymmetric molecule, the iron atoms are each coordinated to four water molecules and two nitrogen atoms of the bpym ligand. Each apical water molecule is hydrogen-bonded to one sulfate counter-ion (Fig. 3). The iron(II) ions are in the HS state and interact antiferromagnetically through bpym ($J = -3.4 \text{ cm}^{-1}$).

This compound can be considered as a precursor of more elaborate bpym-based magnetic systems so that formal substitution of the water molecules by more appropriate peripheral ligands, such as bpym and 2,2'-bithiazoline (bt) together with NCS^- or NCSe^- counter-ions, allows us to fine tune the ligand field strength around the iron(II) atom, resulting in a rich variety of magnetic behaviour in the $\{[\text{Fe}(\text{L})(\text{NCX})_2]_2(\text{bpym})\}$ series.

3 The $\{[\text{Fe}(\text{L})(\text{NCX})_2]_2(\text{bpym})\}$ Series

3.1 Structural Characterisation

The series of compounds $\{[\text{Fe}(\text{L})(\text{NCX})_2]_2(\text{bpym})\}$, where L is bpym or bt and X is S or Se, comprises four complexes, two of which, (bpym, S) and

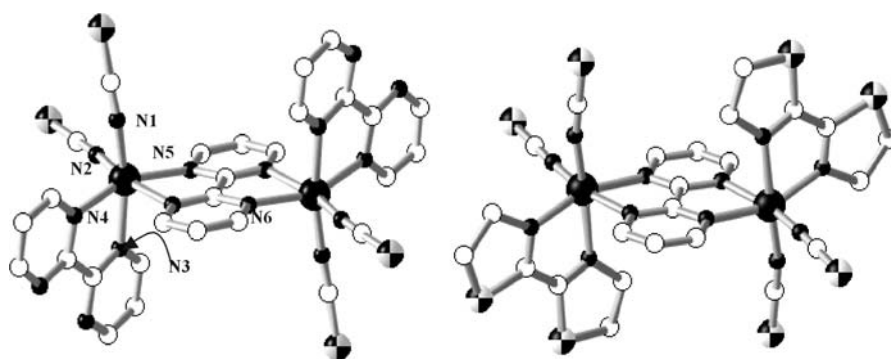


Fig. 4 Molecular structure of $\{[\text{Fe}(\text{bpym})(\text{NCS})_2]_2(\text{bpym})\}$ together with the corresponding atom numbering (**left**) and the same for $\{[\text{Fe}(\text{bt})(\text{NCS})_2]_2(\text{bpym})\}$ (**right**) (adapted from [4, 5])

(**bt**, **S**), have been characterised by x-ray single crystal diffraction. The centrosymmetric dinuclear units $\{[\text{Fe}(\text{L})(\text{NCS})_2]_2(\text{bpym})\}$, where $\text{L}=\text{bpym}$ [4] or **bt** [5], are shown in Fig. 4. Each iron(II) atom is surrounded by two NCS^- anions in *cis* positions, two nitrogen atoms of the bridging bpym ligand and the remaining positions are occupied by the peripheral bpym or **bt** ligands. The $[\text{FeN}_6]$ chromophore is rather distorted with Fe–N bond distances characteristic for an iron(II) ion in the HS state (see Table 1).

No thermal spin transition is observed for the iron(II) complex denoted as (**bpym**, **S**) in the whole range of temperature (see next section). At first sight this is a rather unexpected result, as the iron(II) environment in the dinuclear compound is close to that in $[\text{Fe}(\text{bipy})_2(\text{NCS})_2]$ [6]. However, the average Fe–N bond distance is noticeably greater for (**bpym**, **S**). In contrast, the iron (II) complex denoted as (**bt**, **S**), which shows shorter Fe–N bond distances than (**bpym**, **S**), undergoes a complete spin transition [7]. The remaining members of this family, (**bpym**, **Se**) and (**bt**, **Se**), also undergo spin transitions but their crystal structures have not yet been solved. However, structural information on these compounds has been obtained using x-ray absorption techniques (EXAFS) at 300 and 77 K. The EXAFS data afforded a

Table 1 Fe–N bond distances for the dinuclear compounds (**bpym**, **S**) and (**bt**, **S**)

Bond length (Å)	(bpym , S)	(bt , S)
Fe–N1	2.078(6)	2.069(14)
Fe–N2	2.051(7)	2.041(13)
Fe–N3	2.200(6)	2.239(12)
Fe–N4	2.211(6)	2.112(12)
Fe–N5	2.316(6)	2.195(13)
Fe–N6	2.223(6)	2.256(11)

rather satisfactory description of the iron(II) coordination core both in the HS and in the LS state of these compounds [8].

3.2

Magnetic Properties

3.2.1

Magnetic Behaviour at Ambient Pressure

The magnetic behaviour of this series at ambient pressure (10^5 Pa) is depicted in Fig. 5. As stated before, (**bpym**, S) does not display thermally-induced spin conversion, but exhibits intramolecular antiferromagnetic coupling between the two iron(II) ions through the bpym bridge ($J=-4.1$ cm $^{-1}$, $g=2.18$). When thiocyanate is replaced by selenocyanate the resulting (**bpym**, Se) derivative shows an abrupt spin transition in the 125–115 K temperature region with a small hysteresis loop of 2.5 K width (see Fig. 5). Only 50% of the iron(II) atoms undergo spin transition. The decrease of the $\chi_M T$ values at lower temperatures is due to the occurrence of zero-field splitting of the $S=2$ state (see below). The magnetic properties of (**bt**, S) and (**bt**, Se) are similar to one another and show a complete spin transition with the remarkable feature that it takes place in two steps centred at 197 and 163 K for (**bt**, S) and at 265 and 223 K for (**bt**, Se). In both cases, the plateau corresponds approximately to 50% spin conversion.

These macroscopic steps, also detected by means of Mössbauer spectroscopy and calorimetric measurements, were interpreted in terms of a micro-

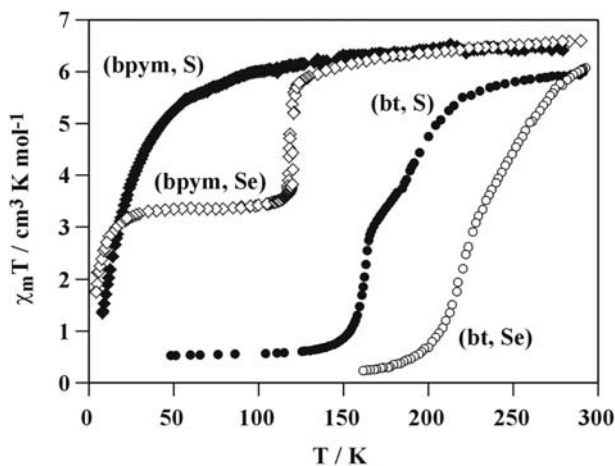


Fig. 5 Temperature dependence of $\chi_M T$ for $\{[\text{Fe}(\text{L})(\text{NCX})_2]_2(\text{bpym})\}$ (L=bpym and X=S (**bpym**, S) or Se (**bpym**, Se) and L=bt and X=S (**bt**, S) or Se (**bt**, Se)) (adapted from [4])

scopic two-step transition between the three possible spin pairs of each individual dinuclear molecule [7]:



The stabilisation of the [HS–LS] mixed-spin pair results from a synergistic effect between intramolecular and cooperative intermolecular interactions (see below).

3.2.2

Influence of Pressure on the Thermal Dependence of Magnetic Susceptibility

The pressure dependence of the thermal variation of $\chi_M T$ has proved to be a useful diagnostic probe to show that the formation of [HS–LS] spin pairs is not fortuitous but that they are the preferentially formed species in the dinuclear-type complexes [9]. It is shown next that application of external hydrostatic pressure can help to unravel features of this whole class of compounds, which usually can be revealed by variation of chemical composition.

It has already been shown that increase in hydrostatic pressure favours the LS state in mononuclear complexes [10], and there is no reason to expect different behaviour for dinuclear systems. Two members of the $\{[\text{Fe}(\text{L})(\text{NCX})_2]_2\text{bpym}\}$ family are particularly suitable candidates in this regard: (**bpym**, S) and (**bpym**, Se). Fig. 6 displays the thermal dependence of $\chi_M T$ at different pressures. At ambient pressure, and over the whole temperature range, (**bpym**, S) contains only the antiferromagnetically coupled [HS–HS] pairs (Fig. 6a). Coexistence of antiferromagnetic coupling and spin cross-over in (**bpym**, S) clearly follows from magnetic susceptibility measurements at $P=0.63$ GPa. When the pressure is increased to 0.63 GPa, a partial conversion from 100% [HS–HS] to 55% [HS–LS] species takes place. The incompleteness of spin conversion is due to the fact that at low temperatures the spin conversion is so slow that the HS state becomes metastable. Therefore antiferromagnetically coupled [HS–HS] pairs and [HS–LS] uncoupled pairs become co-existent in (**bpym**, S) at 0.63 GPa, as reflected in the thermal dependence of $\chi_M T$. Finally, for $P=0.89$ GPa the total conversion to [HS–LS] pairs is accomplished. It is worth noting that, at this pressure, (**bpym**, S) undergoes a similar $[\text{HS} - \text{HS}] \leftrightarrow [\text{HS} - \text{LS}]$ spin transition at $T_{1/2} \approx 150$ K to (**bpym**, Se) at ambient pressure. The effect of pressure on the thermal dependence of the spin state of (**bpym**, Se) seems to be a decrease in the degree of cooperativity (as can be seen from the more gradual $\chi_M T$ function as compared to that under ambient pressure) and a shift of $T_{1/2}$ towards higher temperatures for pressures lower than 0.45 GPa (Fig. 6b). For higher pressures, a second transition appears in addition to the former one, due to the onset of thermal ST in the second metal centre. Between 0.72 and 1.03 GPa a two-step ST function is observed.

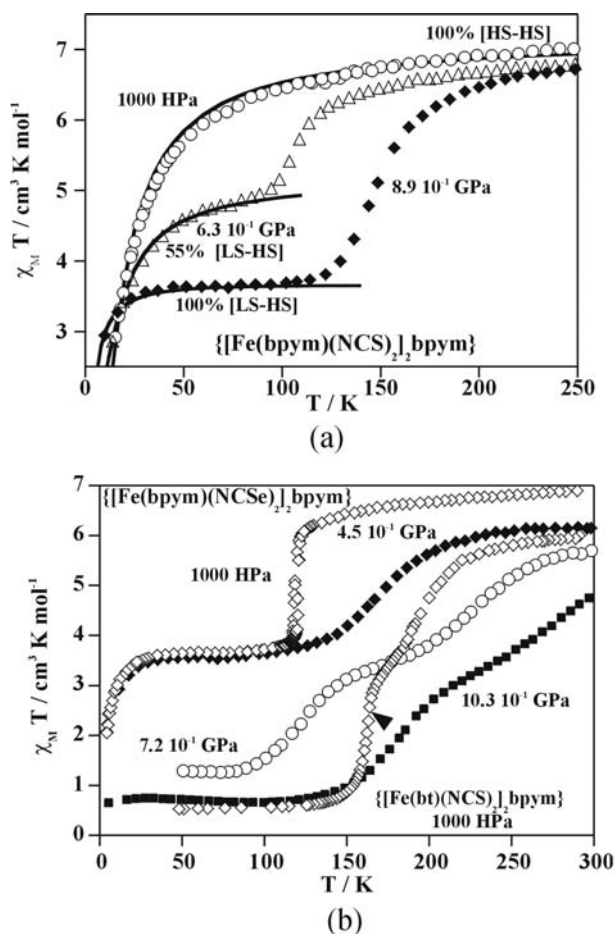


Fig. 6 Temperature dependence of $\chi_M T$ for $\{\text{Fe}(\text{bpym})(\text{NCS})_2\}_2(\text{bpym})$ at different pressures (a). The solid lines, together with estimated concentrations of [HS-LS] and [HS-HS] species, correspond to calculations using the appropriate Hamiltonian. Temperature dependence of $\chi_M T$ for $\{\text{Fe}(\text{bpym})(\text{NCSe})_2\}_2(\text{bpym})$ at different pressures (b). The magnetic behaviour of $\{\text{Fe}(\text{bt})(\text{NCS})_2\}_2(\text{bpym})$ at room pressure has been also included for comparison (adapted from [9])

As mentioned above, the particular characteristics of the spin crossover process in dinuclear compounds is the appearance of a plateau in the spin transition curve. From the analysis of the results of the pressure experiments, it is inferred that the plateau results from successive ST in the two metal centres, leading first to the formation of relatively stable [HS-LS] pairs and then, above a critical pressure, to the formation of [LS-LS] pairs on further lowering of the temperature. The intermolecular interactions between [HS-LS] pairs leads to domains that contribute to the stability of the

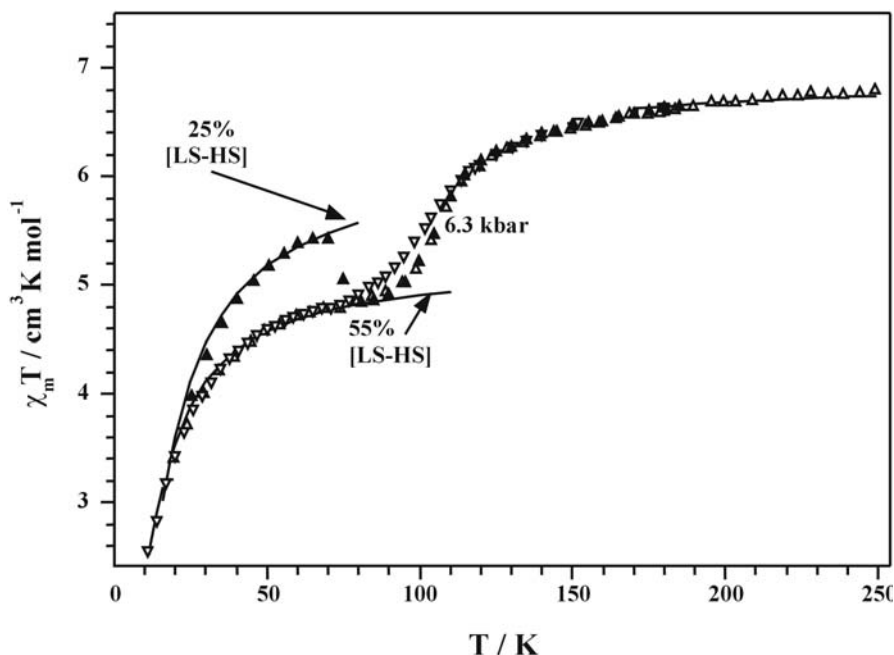


Fig. 7 Quenching experiment at 0.63 GPa: a sample of (**bpym**, **S**) was cooled from 300 K to 4.2 K with a cooling rate of ca. 100 K min⁻¹ and afterwards warmed up to 300 K at 2 K min⁻¹ (filled triangles). The subsequent warming (filled triangles) reveals that a substantial fraction of the HS centres do not convert into the LS state showing the occurrence of magnetic coupling in the additional [HS–HS] pairs. Thermal relaxation to the equilibrium state takes place at ca. 70 K

crystal lattice. Indeed, in the absence of intermolecular interactions, the increase of pressure should decrease the amount of the HS fraction. The pressure-induced low temperature state of (**bpym**, **S**), consisting almost entirely of the [HS–LS] units, is stable up to at least 1.1 GPa. For (**bpym**, **Se**), a pressure of 0.45 GPa shifts $T_{1/2}$ by ca. 50 K upwards without increasing the amount of the LS fraction. Only at higher pressures does the second step appear for this derivative. These experimental data underline the role of intermolecular interactions in the stabilisation of the hypothetical “chequer-board-like” structure consisting of [HS–LS] units as proposed by Spiering et al. [20].

In order to investigate the competition between magnetic interaction and spin transition in (**bpym**, **S**), quenching experiments have been performed at 0.63 GPa. Fig. 7 displays the magnetic behaviour of the quenched sample at increasing temperatures. It can be inferred from the thermal dependence of $\chi_M T$ that [HS–HS] entities can be frozen-in as a metastable state at low temperatures. Heating the sample above ca. 60 K leads to re-formation of

the stable state, which, in this temperature regime, consists mostly of [HS–LS] dinuclear species. Two main factors, namely antiferromagnetic intramolecular interactions and elastic interactions, are believed to play an important role in the stabilisation of the metastable state. Considering the low value of $J \approx -4.1 \text{ cm}^{-1}$ of the former in comparison with the decay temperature of $T \approx 60 \text{ K}$ and the unusually slow kinetics of the relaxation to the stable state, as compared to the relatively fast kinetics of spin transitions taking place at higher temperature, one can conclude that the relaxation is an essentially thermally-activated process and that the crystal lattice is substantially involved. It is the structural rearrangement, associated with the spin changing process, that is responsible for the trapping of the [HS–HS] metastable species and not the magnetic interactions. If the magnetic interactions were responsible, the dynamics of the relaxation to the stable state would be much faster. In other words, elastic interactions rather than magnetic coupling drive the transformations of $[\text{HS} - \text{HS}] \leftrightarrow [\text{HS} - \text{LS}]$ under pressure.

4

The Two-Step Character of the Spin Transition

The special feature of the spin crossover process in all bpym-bridged dinuclear compounds studied so far is the occurrence of a plateau in the spin transition curve. A reasonable assumption to account for this observation is that a thermal spin transition takes place successively in the two metal centres. However, it cannot be excluded that spin transition takes place simultaneously in the dinuclear units leading directly from [HS–HS] pairs to [LS–LS] pairs with decreasing temperature. Therefore, two possible conversion pathways for [HS–HS] pairs with decreasing temperature may be proposed: $[\text{HS} - \text{HS}] \leftrightarrow [\text{HS} - \text{LS}] \leftrightarrow [\text{LS} - \text{LS}]$ or $[\text{HS} - \text{HS}] \leftrightarrow [\text{LS} - \text{LS}]$. The differentiation of the existence of the [LS–LS], [HS–LS], and [HS–HS] spin pairs is not trivial and has recently been solved experimentally by utilisation of magnetisation versus magnetic field measurements as a macroscopic tool [9], and by Mössbauer spectroscopy in an applied magnetic field as a microscopic tool [11].

4.1

Magnetisation Experiments

The observation that $\chi_M T$ of (**bpym**, Se) is temperature-independent between 50 and 110 K and that no maximum in the susceptibility occurs at temperatures below 50 K suggests that no intramolecular antiferromagnetic coupling in pairs remains in this temperature regime. In fact the magnetisation curves [9] of (**bpym**, S) and (**bpym**, Se) at 1.9 K clearly indicate the different nature of the spin pairs involved in each compound in the ground state (Fig. 8).

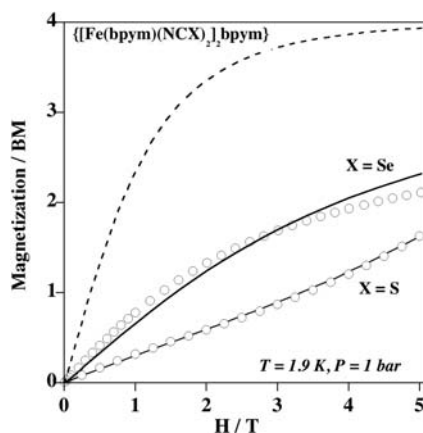


Fig. 8 Magnetisation curves of (bpym, S) and (bpym, Se) at $T=1.9$ K and ambient pressure. The theoretical curve (dashed line) was calculated from the Brillouin function for an $S=2$ ground state with $g=2$. The solid lines correspond to the fit of the experimental data considering the occurrence of zero-field splitting (bpym, Se) and zero-field splitting and magnetic exchange (bpym, S) (adapted from [9])

The M vs. H curve for (bpym, Se) varies linearly with H up to 8 kOe and then progressively tends to saturation. The experimental M values are smaller than the theoretical ones calculated with the Brillouin function for an $S=2$ ground state. In contrast, the magnetisation curve for (bpym, S) increases linearly as the field increases up to 30 kOe. In the range of 35–50 kOe, the slope of the M vs. H curve increases significantly. This effect is due to the crossing of the $M_s=0$ and $M_s=\pm 1$ microstates belonging to the ground and first excited states of the antiferromagnetically coupled [HS–HS] species, respectively. The solid lines represent the fit of the experimental M vs. H data corresponding to $D=|10| \text{ cm}^{-1}$ and $g=2.19$ for (bpym, Se), and $J=-4.1 \text{ cm}^{-1}$, $D=|8| \text{ cm}^{-1}$ and $g=2.2$ for (bpym, S). It follows then that the M vs. H curves allow the distinction between the different ground states [HS–LS] and [HS–HS] of (bpym, Se) and (bpym, S), respectively.

4.2

Direct Monitoring of the Spin State in Dinuclear Iron (II) Coordination Compounds

Previous attempts to distinguish between the different kinds of pairs by applying microscopic methods such as conventional Mössbauer spectroscopy were unsatisfactory, since the Mössbauer spectra corresponding to the HS state of the iron(II) atoms in the [HS–LS] and [HS–HS] spin pairs are indistinguishable. Zero-field Mössbauer spectroscopy applied to the bpym-bridged iron(II) dinuclear compounds only gives access to the total fraction

of HS and LS spin components, irrespective of the nature of the spin pairs involved. However, recently, it has been demonstrated that an unambiguous distinction of different pairs becomes possible if Mössbauer measurements are carried out in an external magnetic field [11].

The effective hyperfine field H_{eff} at the iron nuclei of a paramagnetic non-conducting sample in an external field H_{ext} may be estimated as $H_{\text{eff}} \approx H_{\text{ext}} - [220 - 600(g-2)]\langle S \rangle$ where $\langle S \rangle$ is the expectation value of the atomic spin moment and g the Landé splitting factor [12, 13]. The difference between the expectation values of S for the iron(II) atom in the LS and in the HS states in [HS–LS] and [HS–HS] pairs enables one to distinguish unambiguously between the dinuclear units consisting of two possible spin states in an external magnetic field. To do so, the strength of the external magnetic field should be sufficiently high, and the temperature sufficiently low, in order to avoid magnetic relaxation taking place within the characteristic time window of a Mössbauer experiment. Fig. 9 displays the Mössbauer spectra of (**bpym**, S), (**bpym**, Se) and (**bt**, S) recorded at 4.2 K in zero-field and at 50 kOe, respectively. The zero-field Mössbauer spectrum of the (**bt**, S) complex with only [LS–LS] pairs present at low temperatures shows the expected typical iron(II)–LS quadrupole doublet with isomer shift $\delta_{\text{LS}}(\text{bt}, \text{S}) = 0.19(1) \text{ mms}^{-1}$ and quadrupole splitting $\Delta E_{\text{Q(LS)}}(\text{bt}, \text{S}) = 0.43(2) \text{ mms}^{-1}$ at 4.2 K (Fig. 9a). In an applied magnetic field of $H_{\text{eff}} = 50 \text{ kOe}$, magnetic splitting is observed with a local effective field of $H_{\text{eff}} \approx 50 \text{ kOe}$ as is expected for $\langle S \rangle = 0$ of the [LS–LS] pair (Fig. 9b). The zero-field spectrum of (**bpym**, S) consisting of only [HS–HS] pairs is characterised by a typical HS doublet (Fig. 9c). The presence of an external magnetic field causes a slight broadening of the doublet lines (Fig. 9d). The value of the effective field, H_{eff} , calculated from this spectrum was 15 kOe. The difference between $H_{\text{ext}} = 50 \text{ kOe}$ and the observed field at the nucleus, H_{eff} , arises from the antiferromagnetic nature of the [HS–HS] pairs. In fact, the $\langle S \rangle$ value deduced from the corresponding partition function is around 0.5, which is consistent with the parameters $J = -4.1 \text{ cm}^{-1}$ and $g = 2.2$ for (**bpym**, S) at 4.2 K. The zero-field spectrum of the (**bpym**, Se) complex recorded at 4.2 K reflects the nearly “one-half” spin transition according to the area fractions of the HS (48.0%) and LS (52.0%) components with parameters $\delta_{\text{HS}} = 0.86(1) \text{ mms}^{-1}$, $\Delta E_{\text{Q(HS)}} = 3.11(2) \text{ mms}^{-1}$, and $\delta_{\text{LS}} = 0.22(1) \text{ mms}^{-1}$, $\Delta E_{\text{Q(LS)}} = 0.36(1) \text{ mms}^{-1}$, respectively (Fig. 9e). Measurements in a magnetic field of 50 kOe at 4.2 K reveal features which are not seen in the spectra of paramagnetic compounds in their ground states and may be interpreted as follows. The total spectrum consists of three components as can be seen in Fig. 9f. One of them with relative intensity $x = 52.0\%$ and with isomer shift and quadrupole splitting being equal to $\delta_{\text{LS}}(\text{bt}, \text{S})$ and $\Delta E_{\text{Q(LS)}}(\text{bt}, \text{S})$ is identified as the “fingerprint” of the LS state which has $H_{\text{eff}} \approx H_{\text{ext}}$. The second low-intensity ($y = 4.0\%$) broadened doublet with parameters $\delta_{\text{HS}}(\text{bpym}, \text{S})$ and $\Delta E_{\text{Q(HS)}}(\text{bpym}, \text{S})$ and $H_{\text{eff}} = 14 \text{ kOe}$, corresponds to iron(II) ions in antiferromagnetically coupled

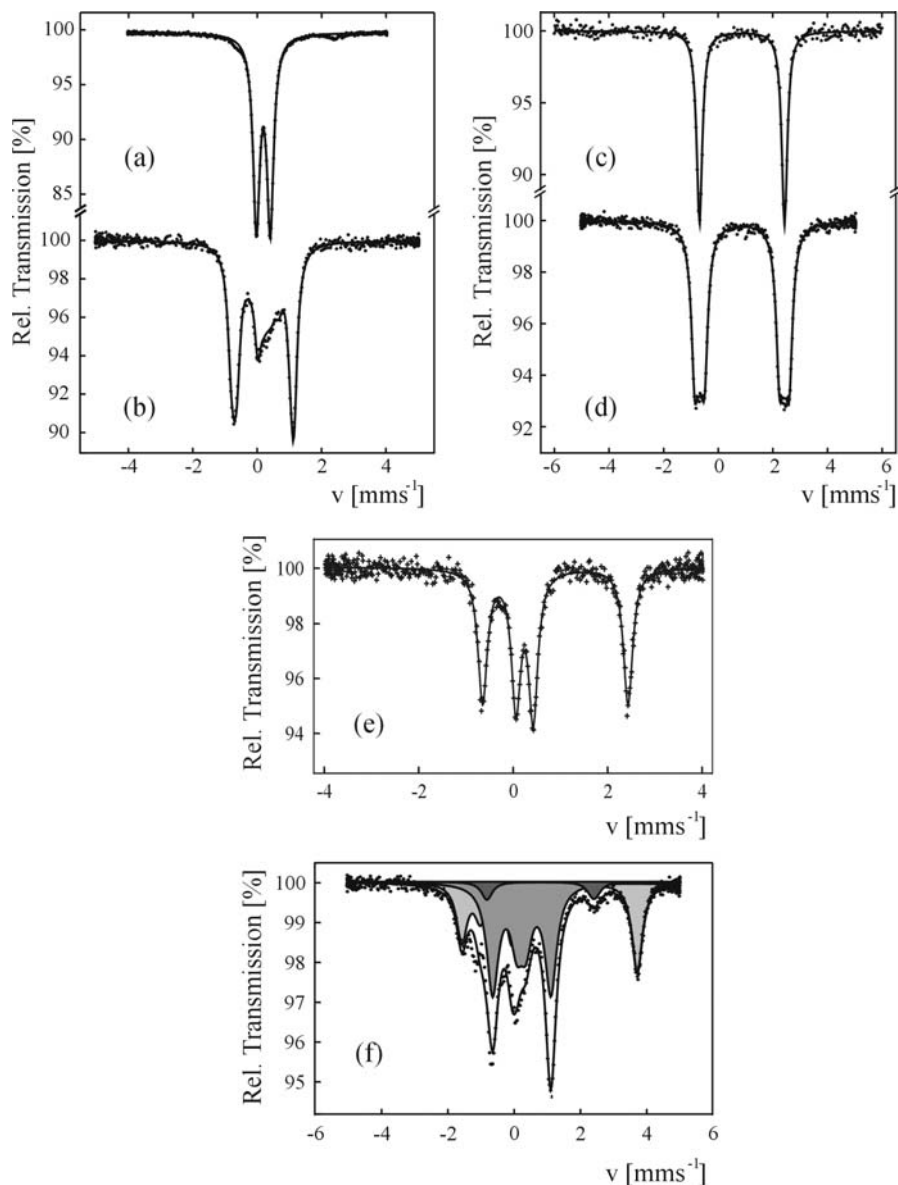


Fig. 9 ^{57}Fe Mössbauer spectra of (bt, S) recorded at 4.2 K in zero-field (a) and in a magnetic field of 50 kOe (b). ^{57}Fe Mössbauer spectra of (bpym, S) recorded at 4.2 K in zero-field (c) and in a magnetic field of 50 kOe (d). ^{57}Fe Mössbauer spectra of (bpym, Se) recorded at 4.2 K in zero-field (e) and in a magnetic field of 50 kOe (f). LS in [HS-LS] and [LS-LS] pairs (grey), HS in [HS-LS] pairs (light grey), HS in [HS-HS] pairs (dark grey) (adapted from [11])

[HS–HS] pairs. The third component (relative intensity $z=44.0\%$) with parameters $\delta_{\text{HS}}(\text{bpym}, \text{S})$ and $\Delta E_{\text{Q(HS)}}(\text{bpym}, \text{S})$ can be unambiguously assigned to the HS state in [HS–LS] pairs, because the measured effective magnetic field at the iron nuclei of 81 kOe clearly originates from a spin quintet ground state of iron(II) ($S=2$). As a result, the complete distinction of dinuclear units becomes possible. It follows from the area fractions of the subspectra intensities that at 4.2 K the sample (**bpym**, **Se**) contains $2z=88.0\%$ [HS–LS], $y=4.0\%$ [HS–HS] and $(x-z)=8.0\%$ [LS–LS] pairs.

The results from Mössbauer spectroscopy in applied magnetic fields clearly prove that the spin transition in the dinuclear compounds under study proceeds via $[\text{HS–HS}] \leftrightarrow [\text{HS–LS}] \leftrightarrow [\text{LS–LS}]$. Simultaneous spin transition in both metal centres of the [HS–HS] pairs converting the dinuclear pairs directly to [LS–LS] pairs can apparently be excluded, at least in the present systems. This is quite surprising in view of the fact that the present dinuclear complexes are centrosymmetric (in other words the two metal centres have identical surroundings, and should therefore experience the same ligand field strength and, consequently, thermal spin transition should occur simultaneously in both centres).

5

Photo-Switching of Spin Pairs

In 1984, Decurtins et al. discovered that the compound $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ ($\text{ptz}=1\text{-propyltetrazole}$) can be converted from the stable LS state to the metastable HS state by irradiation with green light at sufficiently low temperatures [14]. This phenomenon has become known as “light-induced excited spin state trapping” (LIESST) and is dealt with in detail by A. Hauser in a separate chapter in this series. Later, Hauser reported the reverse-LIESST effect, whereby red light is used to convert the compound back into the LS state [15].

Up to now, most of the spin crossover compounds exhibiting LIESST properties have been assemblies of monomeric units with through-space rather than through-bond interactions. A few years ago a form of synergy was pointed out between magnetic interaction and spin conversion in the presence of light in the (**bpym**, **Se**) and (**bt**, **S**) systems making use of the LIESST effect [11, 16]. In these compounds the corresponding ground states [HS–LS] and [LS–LS] were converted partially to the metastable [HS–HS] spin pair state by irradiation with light ($\lambda=514\text{ nm}$ or $\lambda=647\text{--}676\text{ nm}$). As a result, the magnetic properties of the former complexes after LIESST were found to be very close to those of (**bpym**, **S**). This is not unexpected considering the fact that the bridge in (**bpym**, **Se**) and (**bt**, **S**) is strictly the same as that of (**bpym**, **S**), and the interaction parameter, J , in a coupled dinuclear compound depends essentially on the nature of the bridging ligand.

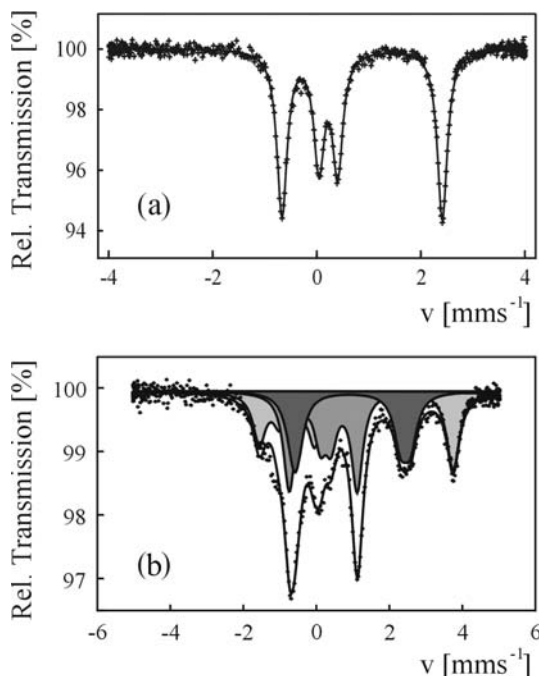


Fig. 10 ^{57}Fe Mössbauer spectra of (**bpym**, **Se**) recorded at 4.2 K in zero-field after irradiation of the sample (a) and in a magnetic field of 50 kOe (b). Mössbauer subspectra correspond to: LS in [HS-LS] (grey), HS in [HS-LS] pairs (light grey), HS in [HS-HS] pairs (dark grey)

According to the results of Sect. 4.2, the ground state of (**bpym**, **Se**) is made up of 48.0% HS and 52.0% LS species, which corresponds to 88.0% [HS-LS], 4.0% [HS-HS] and 8.0% [LS-LS] pairs. After irradiation of the sample for one hour at 4.2 K with light of $\lambda=514$ nm, the Mössbauer spectrum of the paramagnetic compound (**bpym**, **Se**) shows a decrease in the intensity of the LS species (41.0%) in favour of an increase of the HS species (59.0%) as is depicted in Fig. 10a. It was confirmed by Mössbauer experiments with samples of different thickness that irradiation affected not only the surface but also the entire bulk of the sample. The Mössbauer spectrum recorded subsequently in a magnetic field (Fig. 10b) consisted of three components with relative intensities $x=41.0\%$, $y=17.0\%$ and $z=42.0\%$. This indicates an increase of the amount of [HS-HS] pairs ($y=17.0\%$) with a simultaneous decrease of [HS-LS] ($2z=83.0\%$) and disappearance ($x-z\cong 0$) of [LS-LS] species. The expected and observed metastable HS species in the form of [HS-HS] pairs is a consequence of the light irradiation and proves the possible co-existence of magnetic coupling and spin transition in the same compound.

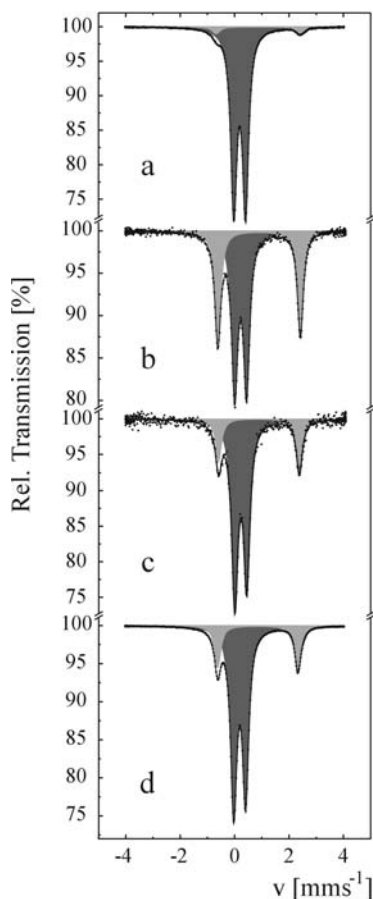


Fig. 11 ^{57}Fe Mössbauer spectra of (**bt**, **S**) recorded at 4.2 K in zero-field before irradiation (a), immediately after irradiation (b), 6 days (c) and 11 days (d) after irradiation. Mössbauer subspectra correspond to: HS species (grey), LS species (dark grey)

The main objective in carrying out LIESST experiments on (**bt**, **S**) was to elucidate the nature of excitations (metastable pairs) which appear at low temperatures after light irradiation of a ground [LS–LS] state. As is illustrated in Fig. 11a, at 4.2 K before irradiation the Mössbauer spectrum of a sample, which was enriched with 20% of ^{57}Fe , reflects the presence of mainly LS species. The Mössbauer parameters obtained from the fitting of the spectrum are: $\delta_{\text{LS}} = 0.357(1) \text{ mms}^{-1}$, $\Delta E_{\text{Q(LS)}} = 0.452(2) \text{ mms}^{-1}$. After irradiation of the sample for one hour ($\lambda = 514 \text{ nm}$) at 4.2 K, the Mössbauer spectrum of (**bt**, **S**) shows a decrease in the intensity of the LS species (62.0%) in favour of an increase of the HS species (38.0%) (Fig. 11b). Time-dependent measurements revealed the decay of the HS component (Fig. 11c, d), which

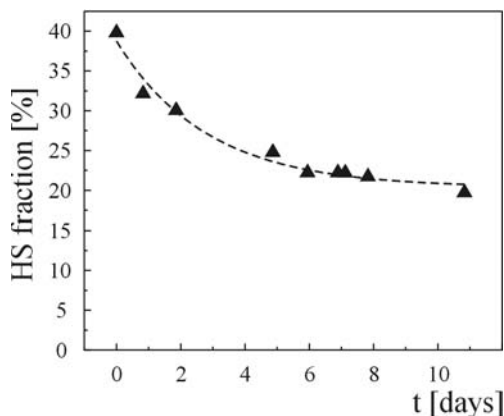


Fig. 12 Time dependence of the fraction of metastable HS molecules for (bt, S)

reached an asymptotic value of ca. 20% within ca. 10 days (Fig. 12). The Mössbauer measurements in a magnetic field of 50 kOe at 4.2 K allows the identification of the nature of the metastable states. As is shown in Fig. 13a, the total spectrum measured after irradiation consists of three components. One of them, with isomer shift and quadrupole splitting values being equal to $\delta_{\text{LS}}(\text{bt}, \text{S})$ and $\Delta E_{\text{Q}(\text{LS})}(\text{bt}, \text{S})$, is identified as the “fingerprint” of the LS state with $H_{\text{eff}} \approx H_{\text{ext}}$. The second low-intensity broadened doublet with parameters $\delta_{\text{HS}}(\text{bpym}, \text{S})$ and $\Delta E_{\text{Q}(\text{HS})}(\text{bpym}, \text{S})$ and $H_{\text{eff}} = 14$ kOe, corresponds to iron(II) ions in antiferromagnetically coupled [HS–HS] pairs. The third component, with parameter values close to $\delta_{\text{HS}}(\text{bpym}, \text{S})$ and $\Delta E_{\text{Q}(\text{HS})}(\text{bpym}, \text{S})$ is unambiguously assigned to the HS state in [HS–LS] pairs, because the measured effective magnetic field at the iron nuclei of 85 kOe clearly originates from a spin quintet ground state of iron(II) ($S=2$). From the time-dependent area fractions of the subspectra of the irradiated sample (bt, S) (Fig. 13a–d) one can derive the dynamics data of transformation of [HS–LS], [HS–HS] and [LS–LS] pairs (Fig. 14).

The important result of the LIESST experiments in (bt, S) is that the photoinduced species are not only [HS–LS] but also [HS–HS] pairs. The appearance of [HS–LS] species should be interpreted in terms of a synergy between intramolecular and intermolecular cooperative interactions which energetically stabilise the mixed pairs. However, the time dependent measurements (Fig. 14) reveal that [HS–HS] pairs are unstable and revert with time to both [HS–LS] and [LS–LS] configurations [17]. This observation is important in the comparative analysis of the two-step transition in (bt, S) (see Sect. 6).

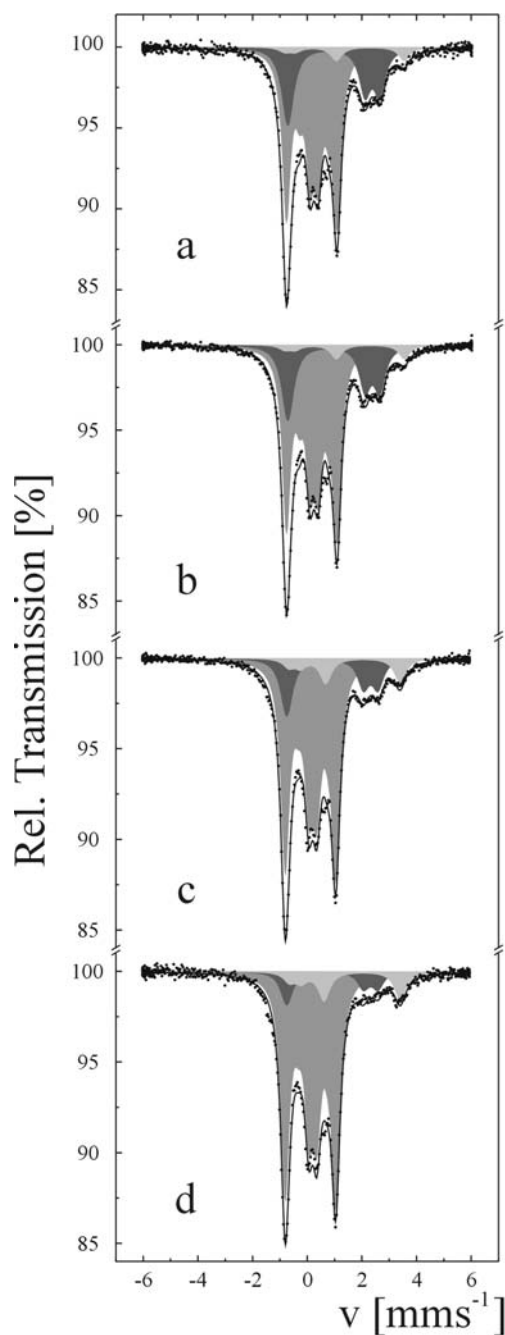


Fig. 13 ^{57}Fe Mössbauer spectra of (bt, S) at 4.2 K in a magnetic field of 50 kOe recorded after **a** 1 day, **b** 2 days, **c** 5 and **d** 6 days after light irradiation. LS in [HS-LS] and [LS-LS] pairs (grey), HS in [HS-LS] pairs (light grey), HS in [HS-HS] pairs (dark grey)

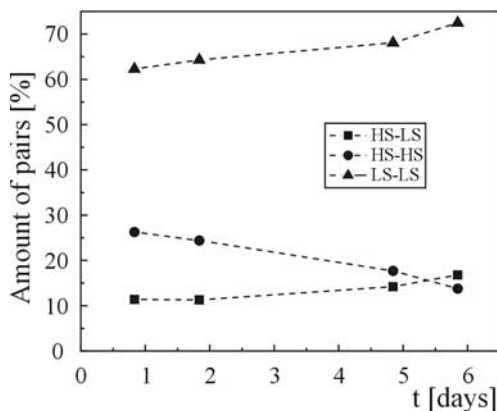


Fig. 14 Time dependence of the fraction of different pairs in (bt, S)

6

The Nature of the Plateau in the Two-Step Spin Transition

As discussed above, from the analysis of the pressure experiments it follows that the nature of the plateau of the two-step transition curve is most probably determined by the formation of [HS–LS] pairs. The application of Mössbauer spectroscopy in an applied magnetic field directly within the plateau region is not possible, because of the relatively high temperature region where the two-step transition takes place in the (bt, S) and (bt, Se) derivatives, $T_{1/2}(1)=197$ K, $T_{1/2}(2)=163$ K and $T_{1/2}(1)=265$ K, $T_{1/2}(2)=233$ K, respectively. The non-negligible thermal population of the upper energetic levels $S=4, 3, 2, 1$ in antiferromagnetically coupled [HS–HS] units yields a similar expectation value of $\langle S \rangle \cong 2$ for both [HS–HS] and [HS–LS] pairs, and consequently very similar values for H_{eff} . Thermal trapping of the species from the plateau region by quenching to helium temperatures would be necessary in order to apply the direct monitoring method as has been performed in (bpym, Se) (Sect. 4.2). However, attempts at thermal quenching from the relatively high temperatures at which the thermal spin transitions in the (bt, S) and (bt, Se) derivatives take place were unsuccessful. The problem did not arise, however, with the dinuclear compound $\{[\text{Fe}(\text{phdia})(\text{NCS})_2]_2(\text{phdia})\}$ (phdia: 4,7-phenanthroline-5,6-diamine) [18], which undergoes an almost complete two-step spin transition at much lower temperatures centred at $T_{1/2}(1)=108$ K and $T_{1/2}(2)=80$ K and accompanied by hysteresis loops of $\Delta T_{1/2}(1)=2$ K and $\Delta T_{1/2}(2)=7$ K, respectively (Fig. 15). This unusual two-step spin transition occurring at relatively low temperatures enables one to elucidate the nature of the species present in the plateau centred at $T_p \cong 100$ K. The composition of the plateau could be identified in a metastable state after quenching from 100 K directly to liquid helium temperature. The room tem-

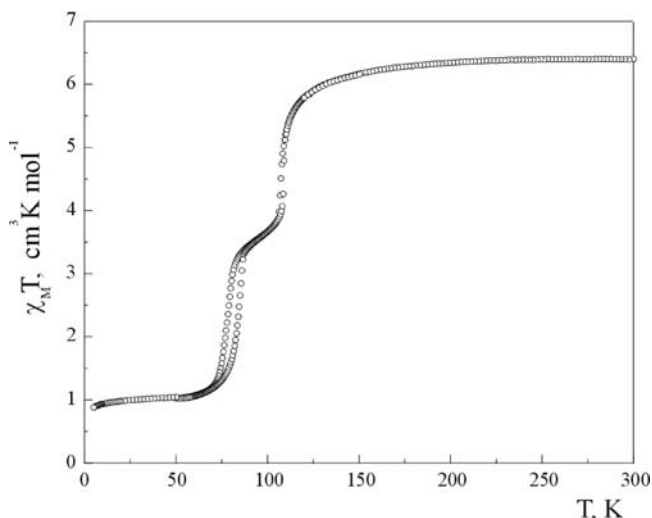
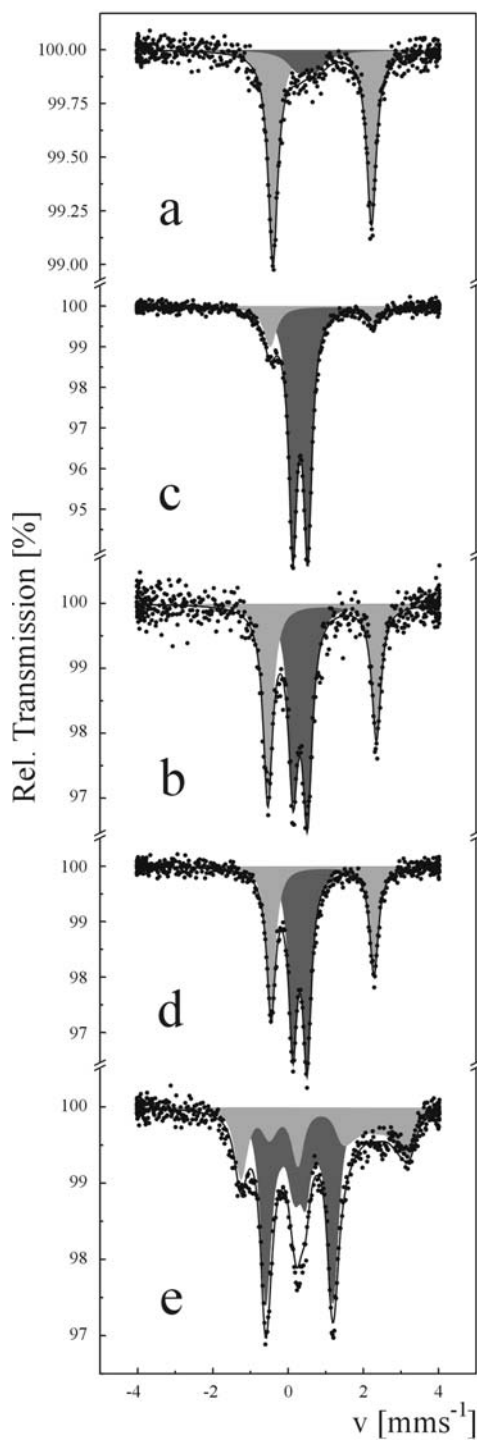


Fig. 15 Thermal dependence of $\chi_M T$ for $\{[\text{Fe}(\text{phdia})(\text{NCS})_2]_2(\text{phdia})\}$

perature Mössbauer spectrum is dominated by a HS doublet, but a LS doublet with relative intensity of ca. 16% is also present (Fig. 16a). The spectrum recorded at 100 K after subsequent slow (<1 K/min) cooling reveals 46.0% of HS and 54.0% of LS species (Fig. 16b). The Mössbauer spectrum recorded at 4.2 K after further slow cooling indicates 84.0% of LS and 16% of HS iron(II) species (Fig. 16c). Rapid cooling at a rate of 100 K/min from 100 K to 4.2 K allowed the trapping of the species existing in the plateau in the metastable state. The Mössbauer spectrum of the metastable state recorded at 4.2 K is essentially similar to that at 100 K with a slight increase of the LS component up to 58% (Fig. 16d). The spectrum in Fig. 16d proves that the thermal quenching was performed effectively. The application of a magnetic field of 50 kOe at 4.2 K revealed the nature of the metastable pairs which determine the plateau in $\{[\text{Fe}(\text{phdia})(\text{NCS})_2]_2(\text{phdia})\}$. The Mössbauer spectrum consists of two subspectra (Fig. 16e). One of them, with an effective value of the hyperfine magnetic field of 50.0 kOe, is the characteristic “fingerprint” of LS species in [HS–LS] and [LS–LS] pairs. The subspectrum with $H_{\text{eff}}=62$ kOe corresponds to the HS species in the [HS–LS] pairs. It follows from the area fractions of the subspectra intensities that the “quenched plateau” consists of 84% [HS–LS] and 16% [LS–LS] pairs. This result experimentally proves the validity of the hypothesis formulated by Real et al. [7], in which the [HS–LS] pair was proposed as an intermediate state in the $[\text{HS} \rightarrow \text{HS}] \leftrightarrow [\text{LS} \rightarrow \text{LS}]$ process instead of a direct spin state transformation. No [HS–HS] pairs have been found in the metastable state at low temperatures. It is therefore safe to conclude that at $T=100$ K the plateau in the transition curve of $\{[\text{Fe}(\text{phdia})(\text{NCS})_2]_2(\text{phdia})\}$ involves mainly [HS–LS] spe-



cies (92%) with the remainder corresponding to [LS–LS] pairs arising from the residual LS fraction detected at 300 K.

Important information relating to the intramolecular interaction in dinuclear units of $\{[\text{Fe}(\text{phdia})(\text{NCS})_2]_2(\text{phdia})\}$ can be drawn from the study of the LIESST effect at low temperature. The Mössbauer spectrum recorded at 4.2 K after slow cooling reveals 16.0% of HS and 84.0% of LS species (Fig. 17a). The spectrum recorded after the irradiation ($\lambda=488$ nm) of the sample for one hour at 4.2 K shows an increase of the intensity of the HS doublet up to 25.0% (Fig. 17b). The spectrum recorded subsequently in a magnetic field reveals no [HS–HS] pairs; it consists of 50.0% of [HS–LS] and 50% of [LS–LS] pairs (Fig. 17c). This is further evidence of the inherent stability of mixed pairs in $\{[\text{Fe}(\text{phdia})(\text{NCS})_2]_2(\text{phdia})\}$.

As was stated at the beginning of this chapter, Real et al. developed a theoretical model based on the above-mentioned hypothesis which satisfactorily explained the two-step character of the spin transition in (bt, S) [7]. In this model it is considered that the enthalpy, H , of the [HS–LS] pair does not correspond exactly to the average enthalpy of the [HS–HS] and [LS–LS] pairs: $H_{\text{HS-LS}} \neq [(H_{\text{LS-LS}} + H_{\text{HS-HS}})/2]$. It is inferred from calculations that the relation $H_{\text{HS-LS}} < [(H_{\text{LS-LS}} + H_{\text{HS-HS}})/2]$ is a necessary, but not sufficient, condition for the occurrence of a two-step transition. The authors concluded that a certain degree of cooperativity from the lattice is required as well. In other words, the two-step character of a transition arises from a synergy between the intramolecular interaction which energetically favours the mixed spin [HS–LS] pairs and the intermolecular interactions favouring the formation of domains consisting of dinuclear entities with identical spin state. The intramolecular interaction, originating from electrostatic and vibronic interactions, is characterized by the parameter $\rho = W/\Delta H$, where ΔH is the enthalpy difference between [HS–HS] and [LS–LS] spin states and W represents the energetic stabilisation of the [HS–LS] pair relative to the enthalpy average of the [HS–HS] and [LS–LS] states ($\Delta H/2$) (Fig. 18). The stronger the intramolecular interaction (the more negative the value of ρ), the more probable the formation of mixed pairs. In this model, a parameter Γ accounts for the intermolecular interactions. At $\rho=0$ a two step transition appears when $\Gamma=332$ cm⁻¹; for the plateau to exist when small intermolecular interactions are present, relatively large negative values of ρ are required. For the (bt, S) compound, good agreement between the experimental and



Fig. 16 ^{57}Fe Mössbauer spectra of $\{[\text{Fe}(\text{phdia})(\text{NCS})_2]_2(\text{phdia})\}$ at room temperature (a), at 100 K after subsequent slow cooling (<1 K/min) (b), at 4.2 K after further slow cooling (c), at 4.2 K after rapid cooling from the plateau with a rate of 100 K/min (d), at 4.2 K in a magnetic field of 50 kOe after quenching from the plateau (e). LS in [HS–LS] and [LS–LS] pairs (grey), HS in [HS–LS] pairs (light grey)

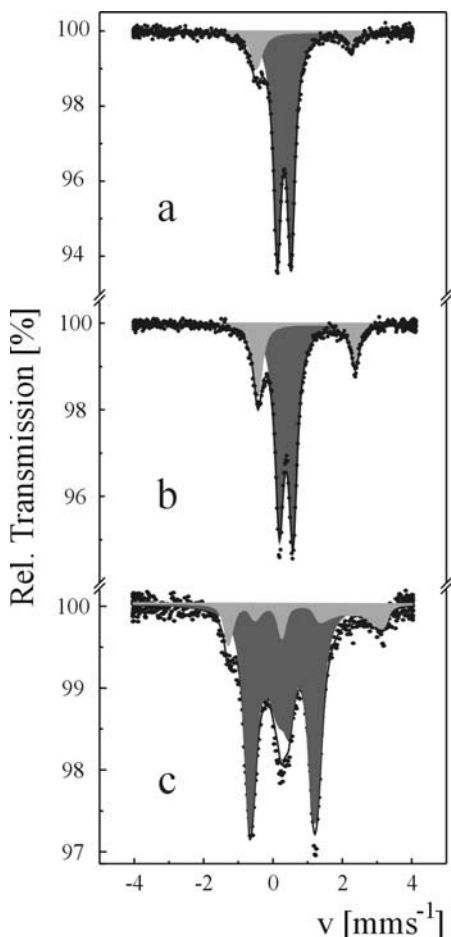


Fig. 17 ^{57}Fe Mössbauer spectra of $\{[\text{Fe}(\text{phdia})(\text{NCS})_2]_2(\text{phdia})\}$ at 4.2 K after slow cooling (<1 K/min) from room temperature (a), at 4.2 K after irradiation (b), at 4.2 K after irradiation in a magnetic field of 50 kOe (c). LS in [HS–LS] and [LS–LS] pairs (grey), HS in [HS–LS] pairs (light grey)

the calculated magnetic data has been obtained at $\Gamma=215\text{ cm}^{-1}$ and $\rho=-0.072$. An important result following from the fit of the magnetic susceptibility is that the plateau in (bt, S) comprises mainly of [HS–LS] pairs. The fraction of [HS–LS] pairs calculated in the middle of the plateau at $T_p \cong 180\text{ K}$ is approximately 70%. From theoretical considerations it follows that the plateau between the steps will be more pronounced with more negative ρ . This conclusion can be experimentally proved by analysing the nature of the metastable pairs, formed from the [LS–LS] ground state by light irradiation. LIESST experiments with the (bt, S) complex described in Sect. 5 re-

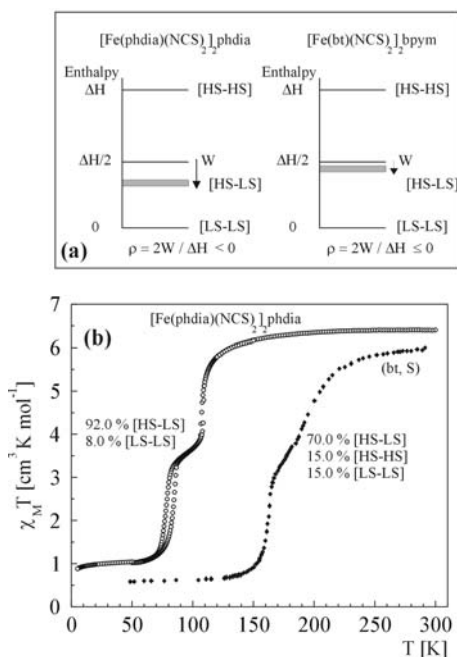


Fig. 18 Representative scheme of the enthalpy of [HS–HS], [HS–LS] and [LS–LS] pairs (a) and comparative magnetic behaviour of (bt, S) and $\{[\text{Fe}(\text{phdia})(\text{NCS})_2]_2\text{phdia}\}$ (b). The composition of the plateau region as a percentage of the pairs is indicated

vealed the appearance of both [HS–HS] and [HS–LS] pairs after light excitation of [LS–LS] pairs. This leads to the conclusion that the parameter ρ is close to zero. This result is in fair agreement with a value $\rho = -0.072$ obtained from magnetic experiments. On the other hand, LIESST experiments carried out on $\{[\text{Fe}(\text{phdia})(\text{NCS})_2]_2(\text{phdia})\}$ demonstrated the inherent stability of [HS–LS] pairs, and therefore a definitive negative value for the parameter ρ . The fact that the intramolecular interaction responsible for the stabilisation of mixed pairs in $\{[\text{Fe}(\text{phdia})(\text{NCS})_2]_2(\text{phdia})\}$ dominates the interaction in (bt, S), qualitatively explains the more extended plateau width in the two-step transition curve for $\{[\text{Fe}(\text{phdia})(\text{NCS})_2]_2(\text{phdia})\}$.

It is worth mentioning that the first stepwise thermal spin transition was observed in the mononuclear compound $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ (2-pic = 2-picolylamine) [19]. The origin of the step in this system, as was later explained by Monte Carlo simulation, lies in competition between short- and long-range interactions, favouring the formation of [HS–LS] species [20]. In the case of dinuclear compounds we have proved experimentally that the plateau of the two-step transition is due to the formation of [HS–LS] pairs. A combination of applied field Mössbauer spectroscopy, together with the LIESST effect, confirmed the inherent stability of the mixed pairs. The synergistic

effect between the intramolecular and intermolecular interactions confers the energetic stabilisation on this mixed spin state, gives rise to the plateau region of a two-step transition curve, and determines its width.

7

Conclusions

Spin crossover research in recent years has increasingly become focused on the design, synthesis and characterization of new materials with suitable physical properties that may ultimately lead to technical applications as sensors, molecular switches or storage devices. Spin state switching at the molecular level, induced by variation of temperature, irradiation with light, application of pressure or electromagnetic fields has been widely recognized as a promising and fundamental physical process. When this occurs along strong cooperative interactions in the solid state, the materials approach the ultimate goal of being suitable for application in devices.

Dinuclear iron(II) compounds of the type presented in this chapter play an important role in bridging the features of intramolecular magnetic interaction and thermal spin transition. The particular interest in exploring these systems has been twofold, gaining a deeper insight into the nature of the near-neighbour interactions within the interplay between these properties on the one hand, and on the other hand the hope that we can make use of this interplay to enhance the response signal in eventual applications. The former has certainly brought about a surprising result in that the thermal spin transition does not set in simultaneously in both iron centres, despite the fact that both have identical surroundings and therefore identical ligand field strengths in the antiferromagnetically coupled state. The model discussed in the last section does hold true, implying that the spin transition to the [HS–LS] pairs as an intermediate state rather than directly to the [LS–LS] pair is favoured by the gain of extra free energy beyond the average free energy of $[(H_{\text{LS-LS}} + H_{\text{HS-HS}})/2]$. It is, however, also likely that the spin transition in the first centre spontaneously induces some change in the bonding properties and/or the geometric environment of the neighbouring iron centre. As a consequence of such changes, the ligand field strength weakens to such an extent that thermal spin transition sets in at a lower temperature than in the first centre. As a result, one observes a more or less pronounced plateau in the spin transition function $\gamma_{\text{HS}}(T)$. Further experiments on other dinuclear SCO systems are underway to explore this phenomenon in more detail.

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Cooperativity in Spin Crossover Systems: Memory, Magnetism and Microporosity

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Abstract This review deals with spin crossover effects in small polynuclear clusters, particularly dinuclear species, and in extended network molecular materials, some of which have interpenetrated network structures. Fe(II)Fe(II) species are the main focus but Co(II)Co(II) compounds are included. The sections on dinuclear compounds include short background reviews on (i) synergism of SCO and spin-spin magnetic exchange (ii) cooperativity (memory effects) in polynuclear compounds, and (iii) the design of dinu-

clear SCO compounds using structural and ligand field concepts. Known examples of dinuclear compounds are reviewed and our new examples are described, these being based on hydrogen-bonded water to pyrazole ligand linkages. Incomplete (half) SCO transitions, due to HS–HS to HS–LS transformations, are commonly observed, with no thermal hysteresis. New and ground-breaking studies of microporous extended network $\text{Fe(II)(NCS)}_2(\text{py})_4$ -type systems reveal reversible host-guest systems which display reversible sorption/desorption of guest molecules and SCO behaviour that varies with exchange of the guests.

Keywords Spin crossover · Polynuclear · Magnetism · Cooperativity · Microporosity

Abbreviations

1,10-phen	1,10-Phenanthroline
2,2'-bipy	2,2'-Bipyridine
2-pic	2(Aminomethyl)pyridine (2-picolylamine)
4,4'-azpy	4,4'-Azodipyridine
bpb	1,4-Bis(4-pyridyl)butadiyne
bpp	2,6-Bis(pyrazol-3-yl)pyridine
bptz	3,6-Bis(2-pyridyl)tetrazine
bpym	2,2'-Bipyrimidine
bt	2,2'-Bi-2-thiazoline
btb	<i>p</i> -Bis((1,2,4)-triazole)benzene
btpa	N,N,N',N'-Tetrakis(2-pyridylmethyl)-6,6'-bis(aminomethyl)-2,2'-Bipyridine
btr	4,4'-Bis(1,2,4-triazole)
btzb	1,4-Bis(tetrazol-1-yl)butane
btzp	1,2-Bis(tetrazol-1-yl)propane
dca [−]	Dicyanamide ($\text{N}(\text{CN})_2^-$)
H ₂ bptz	3,6-Bis(2-pyridyl)-1,4-dihydrotetrazine
HC(pz) ₃	Tris(pyrazol-1-yl)methane
H ₂ fsaen	N,N'-ethylenebis(3-carboxysalicylalimine)
H-bonding	Hydrogen bonding
LIESST	Light-induced excited spin state trapping
LITH	Light-induced thermal hysteresis
<i>p</i> -MeOptrz	4-(<i>p</i> -Methoxyphenyl)-1,2,4-triazole
<i>p</i> -tol-trz	4-(<i>p</i> -Tolyl)-1,2,4-triazole
py	Pyridine
pypz	2-(Pyrazol-3-yl)pyridine
py-trz	4-(2'-Pyridyl)1,2,4-triazole
RT	Room temperature
<i>R</i> -trz	<i>R</i> -substituted triazole in 4-position
SCO	Spin crossover
tcm [−]	Tricyanomethanide ($\text{C}(\text{CN})_3^-$)
tmpdtne	1,2-Bis(N,N'-bis(2-pyridylmethyl)-1,4,7-triazacyclonon-1-yl)ethane
tpa	Tri(2-pyridylmethyl)amine

tpa'	(2-Pyridylethyl)bis(2-pyridylmethyl)amine
tvp	<i>trans</i> -1,2-Bis(4-pyridyl)ethene
2J	Exchange coupling constant ($-2J/S_1S_2$ Hamiltonian)
μ -X	Bridging group X
μ_{eff}	Effective magnetic moment
μ_B	Bohr magneton
χ	Molar magnetic susceptibility
1-D	One-dimensional
2-D	Two-dimensional
3-D	Three-dimensional
k	Boltzmann constant
ΔE°	Difference in energy
Δ	Octahedral ligand-field splitting (10Dq)
B	Racah parameter for interelectronic repulsion
$T_{1/2}$	Transition temperature (at 50% HS, 50% LS)
HS	High-spin
LS	Low-spin

1 Introduction

Our interest in spin-crossover complexes goes back many years, with emphasis at the time being on ligand-field effects, magnetic anisotropy, spin states and spin crossover (SCO) in mononuclear iron(III), d^5 , and cobalt(II), d^7 , Schiff base chelate complexes [1–3]. In the last five or so years our interests have turned more towards molecule-based magnetic materials of the coordination-cluster or coordination-polymer types [4]. The two ‘magnetic’ sub-classes of such compounds are those displaying long-range magnetic order [5] and those displaying spin crossover, with or without magnetic exchange coupling. The latter sub-class forms the basis of this review and the coexistence and/or synergism of SCO and exchange-coupling in polynuclear clusters or extended networks is of particular interest, not only to us [6], but to other groups, some of which contribute to this volume [7–9]. Some of the first studies of SCO in small di- or trinuclear clusters were those on Fe(II)_2 by Real et al. [10] and on Fe(II)_3 by Reedijk et al. [11] while, more recently, tetranuclear 2×2 ‘grid’ Fe(II)_4 species have been investigated by Breuning et al. [12]. Extended polynuclear compounds, particularly those containing bridging triazole or tetrazole groups with 1-D, 2-D or 3-D dimensionalities have been studied by the groups of Kahn [13], Lavrenova [14], Haasnoot [15], Gülich [16] and Rudolf [17], and thermal hysteresis accompanied by thermochromism has been observed at room temperature in some cases. SCO in extended interpenetrated networks was first reported by Real et al. [18] and two-connecting di-pyridyl type ligands were employed. Our inter-

ests in the magnetic order in such extended networks [19] led us to contemplate synthesizing molecular networks containing Fe(II) or Co(II) SCO centres in which magnetic exchange or even magnetic order could also play a part, depending upon such factors as the nature of the bridging ligand, the M–M separation and the metal-ligand orbital overlap.

A new facet of SCO research, in part based on supramolecular chemistry concepts and on CJK's experience and interest in porosity in crystalline molecular networks [20], is that of using the reversible absorption of guest molecules into the channels of the host, in order to switch on, or off, the SCO process. Perturbations such as heat, light (LIESST) and pressure, described elsewhere in this volume, are well known methods of initiating SCO. The more subtle supra- or inter-molecular solid-state effects of solvate molecules, nature of anion, H-bonding and π - π Van der Waals' interactions often also play a key role, sometimes not clearly defined, and often difficult to control in design and synthesis. This new area of SCO in micro- or nanoporous host lattices forms the basis of Sect. 4 of the review. It will be seen that the fine tuning of the SCO "switch" in such materials is sensitive to H-bonding interactions between host framework and exchangeable guest molecule, and to subtle structural changes in the framework, changes which are not enough to lead to collapse or disruption of the structure, a common occurrence in molecular crystals. As in many solvated metal-complex species, the stability of such crystalline phases under normal atmospheric conditions varies greatly. Therefore, with possible applications in molecular sensing, molecular switching, data storage, displays and other electronic devices in mind, the physical and chemical stability (and/or encasement) of these materials will ultimately need to be improved, as will the spin-transition temperature (up to RT) and cooperativity (hysteresis) behaviour.

Cooperativity achieved by the direct linkage of spin crossover sites in crystalline materials leads to a number of interesting features and future possibilities. Structural/electronic cooperativity will sometimes give bistability; in other words the occurrence of abrupt spin transitions accompanied by thermal hysteresis. Magnetic exchange combined with SCO might ultimately lead to spin-crossover magnets. Structural cooperativity within extended networks will yield robust guest-exchange systems. Some recent developments in these aspects of cooperativity are now described. The review is not meant to be exhaustive and so we apologize to those whose work, relevant to these topics, is not cited.

2 Dinuclear SCO Compounds

2.1 Synergism of Spin Crossover and Spin-Spin Exchange Coupling

Three sub-classes of dinuclear SCO compounds can be envisaged. At one extreme, a dinuclear complex (such as Fe(II)Fe(II), Fe(III)Fe(III) or Co(II)-Co(II)) can be designed in which the exchange-coupling will be zero or close to zero. In other words, the value of $2J$, the exchange splitting, will be very small. Therefore SCO on one, or both, metal centres will be the only effect occurring. Such complexes could, for instance, be designed to have no covalent bridging ligand joining the metal ions, leading to no superexchange pathway. One example is an ethane-strapped 2-pyridylmethyl-bis-triazacyclononane system $[\text{Fe}^{\text{II}}_2(\text{tmpdtne})(\text{NCS})_2](\text{ClO}_4)_2$ [21], which, surprisingly perhaps, showed not only no exchange but also no SCO and remained HS-HS at all temperatures, with μ_{eff} per Fe of $5.42 \mu_{\text{B}}$. The Fe-Fe distance was $6.74 \text{ \AA}$. Such designs need to make sure that inter-cluster coupling is zero or weak if intra-cluster cooperativity between the two SCO centres is being investigated. Toftlund has recently discussed the tactics needed to design double-crossover dinuclear systems [22] and is presently investigating dinuclear bipy-linked tri(pyridyl)methylamine (bpta) systems for comparison with the well-known SCO in $\text{Fe}^{\text{II}}(\text{tpa})(\text{NCS})_2$ [23] and the lack of SCO in a mononuclear bpta complex [24] (see also the chapter by Toftlund and McGarvey).

The next class is one in which exchange-coupling is very weak, but measurable (for instance by magnetic studies on HS-HS analogues), and in which SCO on one or both M(II) centres dominates. The best-studied Fe(II)-Fe(II) example is that by Real et al. [7] which contains a covalent-bridging bipyrimidine ligand, one well-studied in d-block cluster compounds for its ability to transmit weak antiferromagnetic exchange coupling (see the chapter on bipyrimidine-bridged dinuclear iron(II) spin crossover compounds by Real et al.). Recently, Ksenofontov et al. have employed applied-field Mössbauer spectroscopy to distinguish antiferromagnetic coupling in the microstates HS-HS, HS-LS and LS-LS [25] which relies fundamentally on very small hyperfine splitting in the antiferromagnetically coupled $S=0$ pair states [26]. LIESST and susceptibility studies have also distinguished $S=0$ (HS-HS) states from $S=0$ (LS-LS) states [9]. While Fe(II)Fe(II) species are restricted to HS-HS states in revealing the size of the exchange coupling, via susceptibility measurements (the LS state is diamagnetic, except for a second-order Zeeman contribution), Fe(III)Fe(III) and Co(II)Co(II) compounds can potentially exhibit the following exchange coupling contributions between SCO microstates: HS-HS, HS-LS, LS-LS. The HS-LS coupling will yield a non $S=0$ ground state, discernable by magnetic, EPR or Mössbauer effect studies at low temperature. The timescale (dynamics) of the

SCO will also play an important, although as yet unknown role. In some pyridazine-bridged Co(II)Co(II) complexes, Brooker et al. [6] observed the coexistence of the HS $\leftrightarrow$ LS SCO and LS-LS(1/2:1/2) exchange coupling by use of $\chi(T)$ studies. Contributions from HS-HS and HS-LS exchange coupling could not be distinguished [6]. Further details are given in Sect. 2.

The final sub-class is one in which medium to strong antiferromagnetic (or ferromagnetic) coupling occurs mediated by a covalent bridge. It is likely that SCO on the two M centres will not be observable [22] although this has yet to be tested. Relationships (synergism) between intra-cluster exchange coupling and intracluster SCO cooperativity (see below), the latter yielding thermal hysteresis loops, have also yet to be tested in detail. Distinguishing intra- from inter-cluster cooperativity effects in solid samples is also not a trivial exercise, especially if H-bonding or other Van der Waals' interactions link the clusters.

The brief summary given above for dinuclear SCO complexes is essentially the same for tri- and tetranuclear SCO compounds, although the latter two will have a greater number of thermally-accessible coupled spin states when exchange coupling is significant.

2.2

Cooperativity in Crystalline Polynuclear SCO Compounds

Cooperativity in solid state mononuclear SCO compounds has been described in detail [16, 27] and theoretical models have been developed to simulate the spin crossover curves (for example of magnetic moment or γ_{HS} vs. temperature) and evaluate thermodynamic parameters [27]. Experimentally, cooperativity is reflected in abrupt (steep) SCO transitions, in which thermal hysteresis loops or two-step transitions can be readily detected. In gradual (broad) SCO the cooperativity is diminished and steps cannot always be detected. Cooperativity in the solid state essentially derives from electron-phonon coupling between the molecules undergoing SCO and the consequent long-range elastic interactions within the crystal lattice [27]. The chapter of this volume by Spiering gives quantitative details of this model. Experimental proof of cooperativity has been provided by microcalorimetric studies, metal (Zn(II)) dilution experiments, relaxation of the decay of optical bands in LIESST experiments, and hysteresis in LITH experiments [16].

In the case of polynuclear metal cluster SCO complexes in the solid state, there will be intra-cluster, as well as inter-cluster cooperativity. To eliminate inter-cluster effects totally, studies must be made in dilute solutions. Williams et al. have done just this for a dinuclear [Fe(II)₂L₃] helicate complex which does not contain a good superexchange pathway between the Fe(II) centre but, rather, three flexible bis-bidentate ligands. A very broad, two step, SCO was observed (LS-LS $\leftrightarrow$ LS-HS $\leftrightarrow$ HS-HS) and fitted to a model for negative cooperativity in which subtle structural changes around each Fe oc-

cur [28]. Piguet et al. [29] used related {bidentate-tridentate} podate ligands to form heterobimetallic species $[\text{LnFeL}_3]^{5+}$ in which SCO in the Fe(II)N_6 compartment occurred, in MeCN solution, with a $T_{1/2}$ of 340 K. Tuning of the σ and π -bonding effects (see Sect. 2.3.2) was important, but the lanthanide ion played only a minor role in SCO.

Distinguishing intra- from inter-cluster cooperativity in the solid state is very difficult. Indeed, the question remains as to how small the cluster must be to observe intra-cluster cooperativity in solids. Other important factors such as the design and rigidity of bridging ligands and of coordination spheres in the dinuclear molecule are discussed below. Two examples are briefly mentioned; the first, by Real et al. [7] deals with bipyrimidine-bridged compounds of type $(\text{NCX})_2(\text{L})_2\text{Fe}(\mu\text{-bpym})\text{Fe}(\text{L})_2(\text{NCX})_2$ (see the chapter by Real et al for details). The two “macroscopic” steps observed in the χT (or γ_{HS} from Mössbauer) vs T plots for $\text{X}=\text{S}$, $\text{L}=\text{bithiazoline}$ reflect the “microscopic” two SCO steps ($\text{LS}-\text{LS} \leftrightarrow \text{LS}-\text{HS} \leftrightarrow \text{HS}-\text{HS}$) occurring in the dinuclear molecules. An Ising-like magnetic exchange model in the mean-field approach was employed to simulate the two-step curve. Short-range intra-cluster and long-range inter-cluster interactions were both found to be important, the former exhibiting negative cooperativity and favouring the LS-HS species [7, 30].

The second example is the 2×2 Fe(II)_4 grid complex of Breuning et al. [12] formed by self-association of four bis-tridentate pyrimidino-bipyridine ligands and four Fe(II) ions. The very broad increase in χT between 30–300 K suggests a non-cooperative one-step SCO transition. However, Mössbauer spectral studies, made under light irradiation of the sample, demonstrated a LITH effect. This indicated that cooperativity among the four Fe(II) centres was occurring via a multistep SCO process, but it was not observable, perhaps due to structural disorder of anion and solvates [12]. Long-range inter-cluster interactions were thought to oppose short-range intra-cluster interactions in this Fe(II)_4 system. Another possibility is that once one Fe(II) site crosses over, this prevents the others from doing so, for steric or electronic reasons.

Polymeric (1-D, 2-D, 3-D) network systems displaying SCO have been proposed by Kahn [31] and Real [7] to yield stronger cooperativity between the covalently-bridged Fe(II) centres than is the case in crystalline mononuclear species in which weak, intermolecular (H-bonding, Van der Waals', π - π stacking) interactions predominate. Of course, these weaker interactions may also occur between chains or sheets of SCO centres. Therefore, this area of SCO research is receiving great interest, as indicated later in Sect. 4, since strong cooperativity would be expected to lead to thermal hysteresis loops (bistability), preferably at RT, and ultimately to the development of useful devices which depend upon colour changes or related changes. These, as yet, little-developed polymeric systems vary greatly in their cooperativity/hysteresis behaviour, which could relate to many factors, both intra- and in-

ter-chain (inter-network) in origin, such as the rigidity/flexibility of the bridged Fe(II) centres along a chain or net. It has been argued that covalent (conjugated) bridging in a chain or network will enhance cooperativity between each SCO centre through the efficient distribution of molecular distortions occurring during SCO [16, 31]. The metal-ligand geometry at each Fe centre must change i.e. shorten the Fe^{II}–N lengths as HS→LS. We contend that this may well occur more readily if the bridging (linking) and terminal groups are flexible rather than rigid.

The triply-1,2,4-triazole bridged chain compounds of type [Fe^{II}(R-trz)₃](anion)₂ yield abrupt SCO transitions and wide thermal hysteresis loops ($\Delta T=35$ K) spanning room temperature [13, 17, 32] (see the chapter by Garcia et al for details). Unfortunately no crystal structure is yet available, at any temperature, although the structure of the Cu derivative is known [33]. The bridging structure is quite rigid. Therefore cooperativity is strong but a full explanation for this is lacking. In contrast, the 2-D bis-triazole derivative *trans*-[Fe(btr)₂(NCS)₂].H₂O has a somewhat more flexible bridging structure, and shows an abrupt SCO with a hysteresis width of 21 K [34]. H-bonding and Van der Waals' forces connect the layers and these will contribute to intermolecular cooperativity. Removal of water led to the compound being HS. The 3-D complex [Fe(btr)₃](ClO₄)₂ shows a two-step SCO with a small hysteresis on the abrupt low temperature step and none on the more gradual transition at higher temperature [35]. Crystal structures at the three plateau regions revealed two distinct Fe(II) sites and details on their spin states. Van Koningsbruggen et al. have also discovered quite different cooperativity in 1-D and 3-D polymeric structures of types [Fe(btzp)₃](ClO₄)₂ and [Fe(btzb)₃](ClO₄)₂, respectively; the former, containing an *i*-propyl-linked ditzazole ligand with Fe–Fe distance of 7.3 Å, gives a very gradual SCO with no hysteresis [36]. The latter, containing the longer *n*-butyl-bridged ditzazole and a probable interpenetrated network structure, gives a sharp, incomplete SCO with hysteresis width of 20 K, but only some of the Fe(II) sites undergo SCO [37]. The authors realized the limitations of a model relating cooperativity to covalent-bridging type, Fe–Fe distance and consequent elastic interactions (see the chapter by van Koningsbruggen).

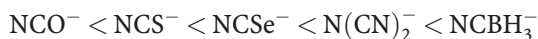
The 2-D and 3-D interpenetrated network systems *trans*-[Fe(tpv)₂(NCS)₂].*x*CH₃OH [7, 18] and *trans*-[Fe(bpb)₂(NCS)₂].0.5CH₃OH [38] contain 2-connecting di-pyridyl ligands with different distances and rigidity between the *p*-pyridyl rings. The tpv complex shows sample dependency in the amount of residual high- and low-spin fractions, and in the slopes of the magnetic moment versus temperature plots for $S=0 \leftrightarrow S=2$ SCO, these being gradual in character. The bpb complex shows a gradual 'half' SCO. Both systems yield no thermal hysteresis, nor does the Fe₂(azpy)₄(NCS)₄ network described later in Sect. 4. The conclusion for this small number of polymeric di-pyridyl-linked network species is that cooperativity is minimal, and we have suggested [39] that their flexibility may facilitate a low-energy pathway

between the HS and LS structures in the appropriate temperature range. Apart from the triazole-bridged chain species $[\text{Fe}^{\text{II}}(\text{R-trz})_3]^{2+}$, it is therefore not possible, at this point, to conclude that covalent-bridging between Fe(II) SCO centres in polymeric compounds will lead to enhanced cooperativity. Qualitatively, there appears to be a bridge-dependence of the cooperativity. The recent work on 2-D and 3-D Hofmann type CN-bridged materials $[\text{Fe}^{\text{II}}(\text{L})\text{M}(\text{CN})_4]\text{xH}_2\text{O}$ (L=pyridine or pyrazine) [40, 41] shows larger hysteresis widths occurring (up to 33 K in 3-D species) than in di-pyridyl-bridged systems and similar to those in the tri-bridged triazoles. Crystallographic phase transitions occur, as well as SCO, in some of the Hofmann phases. Inter-chain and cation-anion effects have yet to be fully defined by crystallography in the triazole bridged 1-D systems.

2.3

Design of Dinuclear (and Polynuclear) SCO Compounds

In their recent review, Gütlich et al. [16] point out that an unambiguous predictive method for designing a new mononuclear SCO complex of Fe(II) is still not available. Experience has led to “rules of thumb” in choosing the successful combination of ligands which will yield the SCO ligand-field around Fe(II), and these are generally aromatic heterocyclic N-donors (pyridyls, triazoles, tetrazoles), either as unidentate ligands or as bi- or tridentate chelating ligands, often in combination with unidentate N-bonded NCX[−] ligands (X=S, Se). “Fine tuning” of the $\{\text{FeN}_6\}$ ligand-field is often required if the SCO condition is not obtained at first attempt. Strategies that are commonly used include (i) incorporation of substituents on to the ligand to induce structural or electronic (such as σ -donor) changes which influence the spin-state, (ii) replacement of six-membered chelate rings by five-membered rings, reducing σ -donor and π -acceptor properties of the ligand, (iii) replacement of conjugated, heterocyclic donor systems by aliphatic-linked donors (the best examples are substitution of 2-pyridyls by amino-methyl groups, for instance in $[\text{Fe}^{\text{II}}(2\text{-picolylamine})_3](\text{anion})_2$ [42], or by 2-pyridyl-methyl arms such as in tpa (for example $\text{Fe}^{\text{II}}\text{tpa}(\text{NCS})_2$) and related multi-dentate chelates [43]), and (iv) variation of the X group in mixed-ligand systems of type *cis*- $\text{Fe}(\text{N-N})_2(\text{NCX})_2$. For the latter, the strength of the ligand-field increases in the following order:



and CN[−] is much stronger (see chapter by Toftlund and McGarvey).

In crystalline SCO complexes the influence of anions, solvate molecules, H-bonding effects and other intermolecular interactions will also influence the nature of SCO and the cooperativity, as has been discussed above.

With these limitations in mind for mononuclear species, the successful design of di- and polynuclear SCO compounds is even more of a challenge.

Even if one can create the SCO ligand-field around one end of a covalently-bridged dinuclear complex, the SCO might influence the ligand-field at the other end. There are many inter-dependent effects to bear in mind of a bonding, electronic and structural kind, and attempts to delineate these are given below. Inter-cluster or inter-chain effects will play difficult-to-control roles in crystalline SCO polynuclear materials, and these have already been alluded to for mononuclear complexes.

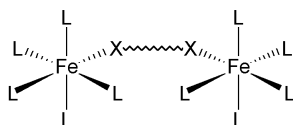
2.3.1

Structural Aspects

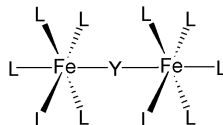
The general dinuclear structural motifs are of the weakly linked, 1, or covalently-bridged, 2, types shown in which



is a long, non-conjugated ligand, possibly chelating at each Fe(II). Y is a covalent-bridge, possibly mono-atomic but commonly multi-atomic and conjugated and usually chelating at each Fe.



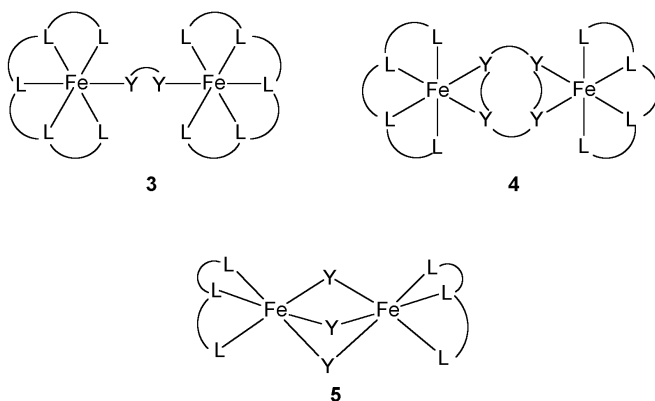
1 ; Weakly linked



2 ; Covalent-bridging

As indicated earlier, type 1 structures will usually lead to zero or weak intra-molecular exchange coupling, while type 2 may lead to weak to strong exchange coupling. The L ligands are defined as the “terminal”, “end” or “capping” groups, and these can have monodentate/chelating combinations. Structural and/or optical isomerism will occur in dinuclear systems containing chelating combination. These are well-recognized and separable in $\text{Ru}^{\text{II}}\text{Ru}^{\text{II}}$ compounds [44–46] but not, at this stage of development, in the more labile $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$, $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}$ or $\text{Co}^{\text{II}}\text{Co}^{\text{II}}$ combinations. The RuRu compounds can be prepared by sequential $\text{L}_4\text{Ru}(\text{bridge}) + \text{RuL}_4$ chemistry. Mixed $\text{Ru}^{\text{II}}\text{Fe}^{\text{II}}$ species are desirable but, as yet, unknown.

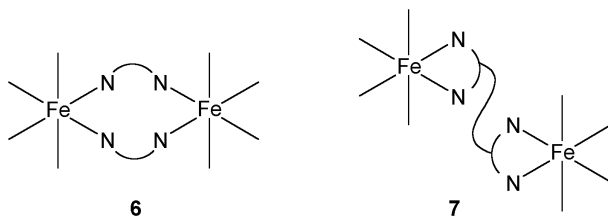
Some years ago, in attempting to expand the small number of known dinuclear SCO compounds of type 2, the known ones being the μ -bipyrimidine $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ compounds of Real [7], we envisaged ligand combinations of the following types: 3, bis-unidentate bridge (or single-atom) bridge plus pentadentate (or other combination) terminal ligands; 4, bis-bidentate bridge plus tetradentate (or other combination) of terminal ligands; 5, bis-tridentate or (three single-atom) bridge(s) plus tridentate (or other combination) of terminal ligands.

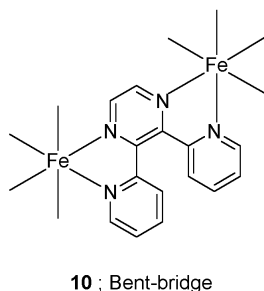
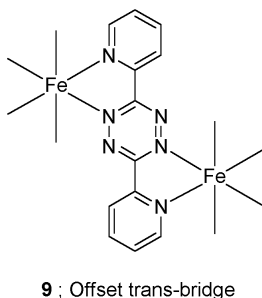
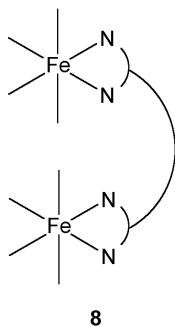


The μ -bipyrimidine compounds are of type 4. Our attempts to obtain new SCO species have also, to date, largely concentrated on type 4, some of which are described below. We were particularly gratified to see a recent successful example of type 3, isolated by Real et al. [47] using the YY bridging groups dicyanamide $(\text{NC-N-CN})^-$ and terminal $(\text{N})_5$ chelator of the Toftlund type [48]. Some details are given later.

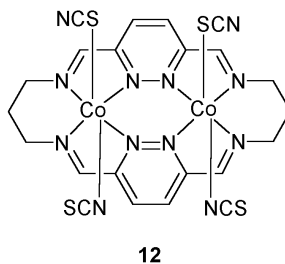
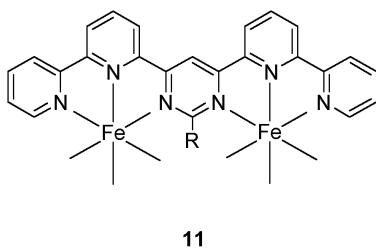
Compounds of structure 5 have yet to be realized but terminal tridentates of the tris(pyrazolyl)hydridoborate [49], tris(pyrazolyl)methane [50] or triazacyclononane [5] types could be contemplated.

Other structural properties of the bridging- or linking-groups have also to be considered. We have already mentioned the rigidity/non-rigidity aspects in the case of non-rigid, CH_2 -linked bis-benzimidazole-pyridyl ligands yielding helical $\{\text{L}_3\text{Fe}^{\text{II}}_2\}$ and $\{\text{LnFe}^{\text{II}}\text{L}_3\}$ complexes [28, 29] and $-\text{CH}_2\text{CH}_2$ -linked bis-tacn Fe^{II}_2 complexes [21], both of type 1, the tacn derivative not showing SCO. In the case of covalent bridges of type 4, the well studied μ -bipyrimidine class has a linear, co-planar motif 6. We are presently studying other motifs such as non-linear and, often, non-coplanar types, 7. Such ligands are of the pyridyl-tetrazine or pyridyl-pyrazine types 9 and 10 and have been used by others to bridge $[(2,2'\text{-bipy})_2 \text{Ru}^{\text{II}}]$ centres [45, 46].





The side-by-side motifs, **8**, are exemplified by the bis-terpy ligand **11** of Breuning et al. [12], used in $[\text{Fe}^{\text{II}}_4\text{L}_4]^{8+}$ grid SCO, and the imino-pyridazine macrocycle, used by Brooker et al. in Co^{II}_2 {SCO-plus-exchange} species, **12** [6]. Interestingly, the Fe^{II}_2 analogue of **12** has only recently been isolated [52].



2.3.2

Bonding and Ligand-Field Aspects

The ligand-field condition $\Delta E^0_{\text{HL}} \sim kT$ (energy difference between potential wells for $\text{H} = {}^5\text{T}_{2g}$, $\text{L} = {}^1\text{A}_{1g}$ states) in the SCO region of mononuclear Fe^{II} complexes has been well described in the chapter by Hauser and in numerous books and reviews [7, 16, 27, 42, 43]. Detailed metal-ligand bonding models specifically applied to the SCO ligand field are less common. Toftlund has briefly summarized the angular overlap model for an MN_6 chromophore

[43]. The ligand-field splitting for this octahedral situation is made up of two contributions

$$\Delta^N = \Delta_{\sigma}^N - \Delta_{\pi}^N \quad (b)$$

where Δ_{σ}^N reflects σ -bonding between the octahedral metal e_g orbitals and the ligand σ -orbitals. It also reflects the basicity of the donor atom. Δ_{π}^N is the π -bonding parameter involving the three t_{2g} orbitals and ligand π -orbitals. In general $|\Delta_{\sigma}|gt;|\Delta_{\pi}|$ and $|\Delta_{\pi}^N|lt;0.2|\Delta_{\sigma}^N|$ for SCO fields. Aliphatic amine N donors have $\Delta_{\pi}^N \approx \text{zero}$, while π -accepting imino N-donors have negative Δ_{π}^N . Therefore Δ^N is high in the latter case and tris-diimines of Fe^{II} are LS, while aliphatic amine FeN_6 complexes have Δ^N low and are generally HS. The combined imino-amine ligand 2-pyridyl methylamine (2-pic) should, therefore give an intermediate Δ^N value leading to SCO, as it does in $[\text{Fe}(\text{2-pic})_3]^{2+}$ complexes [42]. Hyperconjugation to the CH_2 and NH_2 groups in 2-pic has been postulated and tested experimentally [16, 42]. Similar arguments apply to the tripodal, tetradentate ligand tpa. Changing the size of the chelate ring has already been mentioned, 6-rings often leading to LS compounds because of steric-strain effects coming in to play. Increasing steric bulk in the ligand can also induce a smaller Δ^N . Toftlund [43] has also reminded us that the Racah parameter, B , which is used in Tanabe-Sugano calculations and reflects the nephelauxetic effect (covalency and hard/soft effect; soft donors favour LS states) is as important as is Δ in determining the ligand-field and spin-state. The parameter $\Sigma = \Delta/B$ is suggested to be a better representation of relative ligand-field strength. In diimine chelating ligands, the Δ_{σ} and Δ_{π} , and the Σ effects enhance each other. The effect of B is important in the NCX^- series of unidentate ligands. In general, the SCO region requires Δ to be in the range 11600–13400 cm^{-1} for $\text{Fe}(\text{II})$.

Applying these concepts to 'weakly linked' dinuclear compounds of type 1 probably just requires mononuclear bonding conditions. However, complexes of type 2 containing a covalent bridging ligand require extra consideration. First, it is not obvious as to whether the bridging ligand acts in a mechanical/lattice mode, involving phonon coupling effects (as presumably postulated by Kahn in the linear chain μ -triazole compounds [31]) or in an electronic coupling mode, or both. Experimentally, it is known that steps in the SCO magnetic plots do not necessarily require a dinuclear structure, since they also occur in some mononuclear solid systems. For the moment, we assume that the Y or Y–Y ends of the bridge in types 3 to 10 contribute to the individual $\text{Fe}^{\text{II}}\text{N}_6$ ligand-fields of each Fe^{II} . The bridge has to "share" itself and it is likely that, for instance, the ligand-field contribution from one N–N moiety of bridging bipyrimidine is different to the N–N contribution from a terminal (non-bridging) bipyrimidine [7].

If we consider that classical electrostatic arguments may be relevant, we would predict that the net charge on each metal "end" and the distance be-

tween the metal in the dinuclear unit (the bridge length) will influence the ligand-field and spin-state at each metal ion. If one $\text{Fe}^{\text{II}}\text{N}_6$ end is positively charged, then this will weaken the positive charge at the other end. This effect is present, of course, in all dinuclear species. Further, if the bridging ligand is conjugated, a positively charged $\text{Fe}^{\text{II}}\text{N}_6$ end will drag electron density from the bridge, lowering Δ_σ at the other Fe^{II} while making Δ_π more negative. The Δ value will then be modulated. Anionic terminal ligands such as NCX^- will influence these electrostatic effects differently than neutral ligands; for example $(2,2'\text{-bipy})(\text{NCS})_2\text{Fe}^{\text{II}}$ will have a different charge effect than $(\text{tpa})\text{Fe}^{\text{II}}$. Testing such ideas, in practice, can be thwarted by chemical nuances! Therefore, attempts to synthesize a spin-crossover tpa analogue of Real's μ -bipyrimidine compounds, which contain *cis*-(NCX)₂(N-N) as terminal ligands, yielded $[\text{Fe}^{\text{II}}(\text{bpym})_3]^{2+}$ [53] or $[\text{tpaFe}^{\text{III}}\text{OFe}^{\text{III}}\text{tpa}]^{4+}$ as products depending upon reaction conditions. The relative labilities and solubilities of the species in solution (such as $\text{Fe}^{\text{II}}\text{tpa}^{2+}$, HS, labile; $[\text{Fe}(\text{bpym})_3]^{2+}$, LS, inert) determine what is crystallized from solution.

In summary, it can be seen that controlling the ligand-field in the SCO region at each metal centre in a covalently-bridged dinuclear compound is difficult and many factors contribute. As in the mononuclear SCO arena, it is possible to make a good prediction of ligand types, both terminal and bridging, but fine tuning is required if pure HS–HS or LS–LS complexes are first obtained rather than SCO compounds. The effects are very subtle and very small changes are often required to achieve success, particularly in crystalline species where inter-cluster, solvate and anion effects can play a part. Bringing together the structural, bonding and ligand-field ideas outlined in Sect. 2.3.1 and Sect. 2.3.2 led us to believe, for instance, that structural designs of types 9 and 10, in which terminal ligand combinations such as $\{(2,2'\text{-bipy})(\text{NCS})_2\}$ or $\{\text{tpa}\}$ are used, should lead to new dinuclear SCO species in which intramolecular exchange coupling is weak. This is ongoing work and we describe what happened in Sect. 6.

2.4

Examples of Dinuclear SCO Compounds

2.4.1

Weakly Linked Dinuclear Species of Type 1

Some general aspects of linked bis-tacn, bpta and bis-benzimidazole-pyridyl ligand and their $\text{Fe}(\text{II})\text{Fe}(\text{II})$ compounds have been mentioned in Sect. 2.1 and Sect. 2.2 [21, 22, 28]. Only the helical $[\text{Fe}_2\text{L}_3]^{4+}$ bis-benzimidazole-pyridyl complex shows SCO and it was studied in solution. We are pursuing work on weakly linked compounds, with Toftlund, using a butane-linked dinitrile ligand, and this is mentioned in Sect. 6.

2.4.2

Dinuclear SCO Complexes Containing Covalent Bridges and Displaying Weak Exchange Coupling; Types 2–4 and 12

2.4.2.1

Bipyrimidine Bridged Fe(II)Fe(II) SCO Compounds

This topic is dealt with in detail in the chapter by Real et al. In exploring other terminal N,N-chelating ligands in the $[(\text{NCX})_2(\text{N,N})\text{Fe}(\mu\text{-bpym})\text{Fe}(\text{N,N})(\text{NCX})_2]$ system we obtained the hitherto unknown 1,10-phen complex $[\text{Fe}(1,10\text{-phen})(\text{NCS})_2]_2(\mu\text{-bpym})$ [54], albeit without a crystal structure, a common phenomenon in this dinuclear series [7]. Magnetic studies (Fig. 1)

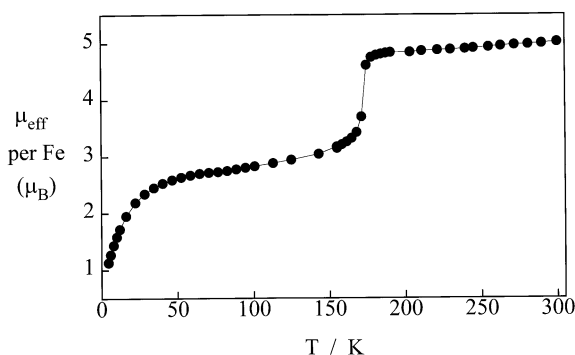


Fig. 1 Magnetic moment, μ_{eff} , per Fe, versus temperature for $[\text{Fe}(1,10\text{-phen})(\text{NCS})_2]_2(\mu\text{-bpym})$ (note the relationship $\mu_{\text{eff}}^2 = 7.997(\chi T)$ where χ is the molar susceptibility per Fe)

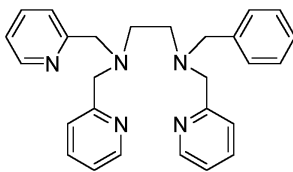
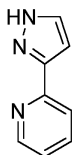
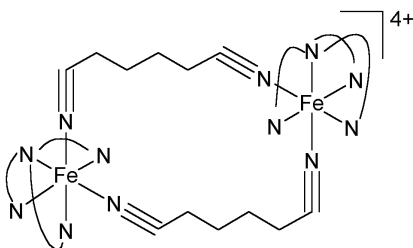
show that this 1,10-phen derivative shows an abrupt half-SCO at 170 K and a decrease in μ_{eff} below 30 K due to zero-field splitting of the quintet state. The $T_{1/2}$ value is lower compared to the HS-HS $\leftrightarrow$ HS-LS transition in the two-step complex $[(\text{NCS})_2(\text{bt})\text{Fe}(\mu\text{-bpym})\text{Fe}(\text{bt})(\text{NCS})_2]$ (197 K) and higher than the 120 K half-SCO transition in $[(\text{NCSe})_2(\text{bpym})\text{Fe}(\mu\text{-bpym})\text{Fe}(\text{bpym})(\text{NCSe})_2]$. The (bpym)(NCS)₂ complex remains HS-HS and weakly antiferromagnetically coupled at all temperatures [7]. There is no hysteresis in the 1,10-phen SCO transition or in those of any other family member. Small changes in the N,N-chelating ligand, and in X, therefore make significant changes to the SCO behaviour, but with the HS-HS $\leftrightarrow$ HS-LS transition being a common feature.

2.4.2.2

Dicyanamide (dca)-Bridged Fe(II)Fe(II) SCO Compounds

As indicated in Sect. 2.3.1, Real et al. [47] have recently isolated new singly-bridged dca compounds of type $[(\text{L})\text{Fe}^{\text{II}}(\mu\text{-1,5-NC-N-CN})\text{Fe}^{\text{II}}(\text{L})](\text{ClO}_4)_3$, in

which L is the N₅-pentadentate ligand **13** [48]. Two structural isomers were isolated but only the one with phenyl rings in the *trans* configuration showed SCO. A very well resolved two-step abrupt transition was observed between 400–4 K resulting from the microstates HS–HS (yellow) ↔ HS–LS ↔ LS–LS (black). Crystal structures were solved at the three plateau temperature regions. Clearly the pentadentate ligand and N(CN)₂[–] yield a ligand-field in the crossover region for each Fe^{II}. There is, presumably, enough structural flexibility in the dinuclear moiety to allow the consecutive crossover processes to occur.

**13****14**; pypz**15**

Finding the appropriate combination of dicyanamide and co-ligand required to yield a ligand-field in the SCO region is not a trivial exercise. The pentadentate N₅ ligand **13** above contains three pyridyl N-donors and two tertiary amine N with three five-membered chelate rings and chirality induced around Fe! Earlier, Real et al. isolated a mononuclear two-step SCO complex containing two terminal (non-bridging) dca ligands and two pyridyl-triazole bidentate chelates in *trans* positions [55]. We had earlier structurally characterized a mixed unidentate dca/triazole mononuclear complex of formula *trans*-[Fe^{II}(py-trz)₂(N(CN)₂)₂(H₂O)₂] but which remains HS because of the overall weaker ligand-field in the absence of six N-donors [56]. We have not been able to replace the H₂O molecules with pyridines.

2.4.2.3

Macrocyclic Double Pyridazine-Bridged Co(II)-Co(II) SCO Compounds

Two examples of the structural type **12** are now known which display, simultaneously, a gradual $S=3/2 \leftrightarrow S=1/2$ crossover and, at lower temperature, $S=1/2:S=1/2$ antiferromagnetic coupling [6, 57]. The axial ligands, Y, in

$[\text{Co}_2\text{L}(\text{Y})_4]^{2+}$, are $(\text{MeCN})_4$ or $(\text{NCS})_2(\text{SCN})_2$. $2J$ values of -14.2 cm^{-1} and -11.7 cm^{-1} , respectively, were obtained by fitting the maximum in χ , observed at $\sim 10\text{ K}$, to a $S=1/2:S=1/2$ model. Other combinations of the Y ligands and anions were structurally characterized and displayed HS–HS coupling with $2J$ values of ca. -20 cm^{-1} . One of the best-known and abrupt $S=3/2 \leftrightarrow S=1/2$ transitions in mononuclear Co(II) complexes was observed in $[\text{Co}(\text{H}_2\text{fsaen})(\text{py})_2]$ [58]. It would be intriguing to monitor the SCO behaviour as a second Co(II) (or other paramagnetic M(II)) ion is incorporated into the outer {O,O} compartment of this compartmental ligand, thereby introducing exchange coupling via the phenoxo bridging oxygens.

2.4.2.4

Pseudo-Dimer Fe(II)Fe(II) SCO Compounds Involving Ligand to Solvate Hydrogen Bonding

Examples of solvate (such as water) H-bonding interactions on the SCO transition have been briefly mentioned in Sect. 1 and Sect. 2.2. The influence of solvate removal upon SCO has been investigated in cases such as in the 2-D compound $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ [34] and in the monomers $[\text{Fe}(\text{pic})_3]\text{Cl}_2 \cdot \text{solvate}$ [16, 42] and in various pyridyl-pyrazole chelates of type $[\text{Fe}(\text{bpp})_2](\text{BF}_4)_2 \cdot 3\text{H}_2\text{O}$ [16, 59, 60]. To date, most examples relate to mononuclear or polynuclear crystalline species. Here we describe some novel discrete dimers obtained, initially, by attempted recrystallization of μ -bpym complexes. They were then made in larger quantities by reaction of $\text{Fe}(\text{NCS})_2$ in methanol, under nitrogen, with two moles of the bidentate ligand 2-pyrazolylpyridine 14 (pypz) which has been previously employed in octahedral $[\text{FeL}_3]^{2+}$ SCO compounds [16, 59, 61]. Dimeric and monomeric complexes $\{[\text{Fe}(\text{pypz})_2(\text{NCS})_2]_2(\mu\text{-OH}_2)(\text{H}_2\text{O})_2\} \cdot \text{H}_2\text{O} \cdot \text{MeOH}$ and *cis*- $[\text{Fe}(\text{pypz})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ were sequentially crystallized, but only the dimer was obtained in the isostructural NCSe case [62]. In this formula for the dimer, $\mu\text{-OH}_2$ does not imply bridging of water to the Fe atoms, but to the pypz ligands. $[\text{Fe}(\text{pypz})_2(\text{NCS})_2]$ has been reported previously and found to be HS [59]. The structures of the NCS-complexes are shown in Fig. 2. H_2O to pyrazole O–H–N hydrogen-bonding is clearly occurring in both bridging-water and terminal-water modes of the dimer. The average Fe–N distance is $2.161(4)\text{ \AA}$ in the NCS and NCSe dimers, typical of HS Fe(II) bond lengths. It reduces to $2.098(7)\text{ \AA}$ in the NCSe complex when determined at 123 K . The water and methanol molecules that are not H-bonded to the dimer are H-bonded to each other. Magnetic measurements on the dimeric and monomeric forms of the pypz/NCS complexes show HS behaviour at all temperatures. In all such cases, μ_{eff} (per Fe) remains constant ($\sim 5.2\text{ }\mu_{\text{B}}$) between $300\text{--}40\text{ K}$, then decreases rapidly due to zero-field splitting. However, the complex $\{[\text{Fe}(\text{pypz})_2(\text{NCSe})_2]_2(\mu\text{-OH}_2)(\text{H}_2\text{O})_2\} \cdot \text{H}_2\text{O} \cdot \text{MeOH}$ shows a gradual SCO over the range 170 and 70 K (Fig. 3) due to the HS–HS $\leftrightarrow$ HS–LS transi-

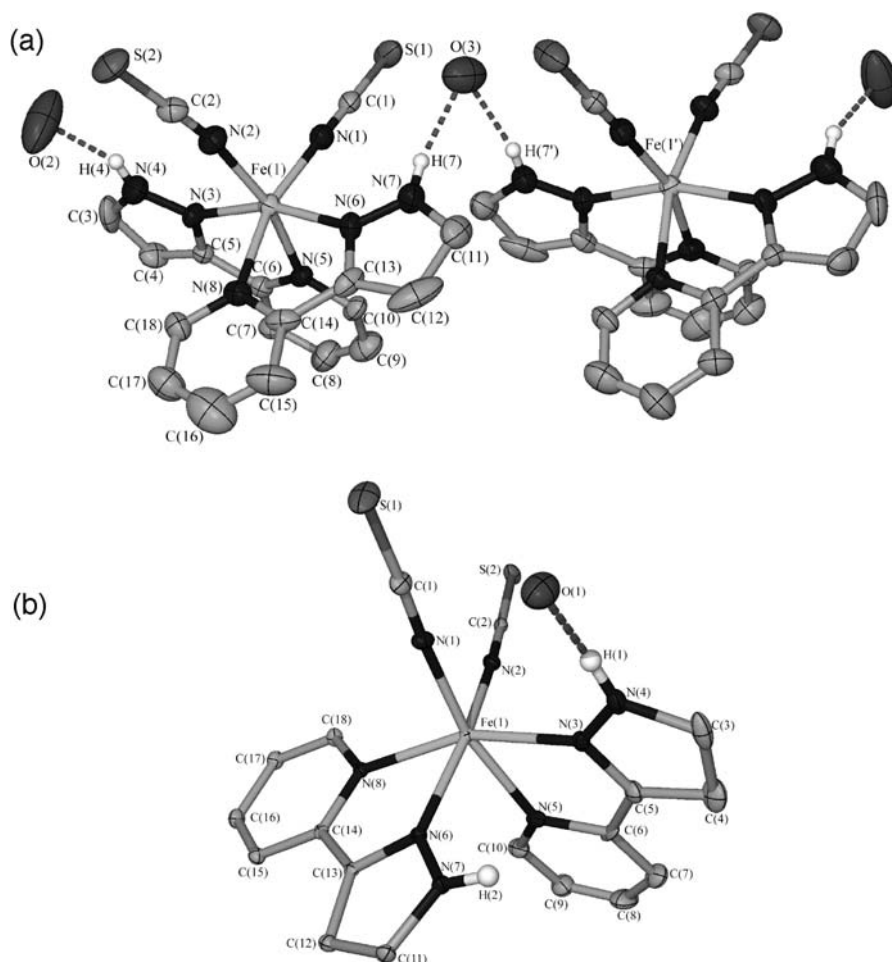


Fig. 2 ORTEP diagrams of **a** $\{[\text{Fe}(\text{pypz})_2(\text{NCS})_2]_2(\mu\text{-OH})_2(\text{H}_2\text{O})_2\} \cdot \text{H}_2\text{O} \cdot \text{MeOH}$. The NCS complex is isostructural. Note that the lattice H_2O and MeOH are not shown. They do not hydrogen-bond to the dimer but to each other. **b** *cis*- $[\text{Fe}(\text{pypz})_2(\text{NCS})_2]\text{H}_2\text{O}$

tion. No hysteresis is observed. This compound provides yet another, rather novel, example of a half-SCO in an Fe(II)Fe(II) system. Upon desolvation, in vacuo, the compound is HS–HS at all temperatures. Therefore the H-bonding plays a pivotal role in the SCO process. A crystal structure of the anhydrous material would be needed, however, to monitor any structural changes which occur within the dimeric units, assuming they are retained, and around the metal centres. Work is in progress to confirm that all five solvate molecules have been removed, since we believe that removal of H-bonded water causes the HS state to be stabilized. In this context, Goodwin et al. [16, 59, 60] have postulated that the stabilization of $\text{LS}(^1\text{A}_{1g})$ states in the hy-

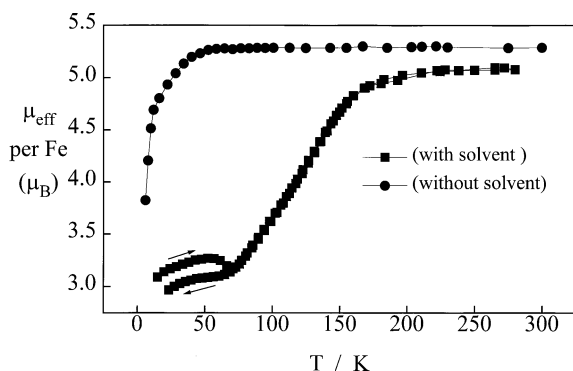


Fig. 3 Magnetic moment, μ_{eff} per Fe, versus temperature for $\{[\text{Fe}(\text{pypz})_2(\text{NCSe})_2](\mu\text{-OH}_2)(\text{H}_2\text{O})_2\} \cdot \text{H}_2\text{O} \cdot \text{MeOH}$ (filled squares), and for its desolvated product (filled circles)

drates of mononuclear chelated pyrazoles and triazoles, $[\text{FeL}_3](\text{anion})_{2 \cdot x} \text{H}_2\text{O}$, is due to an increase in the σ -electron density at the azole N-donor, and this is brought about by increased acidity at the neighbouring H-bonded NH group. This explanation is not sufficient in itself, in the present pypz/NCS dimer, to induce SCO.

3 SCO Cationic Complexes Encapsulated in Magnetically Coupled Anionic Networks

There is considerable interest in studying the electronic and structural effects that a 2-D or 3-D exchange-coupled anionic network might impart upon a six-coordinate SCO complex which is held between, or within, layers or between 3-D networks. Apart from synthetic challenges faced when assembling what are generally labile cationic complexes within such polymer networks, the latter often formed by use of the cation as a template, there is the choice to be made of the use, as starter cation, of a LS, HS or SCO complex. It is anticipated that (smaller) LS precursors will remain LS while HS precursors might be “squeezed” by the chemical pressure of the network cavities and produce SCO behaviour. A SCO precursor, particularly one that shows an abrupt transition in “normal” (ClO_4^- , BF_4^-) salts, might be expected to be less abrupt when the cations are separated by the network milieu, unless some new kind of cooperative behaviour occurs. In the case of simple double-salts in which the individual anions are paramagnetic (for instance $\text{M}(\text{C}_2\text{O}_4)_3^{3-}$), we had shown that the cation could retain its SCO behaviour [4].

Hauser and Decurtins et al. [63] were the first to observe $S=1/2 \leftrightarrow S=3/2$ SCO in the $[\text{Co}(2,2'\text{-bipy})_3]^{2+}$ cation, when it was incorporated into cavities

formed in the 3-D oxalate net in $[\text{Co}(2,2'\text{-bipy})_3][\text{LiCr}(\text{C}_2\text{O}_4)_3]$. The SCO process was very gradual over the range 50–300 K and so cooperativity was minimal. Crystal structures at 290 K and 10 K monitored Co–N bond length and other geometrical changes. The Na^+ analogue remained HS. Recently, temperature dependent visible spectra and magnetic susceptibility measurements on $[\text{Co}(2,2'\text{-bipy})_3][\text{LiRh}(\text{C}_2\text{O}_4)_3]$ were also reported to show SCO for the Co(II) centre [64]. Coronado et al. [65] have inserted a cationic Fe(III) Schiff base complex, which in simple salts displays a full d^5 HS to LS cross-over, into the layers of the ordered network $[\text{Mn}^{\text{II}}\text{Cr}^{\text{III}}(\text{C}_2\text{O}_4)_3]^-$. The SCO transition is less obvious in the resulting hybrid species.

We are investigating the template formation of 2-D and 3-D metal-dicyanamide anionic networks, for instance of type $\text{M}^{\text{II}}(\text{dca})_3^-$, by use of $[\text{M}(\text{N}_3)_3]^{n+}$ cations such as $[\text{M}(2,2'\text{-bipy})_3]^{2+}$. A hexagonal sheet network was formed in $[\text{Fe}^{\text{II}}(2,2'\text{-bipy})_3][\text{Fe}^{\text{II}}(\text{dca})_3]_2$ in which the cations fitted beautifully within the hexagonal windows. The cation remained LS between 4–300 K [66]. Attempts to make the $\text{Co}^{\text{II}}(2,2'\text{-bipy})_3^{2+}$ analogue unfortunately led to dissociation of dca and bipy and formation of a zig-zag chain structure in the weakly-coupled HS complex $[\text{Co}^{\text{II}}(\text{dca})_2(2,2'\text{-bipy})_2]_n$. The complex $[\text{Fe}^{\text{II}}(\text{propyl-tetrazole})_6]^{2+}$, which has a very sharp SCO transition [42], unfortunately did not yield a network product.

However, $[\text{Fe}^{\text{II}}(\text{pz}_3\text{CH})_2](\text{ClO}_4)_2$, which shows the beginnings of a $S=0 \leftrightarrow S=2$ SCO near room temperature [50], forms, in methanol, a 3-D NbO-type network in $[\text{Fe}^{\text{II}}(\text{pz}_3\text{CH})_2][\text{Mn}^{\text{II}}(\text{dca})_2(\text{MeOH})_2]_3\text{Cl}_2$ in which the cation occupies space between the chains of the network. The Fe^{II} cation remained LS at all temperatures, and so very weak antiferromagnetic coupling of the Mn^{II} centres can be detected from the 4–350 K Curie-like susceptibility data [67]. Work in progress shows that a tris-(2,2'-bi-1,4,5,6-tetrahydropyrimidine)Fe(III) cation [68] retains its SCO behaviour when it is held in cavities of a rare lonsdaleite network containing $\text{Fe}^{\text{II}}(\text{dca})_3^-$ and Cl^- .

While the encapsulation of SCO cations within anionic networks needs further development, particularly by use of cations having abrupt SCO transitions, the results to date show that the cationic and anionic networks remain independent, magnetically, with little cooperativity being evident.

4 Microporous Spin Crossover Systems

The above-mentioned interest in the synthesis of extended 1-D, 2-D and 3-D networks containing SCO centres, which is driven largely by a desire to maximise steric and electronic cooperativity between metal centres, has arisen in parallel with a much broader range of research interests in 1-D, 2-D and 3-D coordination framework materials. Within this broader per-

spective, the impetus for the formation of molecular frameworks has been largely two-fold: firstly, the generation of novel lattice topologies, including with an element of rational design (or “crystal engineering”) that derives from the use of complementary building units that display well-defined, highly directional interactions [69–71]; and secondly, the achievement of materials having novel physical properties that relate to the considerable structural and electronic/magnetic cooperativities of coordination framework lattices. Examples corresponding to the second broad aspect include molecular magnets [72–75], bistable spin-crossover systems, as discussed above and elsewhere in this volume, and porous frameworks that house solvent molecules within their lattices [76]. Recent work on the latter class of materials has demonstrated microporosity, as evidenced by their ability to support extensive void micropore volume [20, 77–79], to display high degrees of selectivity and reversibility in their guest-exchange chemistry [80–83], and to possess heterogeneous catalytic activity [84, 85]. These properties have prompted speculation that coordination frameworks may find application in areas such as molecular separations, sensing and catalysis, by analogy with the performance of conventional porous solids such as zeolites.

The realisation of microporosity in coordination frameworks has opened up the interesting possibility of exploiting the many unique electronic aspects of molecular chemistry to impart specific electronic function to these host-guest systems. This issue has been explored to some extent in molecular magnets, with examples including a range of “molecular sponges” [86–88], for which reversible dehydration/rehydration leads to substantial changes in the magnetic properties due to proposed changes to the framework connectivity with loss of crystalline solvent, and pillared-layer materials based on magnetic transition metal hydroxide layers [89–91]. The guest-dependent properties of conducting molecular charge-transfer salts [92] and porous luminescent frameworks [93, 94] have also recently been explored. We discuss here the synthesis and properties of the first porous molecular framework lattices containing SCO centres.

The majority of the known mononuclear SCO centres lend themselves to convenient incorporation into framework lattices through the replacement of some or all of the terminal ligands by multitopic ligands (or complexes) that bridge the metal centres. Examples include materials with the $\text{Fe}^{\text{II}}\text{L}_6$ [35, 37, 95–100] and $\text{Fe}^{\text{II}}(\text{NCX})_2\text{L}_4$ [18, 34, 36, 38, 101, 102] SCO centres (L =2-connecting aromatic imines such as those containing pyridyl, pyrrolyl, pyrazolyl, triazolyl, tetrazolyl and/or imidazolyl groups), and the Hofmann Clathrates $[\text{Fe}^{\text{II}}\text{L}_2\text{M}^{\text{II}}(\text{CN})_4]_x\{\text{guest}\}$ (L =pyridine or pyrazine type bases; M =Ni, Pd, Pt) which consist of cyano-bridged mixed-metal square grid layers [40, 41, 103]. Many of these materials contain solvent of crystallisation within the lattice, and the influence of dehydration/desolvation on SCO has been explored in a number of cases [97, 102]. Notably, the Hofmann Clath-

rates are also well-known for displaying a rich inclusion chemistry, including with reversible guest-exchange [76, 104]. Conventional tetrahedra-based porous materials such as zeolites offer little scope in this area, although it is notable that an open-framework iron phosphate displaying SCO has recently been reported [105].

The formation of frameworks that display true microporosity (the reversible exchange of guest molecules and lattice stability in the absence of guests) requires that the framework must crystallize with accessible pore volume, and that the framework linkages be of sufficient strength and arrangement to confer robustness to the empty framework lattice. Our efforts to incorporate SCO centres into such lattices have focused principally on the $\text{Fe}^{\text{II}}(\text{NCX})_2\text{L}_4$ ($\text{X}=\text{S}, \text{Se}, \text{BH}_3, \text{CH}_3$) centre, where incorporation of multiply-coordinating aromatic imines has led to the formation of a range of 1-D, 2-D and 3-D framework architectures. Here we discuss in detail one of a number of microporous materials synthesised to date, $\text{Fe}_2(\text{azpy})_4(\text{NCS})_{4\cdot x}(\text{guest})$ [39], which retains single crystallinity with desorption of guest molecules and displays SCO behaviour that is sensitive to the presence of the sorbed guest. In Sect. 6 we also briefly describe on-going work on a number of other porous phases to contain the $\text{Fe}^{\text{II}}(\text{NCX})_2\text{L}_4$ centre, many of which undergo SCO.

4.1

$\text{Fe}_2(4,4'\text{-azpy})_4(\text{NCS})_{4\cdot x}(\text{Guest})$

The $\text{Fe}_2(4,4'\text{-azpy})_4(\text{NCS})_{4\cdot x}(\text{guest})$ phase [39] consists of the double interpenetration of 2-D square grids formed by the linking of *trans*- $[\text{Fe}^{\text{II}}(\text{NCS})_2(\text{py})_4]$ centres by 4,4'-azpy ligands. These grids interpenetrate with one another in a diagonal fashion to give 1-D, guest-filled channels that occupy ca. 12 % of the crystal volume (Fig. 4). The structure contains two distinct Fe(II) centres with closely similar ligand binding geometries but differing second coordination spheres due to a hydrogen-bonding interaction between the guests and the thiocyanate ligands bound to one of the Fe(II) centres.

The removal of the guest molecules from the framework occurs without destruction of the single crystallinity, and is a reversible process, the desorbed material being capable of sorbing a range of different guests either through the vapour or liquid phase. With guest removal the general structural motif of interpenetrating grids remains intact but the structure undergoes a number of changes (Fig. 4), the grids displaying both a hinging motion and a slippage with respect to each other. The relative geometries of both the 4,4'-azpy and thiocyanate units change appreciably with desorption, the thiocyanate units straightening and the pyridyl groups rotating considerably. Structural studies on a range of different sorbed phases indi-

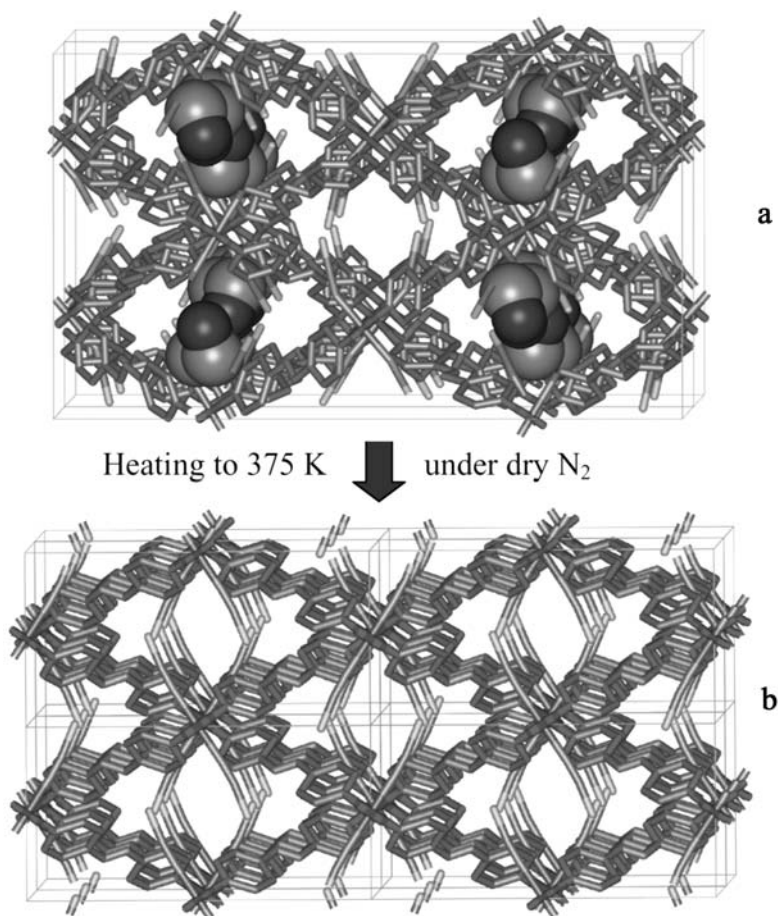


Fig. 4 The structures of **a** $\text{Fe}_2(4,4'\text{-azpy})_4(\text{NCS})_4(\text{EtOH})$ and **b** $\text{Fe}(4,4'\text{-azpy})_2(\text{NCS})_2$, viewed approximately down the 1-D channels. Framework atoms are represented as sticks and atoms of the ethanol guests as spheres. In $\text{Fe}_2(4,4'\text{-azpy})_4(\text{NCS})_4(\text{EtOH})$ the ethanol guests occupy every second 1-D channel in a "chess board" arrangement. Removal of ethanol by heating gives single crystals of $\text{Fe}(4,4'\text{-azpy})_2(\text{NCS})_2$, which has empty, equivalent 1-D channels and a concomitant quartering of the unit cell. Hydrogen atoms are omitted for clarity. Reprinted with permission from [39]. Copyright 2002 American Association for the Advancement of Science

cate that the extent of opening of the hinged framework is subtly dependent on the size/shape of the guest molecules.

The framework displays very interesting guest-dependent SCO properties. The fully desorbed material, $\text{Fe}(4,4'\text{-azpy})_2(\text{NCS})_2$, remains HS to low temperature, whereas the guest-loaded phases $\text{Fe}_2(4,4'\text{-azpy})_4(\text{NCS})_4\{\text{guest}\}$ (guest=methanol, ethanol, 1-propanol, acetonitrile and acetone) display

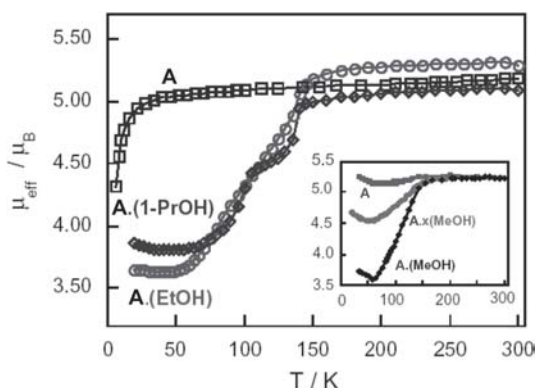


Fig. 5 Magnetic moment, μ_{eff} , versus temperature for $\text{Fe}_2(4,4'\text{-azpy})_4(\text{NCS})_{4-x}\{\text{guest}\}$ (denoted $\text{A}_x\{\text{guest}\}$), showing 50% SCO between 50 and 150 K for the fully loaded phases and no SCO for the fully desorbed phase. The ethanol and methanol loaded phases undergo a single-step spin crossover whereas the 1-propanol adduct shows a two-step crossover with a plateau at 120 K. The inset shows the effect of partial and complete removal of methanol from A (MeOH). Reprinted with permission from [39]. Copyright 2002 American Association for the Advancement of Science

broad half-SCO transitions that are centered about ca. 100 K (see Fig. 5 for the methanol, ethanol and 1-propanol analogues). These transitions have subtly different temperature dependencies, the 1-propanol adduct, for example, undergoing a two-step half-SCO. Low temperature structural studies on the ethanol phase indicate that it is the iron centre involved in H-bonding to the guest that undergoes SCO.

To explore the relative importance of the local second-sphere metal-guest interactions, and the structural influence of the guest on the framework and therefore coordination geometry, partially solvated materials were investigated. Partial removal of methanol causes a gradual disappearance of the crossover and replacement by $S=2$ behaviour for the desorbed material, rather than a shift of the transition temperature (see inset to Fig. 5). This suggests that it is principally the local interaction of the guest molecule, rather than its influence on the overall framework geometry that influences the SCO properties, although further studies on partially loaded phases will be needed to verify this. The closely similar unit cell parameters for each of the five guest-loaded phases explored to date, and their similar crossover temperatures, sheds little light on the steric influence of the guest on framework geometry and SCO behaviour. Further variation in the included solvent, both in its size and shape, to influence the framework geometry, and in its electrostatic potential (such as its polarity and hydrogen-bonding ability) to directly influence the ligand field splitting at the metal sites through second-sphere effects, are in progress.

5 Conclusions

In Sect. 2 we provided a background and framework for the design of dinuclear SCO compounds and reviewed the chemical systems that we have obtained to this point. Despite the difficulties experienced in obtaining SCO materials even when all design criteria appear to have been met (we often observe HS–HS states), a number of new systems have been discovered, particularly of the pseudodimer type involving hydrogen-bonding between solvate and ligand. On-going work involving new weakly-linked and covalently-bridged dinuclear species is briefly described in Sect. 6. The half-(incomplete) spin transition from HS–HS to HS–LS states has been observed by us and others in a number of Fe(II)–Fe(II) examples, and appears to be particularly common in dinuclear species. These dinuclear compounds display gradual SCO with little or no thermal hysteresis at the spin transition. Therefore, there is minimal cooperativity within these small clusters or between them. This is also the case in extended network SCO compounds, as judged by a brief literature review and our own work on the azpy-linked networks, summarized below. Therefore, we believe that, in the absence of systematic evidence to relate cooperativity to the covalent-bridging of SCO centres, much more experimental work is needed in this area, and theoretical models for cooperativity in polynuclear species are urgently needed to complement those presented in this volume for mononuclear SCO compounds.

The present status of attempts to encapsulate SCO complex cations in magnetically coupled anionic frameworks was described in Sect. 3. To date, there is no evidence for magnetic or cooperative interactions between cation and host network, for the anionic oxalato or dicyanamido types.

One of the most significant advances in our work is that we have shown, for the first time, that it is possible to make microporous frameworks that display SCO. In such systems the reversible exchange of guest species provides a unique mechanism with which to conveniently perturb the geometry and local electronic environment of SCO centres, thereby introducing a new approach for the systematic investigation of the SCO phenomenon. We envisage that future work may also shed some light on the lattice features that favour sharp and hysteretic transitions, with the energetics of lattice transformations/transitions potentially being modified by exchange of the guest species. Notably, the desorption and resorption of guests promises to provide a new stimulus for SCO, suggesting possible application in areas such as molecular sensing (change in the colour, magnetism, size, shape, and so on of the host with guest sorption). In such an application, selectivity could potentially be achieved both through the direct steric and electronic influence of the guest on the metal centres, and also through the highly selective sorption displayed by molecular frameworks. Of further interest is the gen-

eration of materials having hysteresis in their desorption/sorption chemistry (Type IV and V behaviour), as is common for flexible molecular frameworks [106–108]; if accompanying SCO, it is anticipated that such a feature would provide a second structural mechanism for electronic bistability. From the viewpoint of the porous hosts themselves, SCO induced by external stimuli (temperature, pressure and light irradiation) may provide the first microporous hosts where the size, shape and electronic potential of the pores and pore windows could be manipulated in a switchable fashion. An important consequence of SCO is a contraction of the framework lattice due to the decrease in Fe–N distances; the average intra-framework Fe–Fe distances in the square grid phases, for example, decreasing by 0.1 to 0.4 Å. Such behaviour may have interesting influences on the host-guest chemistry, and could feasibly be used to manipulate the uptake and release of guest molecules. Moreover, the controlled modification of guest environment through stimulated lattice SCO could potentially be used to modify the chemical (reactive) and physical (spectroscopic, magnetic) properties of the guest species. In the longer term, it is anticipated that the inclusion of guest/template species with specific electronic function into molecular lattices having controllable switching, including communication between these switching centres through coordination linkages, may lead to more advanced materials having other unique and potentially useful physicochemical properties.

6

On-Going Work and Future Directions

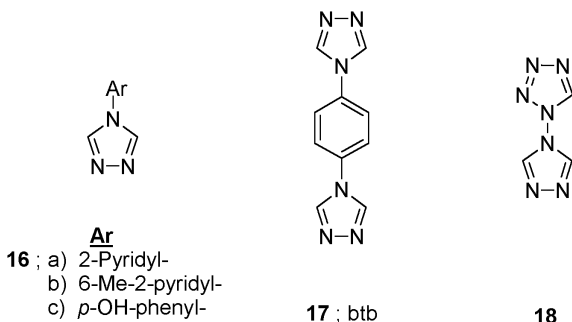
6.1

Dinuclear and Dimeric SCO Compounds

The main aims are to isolate and characterize new dinuclear compounds of types 1 to 10 possessing a variety of bridging types and geometries and a variety of terminal groups. In this way, as well as being able to make comparisons with Real's μ -bipyrimidine series [7], knowledge will be gained about the synergy between magnetic exchange and SCO, about reasons for the stability of the HS–LS state, which is the state commonly obtained to date, and about cooperativity, or lack thereof, in dinuclear (and other polynuclear) species. Some valuable advances have already been achieved. In conjunction with Toftlund, weakly-linked complexes of general type 1, incorporating flexible dinitrile linking ligands and terminal tpa ligands, viz 15, have been structurally characterized and shown to display $S=0 \leftrightarrow S=2$ SCO above 300 K. Further examples of the covalently-bridged μ -bipyrimidine Fe(II)Fe(II) compounds of general type 4 have been obtained, containing different chelating “end” groups viz $[(NCX)_2(pypz)Fe(\mu\text{-bpym})Fe(pypz)(NCX)_2]$, where

X=S or Se. The X=S compound remains HS–HS at all temperatures with weak coupling ($J=-4\text{ cm}^{-1}$) and the X=Se compound shows a broad half-SCO, to the HS–LS state, between 200–100 K, with no hysteresis. Interestingly, attempts to crystallize these compounds led to loss of bipyrimidine and formation of water-bridged chain species $\{[\text{Fe}(\text{pypz})_2(\text{NCS})_2](\mu\text{-OH}_2)\}_n$, from which the H-bonded water-bridged dimers described in 2.4.2.4 were developed.

Doubly bridged $\mu_{1,5}$ -dca and $\mu_{1,5}$ -tcm dinuclear Fe(II)Fe(II) complexes containing $\{\text{HC}(\text{pz})_3 + \text{dca}\}$ and tpa' end groups, respectively, have been structurally characterized. They remain HS–HS at all temperatures, with weak antiferromagnetic coupling. This contrasts with the singly bridged $\mu_{1,5}$ -dca SCO example [47] described in Sect. 2.4.2.2. Finding the precise combination of N donors around each Fe(N)_6 chromophore, with their requisite σ and π -bonding contributions, is an elusive exercise. We note that structures of type 5, such as $[\text{LFe}^{\text{II}}(\mu_{1,5}\text{-dca})_3\text{Fe}^{\text{II}}\text{L}]\text{BF}_4$ have recently been reported [109] but the tripodal triphosphine ligand, L, which was used, created a ligand field that was too strong and led to LS–LS behaviour. It should be possible to tune the ligand field at each Fe^{II} and achieve SCO.



We are making extensive studies of triazole-bridged Fe(II) cluster complexes using the little studied 4-aryl substituents in the 1,2,4-triazole ring, some of the ligands being shown in structures 16 to 18. The linked bis-(triazole)benzene, 17, (btb) and the 4,4'-triazole-tetrazole, 18, are being explored to see if they form 2-D or 3-D polymers in the way that the 4,4'-bis-triazole, btr, and alkane-linked bis-triazoles and bis-tetrazoles do [34–38]. Ligand 18 yields thermochromic (white $\leftrightarrow$ violet) Fe(II) compounds and a corresponding gradual, incomplete SCO between 220–70 K. Crystals of $[\text{Fe}_2^{\text{II}}(\mathbf{16b})_5(\text{NCS})_4]$, containing three N1,N2-triazole bridges, remain HS–HS with weak antiferromagnetic coupling. This contrasts with a sharp HS $\rightarrow$ LS transition at $T_{1/2}=111\text{ K}$ reported for a very similar dinuclear complex $[\text{Fe}_2^{\text{II}}(4\text{-}p\text{-tol-trz})_5(\text{NCS})_4]$, although the latter was cocrystallized within a pentanuclear assembly [100]. Another example which shows how very subtle changes in triazole and anion can influence the occurrence of SCO is the trinuclear complex $[\text{Fe}_3(\mathbf{16c})_6(\text{H}_2\text{O})_6](\text{ClO}_4)_6$. It remains HS–HS–HS at all temperatures,

with weak antiferromagnetic coupling, as does the 4-*p*-methoxyphenyltriazole/BF₄[−] analogue [8], both contrasting with the SCO occurring on the central Fe(II) ion in other 4-aryl and 4-alkyl analogues [8, 11, 110].

New covalently bridged dinuclear Fe(II) complexes containing “offset” bridges of the pyridino-tetrazine bptz type, **9**, and of its 1,4-dihydropyridine congener, H₂bptz [111], have been isolated and contain tpa as the terminal N₄ donor set. The μ -bptz complex remains LS–LS between 4–300 K, whereas the μ -H₂bptz complex displays a gradual half-SCO transition at 135 K, similar to those observed in the μ -bipyrimidine compounds [7], but without the rapid decrease in magnetic moment at very low temperatures, perhaps indicative of lower zero-field splitting in the HS–LS state.

In Sect. 2.4.2.4 we showed the importance of solvate-to-ligand H-bonding effects within pseudo-dimeric species and how it influences SCO. This phenomenon has long been recognized in mononuclear Fe(II) compounds [16, 42], but hard to quantify. We are exploring H-bonding and other supramolecular influences on crystalline mononuclear, small cluster SCO and extended network SCO compounds, aspects of the latter being described in Sect. 4. A range of chelating ligands is being employed which contain non-coordinating NH groups capable of forming H-bonds to solvate and/or anion, therefore influencing the MN₆ ligand-field in their Co(II), Fe(II) or Fe(III) complexes.

6.2

Microporous Spin Crossover Systems

On-going research in this area involves a range of host/guest combinations with the principal aim of achieving materials for which the SCO and desorption/sorption temperature ranges overlap. We anticipate unusual guest-exchange chemistries for such materials, since the switching of the lattice geometry is expected to have considerable influence on the energetics of sorption/desorption. Although syntheses to date have focused on the Fe^{II}(NCS)₂L₄ centre, we note the promise of many other systems as porous hosts, in particular the Hofmann Clathrates and those based on the tris(dithiocarbamate) Fe(III) centre. Our interests have also recently extended to other classes of host-guest systems, including hydrogen-bonded lattices, which have also been shown to display reversible guest-exchange and microporosity [112, 113], and soluble mono- and polynuclear SCO systems having supramolecular host-guest chemistries, for which guest-binding in solution could potentially be used to stimulate SCO.

At the time of writing, we have synthesized a large number of other porous phases of the interpenetrating square grid topology by variation of the guest molecules, the terminal NCX groups, and the di-pyridyl ligands. Investigations into the guest-dependent structures and SCO behaviours of these phases have yielded a number of interesting preliminary observations. Vari-

ation of both the di-pyridyl ligands and the solvent of inclusion has seen the angle of interpenetration of the grids range from 53.6 to 90°, the orthogonal grid structures being analogous to one reported by Real et al. with tvp [18]. The subtle scissor-type action observed in the 4,4'-azpy phase with guest desorption/sorption [39] and the considerable variation of the interpenetration angle seen in these phases raises the question of whether a single phase may undergo a more pronounced variation in geometry with guest exchange, thereby potentially favouring a greater guest-dependence in the SCO behaviour. The materials measured to date display partial or full crossovers over a range of temperature intervals, all having comparatively broad transitions (over a 50 to 100 K range) and, at most, negligible hysteresis. We speculate that the absence of any significant hysteresis about the SCO transitions in these materials may arise with the existence of low energy pathways between the HS and (partial or full) LS structures in the crossover temperature ranges. Such a flexibility is not unexpected given the considerable structural distortions that occur at higher temperatures with guest desorption/sorption. Further, it seems likely that the comparative broadness of the transitions seen in the guest-loaded phases may be influenced by the gradual decrease in the kinetic volumes of the guest molecules with cooling; SCO necessitates a decrease in the pore size due to a ca. 0.1–0.4 Å decrease in the intra-grid Fe–Fe distances, and so the temperature-dependent size requirement of the guest molecules may act to limit the sharpness of the SCO in these materials.

Variations in the solvent of crystallization and conditions of synthesis have led also to the formation of a number of 2-D layered SCO materials. As with the interpenetrated phases, these materials contain extended 2-D grids that stack on one another, but without the interpenetration by a second set of parallel layers. Accordingly, the materials generally have larger pores and greater pore volumes than the interpenetrated materials, and their guest desorption/sorption behaviour, which involves interlayer collapse, is more reminiscent of intercalation materials than that of truly microporous systems. We anticipate that the SCO will display a greater guest-dependence in such systems.

The considerable structural flexibility of the abovementioned 2-D porous phases has prompted us to also explore the generation of frameworks with 3-D connectivity, for which more robust lattice behaviour is generally expected. This has been successfully achieved using two separate approaches: firstly, through the use of 2-connecting ligands for which a large torsion between the imine groups disfavours the formation of flat 2-D grids; and secondly, the use of 3-connecting tris(imine) ligands. A very high degree of robustness to resorption and guest-exchange has been observed, and it will be interesting to determine, through comparison of these phases with the more flexible analogues, to what extent the robustness of the lattice suppresses the guest-sensitivity of the SCO transition.

7

Note Added in Proof

We have recently synthesized and structurally characterized a new covalent-bridged diiron(II) complex of structural type **6**, at temperatures above and below a SCO transition temperature of 225 K [114]. The complex, $[(\text{pypz})(\text{NCSe})\text{Fe}(\mu\text{-pypz})(1\text{-})2\text{Fe}(\text{NCSe})(\text{pypz})]$, incorporates ligand **14**, 2-pyrazolylpyridine, acting both as a μ -pyrazolate bridge and as a neutral capping ligand. In contrast to members of the μ -bipyrimidine family of Real et al. [7] which show a two-step [HS-HS] to [HS-LS] to [LS-LS] transition, this compound displays a sharp, single [HS-HS] to [LS-LS] transition. Recently, Real et al. [115], have also reported a one-step example in the μ -bipyrimidine series, containing two NCS^- and a 2,2'-dipyridylamine as end groups. However, the continuous spin crossover behaviour in this case occurred over the range 400 to 50 K. They have reviewed their work in regard to cooperativity [116].

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Spin Crossover in 1D, 2D and 3D Polymeric Fe(II) Networks

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Abstract In this chapter, structural and spin transition aspects of the most important families of polymeric Fe(II) compounds are reviewed. These coordination compounds contain N-donor heterocyclic 1,2,4-triazole, 1-R-tetrazole and bis monodentate pyridine-like bridging ligands. Recent results involving new series of polymeric compounds formed by the combination of organic and inorganic tetra- and dicyanometallate complex bridging ligands are also discussed.

Keywords Spin transition · Coordination polymers · Bistability · Hofmann-like clathrates · Supramolecular networks

List of Abbreviations and Symbols

azpy	<i>trans</i> - 4,4'-azopyridine
bpb	1,4-bis(4-pyridyl-butadiyne)
bpe	Bispyridylethylene
btr	4,4'-bis-1,2,4-triazole
btzb	1,4-bis(tetrazol-1-yl)butane
btze	1,2-bis(tetrazol-1-yl)ethane
btzp	1,2-bis(tetrazol-1-yl)propane
etrz	4-ethyl-1,2,4-triazole
EXAFS	Extended X-ray Absorption Fine Structure
HS	High-spin
Htrz	1 <i>H</i> -1,2,4-triazole
hyetrz	4-(2'-hydroxy-ethyl)-1,2,4-triazole
hyptrz	4-(3'-hydroxy-propyl)-1,2,4-triazole
iptrz	4-(isopropyl)-1,2,4-triazole
LIESST	Light Induced Excited Spin State Trapping
LS	Low-spin
N(entz) ₃	Tris[(tetrazol-1-yl)-ethane]amine
py	Pyridine
pz	Pyrazine
SCO	Spin crossover
Solv	Solvent
ST	Spin transition
T _{1/2}	Spin transition temperature
totrz	4-(<i>p</i> -tolyl)-1,2,4-triazole
trz	1,2,4-triazolato
TSCO	Thermal spin crossover
WAXS	Wide Angle X-ray Scattering
γ _{HS}	High-spin molar fraction
γ _{LS}	Low-spin molar fraction

1**Introduction**

Most Fe(II) compounds showing spin crossover (SCO) behaviour in the solid state are mononuclear neutral or cationic molecules. Although the origin of the SCO phenomenon is molecular, its cooperative manifestation depends on the coupling between the SCO species in the crystal lattice. Indeed, the molecular structural changes occurring upon SCO may spread cooperatively throughout the whole solid when SCO centres are strongly coupled via intermolecular interactions. In such a situation first-order phase transitions and hysteresis effects may be observed, i.e. magnetic, optical and structural properties change dramatically conferring a bistable character to the com-

pound, which could be useful for designing new classes of multifunctional materials.

Strong intermolecular interactions between active SCO mononuclear building blocks stem from the presence of efficient hydrogen-bonding networks or π - π stacking interactions and have led to abrupt spin transitions [1], sometimes with associated hysteresis [2–4]. Despite the important efforts made by crystal engineers in establishing reliable connections between molecular and supramolecular structures on the basis of intermolecular interactions, the control of such forces is, however, difficult and becomes even more complicated when uncoordinated counter-ions and/or solvent molecules are present in the crystal lattice.

An alternative approach to enhance the coupling between active centres is to replace intermolecular interactions by more strongly bonding forces. That is, the self-assembly of polymeric networks of varying dimensionality and topology, driven by coordination of bridging ligand molecules to Fe(II) ions [5]. The use of suitable bridging ligands between Fe(II) sites should allow structural distortions accompanying the ST to be efficiently communicated [6]. In this chapter, we will consider structural and ST aspects of the most representative series of polymeric SCO compounds obtained from the assembly of Fe(II) and N-donor heterocyclic bridging ligands such as 1,2,4-triazole, 1-*R*-tetrazole or polypyridine-like derivatives as well as tetra- or di-cyanometallate complex ligands.

2

1,2,4-Triazole Systems

Research on Fe(II) 1,2,4-triazole polynuclear SCO complexes has undergone renewed activity over the last ten years since their potential for being incorporated in memory devices and displays was outlined by Kahn in collaboration with an industrial partner [7]. Towards this end, spin transition (ST) materials showing wide hysteresis effects around room temperature along with thermochromic behaviour are currently being sought [8].

2.1

Oligonuclear Systems

We first describe the crystal structure and magnetic properties of some examples of SCO oligomers that can be considered as model systems for the polymers.

2.1.1

Dinuclear Complexes

$[\text{Fe}_2(4\text{-R-1,2,4-triazole})_5(\text{NCS})_4] \cdot n\text{H}_2\text{O}$ ($\text{R}=\text{C}_6\text{H}_5$, $n=2.5$ [9]; $\text{R}=\text{NH}_2$, $n=2$ [10]) are Fe(II) dinuclear compounds with bridging 4-*R*-1,2,4-triazole. Both exhibit a one step thermal SCO below 300 K without hysteresis.

The crystal structure of $[\text{Fe}_2(\text{totrz})_5(\text{NCS})_4]_2[\text{Fe}(\text{totrz})_2(\text{NCS})_2(\text{H}_2\text{O})_2] \cdot n\text{-H}_2\text{O}$, a compound obtained by self-assembly of 4-(*p*-tolyl)-1,2,4-triazole

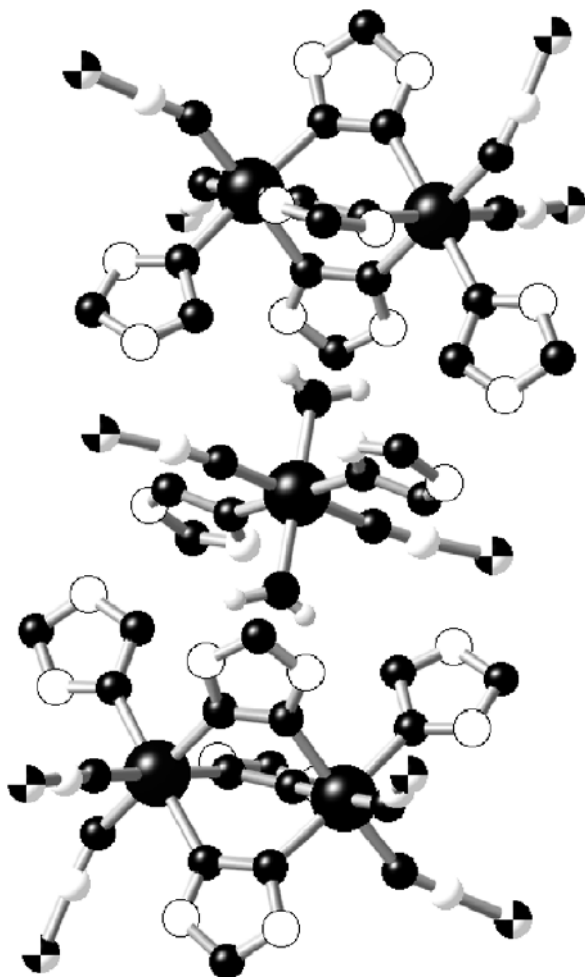


Fig. 1 View of the pentanuclear assembly of $[\text{Fe}_2(\text{totrz})_5(\text{NCS})_4]_2[\text{Fe}(\text{totrz})_2(\text{NCS})_2(\text{H}_2\text{O})_2]$ (*p*-tolyl groups and hydrogen atoms of the triazole have been omitted for clarity). *Shining black, white, and black and white small spheres correspond to nitrogen, carbon and sulfur atoms, respectively. The larger black spheres correspond to iron(II) ions*

(totrz) with $\text{Fe}(\text{NCS})_2$, reveals a pentanuclear arrangement formed by two dinuclear SCO units, hydrogen bonded to a central high-spin (HS) mononuclear unit (Fig. 1) [11]. Three $\text{N1,N2-1,2,4-triazole}$ molecules bridge the Fe ions of the dinuclear units with Fe-N distances between 2.151(8) Å and 2.223(8) Å, which are typical for HS Fe(II). Two thiocyanate anions in *cis* positions and a monodentate totrz ligand complete the coordination sphere leading to a distorted octahedral FeN_6 chromophore. Hydrogen-bonding is found between non-coordinated N atoms of the monodentate triazole and water molecules coordinated to the central mononuclear unit (see Fig. 1). The Fe(II) ion of the central unit is located on an inversion centre and octahedrally surrounded by two water molecules, two monodentate totrz ligands at 2.194(9) Å, and two thiocyanate anions in *trans* positions at 2.095(1) Å, forming a FeN_4O_2 chromophore. This compound displays an abrupt ST ($T_{1/2} = 111$ K) which is confined to the four FeN_6 centres. The central FeN_4O_2 chromophore remains HS over the whole temperature range as a consequence of the much weaker ligand field in this unit [9, 11, 12]. The bridge between the dinuclear units via hydrogen bonding presumably contributes to the observation of a one step transition.

2.1.2

Trinuclear Complexes

Trinuclear SCO coordination compounds of formula $[\text{Fe}_3(4\text{-}R\text{-}1,2,4\text{-triazole})_{12-\gamma}(\text{H}_2\text{O})_\gamma](\text{anion})_6 \cdot n\text{H}_2\text{O}$ have been reported. Their SCO characteristics are listed in Table 1.

In the crystal structure of $[\text{Fe}_3(\text{etrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ (etrz = 4-ethyl-1,2,4-triazole) the central Fe(II) ion is surrounded by six triazole ligands thus establishing an FeN_6 chromophore. These triazole ligands are N1,N2-

Table 1 SCO characteristics of $[\text{Fe}_3(\text{Rtrz})_{12-\gamma}(\text{H}_2\text{O})_\gamma](\text{anion})_6 \cdot n\text{H}_2\text{O}$

R substituent	γ	Anion	n	$T_{1/2}$	Ref
Ethyl	6	CF_3SO_3	0	202	13
2'-Hydroxy-ethyl	6	CF_3SO_3	0	290	14
Isopropyl	6	CF_3SO_3	0	187	15
Isopropyl	6	I^-	0	195	16
Isopropyl	6	BF_4^-	0	194	16
Isopropyl	6	Otos	2	242	15
Isopropyl	6	Br^-	4	355	16
Isopropyl	4	I^-	8	195	16
Dimethylamino	6	ClO_4^-	2	175	17
<i>m</i> -Tolyl	6	Otos	0	200	18
<i>m</i> -Tolyl	6	BF_4^-	0	-	18
<i>p</i> -Anisyl	6	Otos	4	245	18
<i>p</i> -Anisyl	6	Otos	0	330	18
<i>p</i> -Anisyl	4	BF_4^-	2	-	18

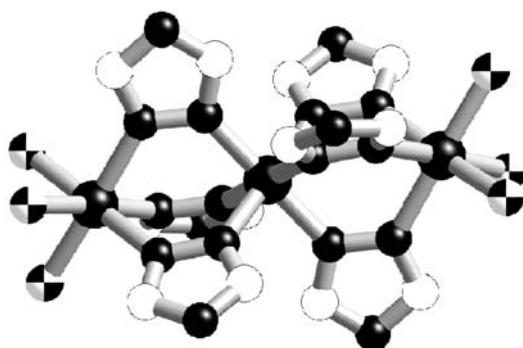


Fig. 2 View of the trinuclear unit of $[\text{Fe}_3(\text{etrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ at 105 K (hydrogen atoms and anions have not been depicted). *Shining black, white, black and white small spheres correspond to nitrogen, carbon and oxygen atoms, respectively. The larger black spheres correspond to iron(II) ions*

bridged to two external Fe(II) ions that are also coordinated to three water molecules giving an FeN_3O_3 chromophore (Fig. 2) [13]. Additionally, non-coordinated trifluoromethanesulfonate anions are connected by hydrogen bonds to the coordinated water molecules via their sulfonate groups. The crystal structures determined at 300 K and 105 K have confirmed the presence of a ST for the central Fe(II) ion with $\text{Fe-N} = 2.174(3) \text{ \AA}$ at 300 K (HS) decreasing to $\text{Fe-N} = 2.031(6) \text{ \AA}$ at 105 K (low-spin, LS). The Fe-Fe intramolecular distance also significantly decreases from $3.840(1) \text{ \AA}$ at 300 K to $3.795(2) \text{ \AA}$ at 105 K. The temperature dependence of the magnetic properties has revealed a gradual and incomplete SCO around $T_{1/2} \sim 202 \text{ K}$. The large residual HS fraction (66%) can be attributed to the external Fe(II) ions that are coordinated to water molecules and thus experience a weaker ligand field. This trinuclear compound has been functionalised by the introduction of hydroxy groups in $[\text{Fe}_3(\text{hyetrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ (hyetrz = 4-(2'-hydroxyethyl)-1,2,4-triazole). A similar crystal structure is obtained with trinuclear units which are now linked to each other by hydrogen bonding interactions, between the hydroxy groups of the ligands and coordinated water molecules. The SCO curve centred on the room temperature region is smoother than the one of the etrz derivative. It is believed that the greater flexibility of the hydrogen bonding network in $[\text{Fe}_3(\text{hyetrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ is responsible for the reduction in the degree of cooperativity [14].

A further example illustrating the importance of lattice effects on the SCO behaviour of these trinuclear compounds is given by $[\text{Fe}_3(\text{iptrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ (iptrz = 4-(isopropyl)-1,2,4-triazole). A strong influence of the ST of the central Fe(II) ion on both external Fe(II) ions has been found by Mössbauer spectroscopy, as detected by the perturbation of their quadrupole interactions [15]. The nature of this phenomenon has been proposed to

be linked to the rigid lattice structure connecting the trinuclear units. This result demonstrates that, despite the fact that only one of the three Fe(II) centres is SCO active, propagation of cooperative effects throughout the whole trinuclear unit can be effective.

2.2

One-Dimensional Fe(II) 1,2,4-Triazole Chain Compounds

We consider 1D Fe(II) chain compounds of formula $[\text{Fe}(\text{Htrz})_2\text{trz}](\text{anion})$ and $[\text{Fe}(4\text{-}R\text{-}1,2,4\text{-triazole})_3](\text{anion})_2 \cdot n\text{Solv}$ where n denotes the number of non-coordinated solvent molecules Solv, Htrz =4-H-1,2,4-triazole and trz =1,2,4-triazolato. So far, no single crystal suitable for X-ray diffraction could be obtained. It has been possible, however, to obtain structural information from EXAFS (Extended X-ray Absorption Fine Structure) at the iron K edge [19–26] and WAXS (wide angle X-ray scattering) [27] spectra. These materials are made up of linear chains in which the adjacent Fe(II) ions are linked by three N1,N2-1,2,4-triazole bridges [20]. This arrangement has been

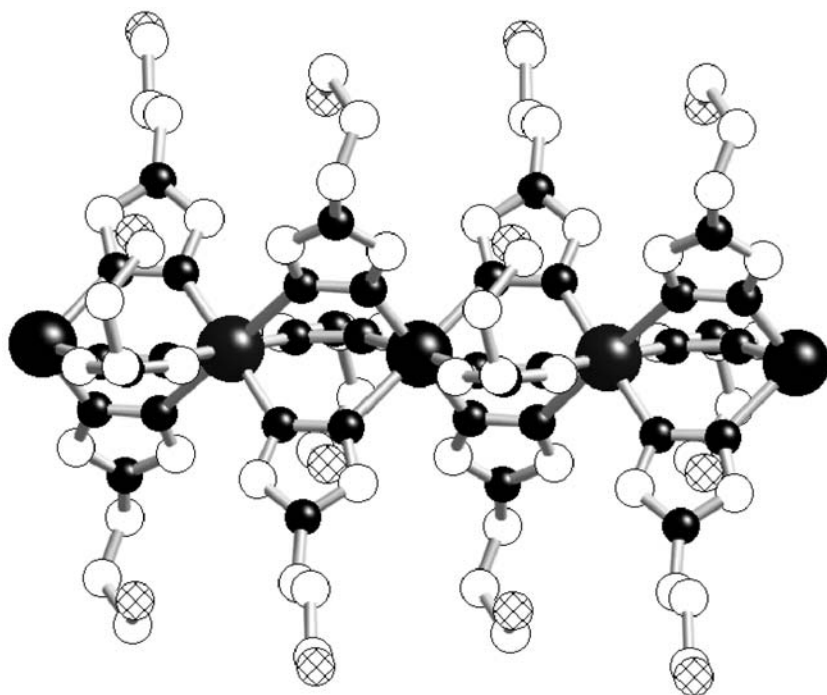


Fig. 3 View of the cationic chain in $[\text{Cu}(\text{hyptrz})_3](4\text{-chloro-3-nitrophenylsulfonate})_2 \cdot \text{H}_2\text{O}$. Counter anions and water molecules have been omitted for clarity. *Shining black, white, and hatched small spheres correspond to nitrogen, carbon and oxygen atoms, respectively. The larger black spheres correspond to copper(II) ions*

confirmed in the crystal structure of related $[\text{Cu}^{\text{II}}(4\text{-}R\text{-}1,2,4\text{-triazole})_3](\text{anion})_2 \cdot n\text{H}_2\text{O}$ chain compounds where, additionally, non-coordinated water molecules and counter-anions were found between the polymeric chains (Fig. 3) [22, 26, 28–30]. Recent Rietveld refinements of the X-ray powder spectra of $[\text{Fe}(\text{Htrz})_3](\text{ClO}_4)_2 \cdot 1.85\text{H}_2\text{O}$ have yielded cell parameters similar to those of $[\text{Cu}(\text{hyetrz})_3](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ [31].

In these polymeric species, the $N1,N2$ -1,2,4-triazole linkage is rigid, and allows an efficient transmission of cooperative effects. Consequently, abrupt ST with broad thermal hysteresis loops have been observed [26, 32–34]. The absorption spectra of these compounds show a broad band at 520 nm corresponding to the $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ d-d transition in the LS state whereas no band is found in the visible region in the HS state, the $^5\text{T}_{2g} \rightarrow ^5\text{E}_g$ transition being located around 850 nm [7a]. The ST is thus accompanied by a thermochromic effect, purple (LS) and white (HS). These characteristics make these compounds potential candidates for practical applications, e.g. thermal display devices [7, 8, 17]. Such behaviour has been observed, for example, in the compound $[\text{Fe}(4\text{-amino-}1,2,4\text{-triazole})_3](\text{NO}_3)_2$ [32] whose SCO is associated with a hysteresis loop of width ~ 35 K, centred above room temperature [8].

Temperature dependent EXAFS experiments have suggested that the linearity of these chains is preserved in both the LS and HS states [25, 26] ruling out a possible chain twisting in the HS state [20, 27], which could account for a crystallographic phase transition. Recent powder diffraction spectra recorded using synchrotron radiation for both spin states of $[\text{Fe}(\text{Htrz})\text{trz}](\text{BF}_4)$, confirmed the absence of a crystallographic phase transition [35]. This suggests that the observed thermal hysteresis associated with the transition in these materials originates from strong elastic cooperative interactions [6].

Abrupt spin transitions with hysteresis loops of width about 10 K are generally observed for this family of chain compounds [24, 36–41]. This width is not sufficient to meet application criteria, as ~ 50 K is considered to be ideal [7a]. The influence of molecular parameters of these 1D chain compounds on the ST is currently being studied in order to control not only the cooperative effects (the width of the hysteresis loop and the steepness of the ST curves) but also the ST temperature range. A direct correlation between the transition temperatures and the radii of the non-coordinated anions has been obtained [38, 40]. As the size of the anion increases in $[\text{Fe}(\text{hyetrz})_3](\text{anion})_2$, the transition temperatures decrease but the hysteresis width remains practically constant (~ 10 K) (Fig. 4). Selecting a relatively small anion such as iodide afforded $[\text{Fe}(\text{hyetrz})]\text{I}_2$ which does show a bistability domain centred around room temperature [40]. Ligand and/or counter-ion substitution has also been used to tune the SCO region in mixed systems $[\text{Fe}(\text{Rtrz})_{3-3x}(\text{R}'\text{trz})_{3x}]\text{A}_{2-2y}\text{A}'_{2y} \cdot n\text{H}_2\text{O}$, so as to centre the bistability domain around room temperature [7b, 17, 42].

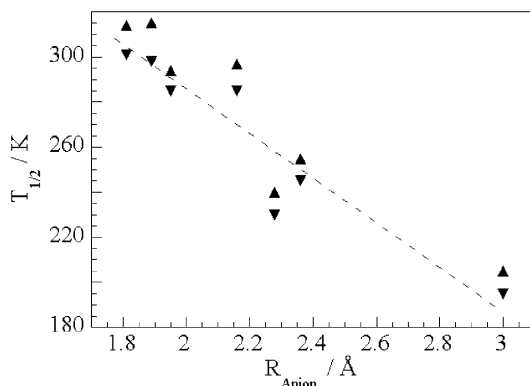


Fig. 4 Plot of the transition temperatures $T_{1/2}$ on heating (filled triangles) and cooling (filled upside down triangles) vs the anion radii for the series $[\text{Fe}(\text{hyetrz})_3](\text{anion})_2$

Insertion of non-coordinated solvent molecules in these networks can stabilise the LS state. For instance, the transition temperatures of the system $[\text{Fe}(\text{hyetrz})_3](3\text{-nitrophenylsulfonate})_2\cdot\text{Solv}$ depend dramatically on the nature of the solvent as follows: $\text{Solv}=0$ ($T_{1/2}\sim 105$ K) $<$ DMA ($T_{1/2}\sim 145$ K) $<$ MeOH ($T_{1/2}\sim 175$ K) $<$ DMF ($T_{1/2}\sim 235$ K) $<$ 3 H_2O (LS at room temperature) [43]. A similar influence of non-coordinated solvent molecules was first reported for the mononuclear complexes $[\text{Fe}(2\text{-picolylamine})_3]\text{Cl}_2\cdot\text{Solv}$ [44]. The hydrate $[\text{Fe}(\text{hyetrz})_3](3\text{-nitrophenylsulfonate})_2\cdot 3\text{H}_2\text{O}$ loses water when heated and this is accompanied by a change to the HS state [45]. The significant feature of this system is that the HS anhydrous sample does not re-absorb water under a normal atmosphere. Thus it can be the basis for single use applications. Several other examples of changes in spin state induced by water removal have been identified for 1D polymeric chain compounds following this discovery [46–49].

The influence of pressure has also been used to tune the ST properties of these 1D chain compounds. Application of hydrostatic pressure (~ 6 kbar) on $[\text{Fe}(\text{hyptrz})_3](4\text{-chlorophenylsulfonate})_2\cdot\text{H}_2\text{O}$ (hyptrz=4-(3'-hydroxypropyl)-1,2,4-triazole) provokes a parallel shift of the ST curves upwards to room temperature (Fig. 5) [41]. The steepness of the ST curves along with the hysteresis width remain practically constant. This lends support to the assertion that cooperative interactions are confined within the Fe(II) triazole chain. Thus a change in external pressure has an effect on the SCO behaviour comparable to a change in internal electrostatic pressure due to anion-cation interactions (e.g. changing the counter-anion). Both lead to considerable shifts in transition temperatures without significant influence on the hysteresis width. Several theoretical models have been developed to predict such SCO behaviour of 1D chain compounds under pressure [50–52]. Figure 5 (bottom) also shows the pressure dependence of the LS fraction, γ_{LS} , of

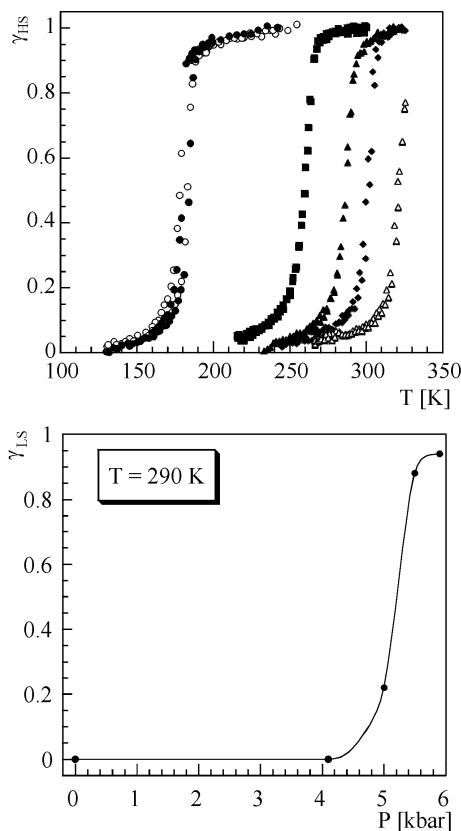


Fig. 5 (Top) γ_{HS} vs T plot for $[\text{Fe}(\text{hyptrz})_3](4\text{-chlorophenylsulfonate})_2 \cdot \text{H}_2\text{O}$ at different pressures. (Filled circles, $P=1$ bar; filled squares, $P=4.1$ kbar; filled triangles, $P=5$ kbar; filled diamonds, $P=5.3$ kbar; empty triangles, $P=5.9$ kbar; empty circles, $P=1$ bar after releasing the pressure). (Bottom) γ_{LS} vs P plot for $[\text{Fe}(\text{hyptrz})_3](4\text{-chlorophenylsulfonate})_2 \cdot \text{H}_2\text{O}$ at 290 K

$[\text{Fe}(\text{hyptrz})_3](4\text{-chlorophenylsulfonate})_2 \cdot \text{H}_2\text{O}$. A very steep HS $\rightarrow$ LS transition is observed at room temperature around ~ 5 kbar accompanied by a colour change from white to deep purple. This property could be used for an application such as a pressure sensor or display [53].

It should also be noted that the LIESST phenomenon has been recently observed on these materials [53–55]. This discovery may lead to a new wave of photomagnetic investigations of these bistable materials in view of potential applications. The shape of the relaxation curves after LIESST could be modelled within the framework of a revised 1D Ising like model [56].

2.3

Two- and Three-Dimensional Bis-1,2,4-Triazole Compounds

$[\text{Fe}(\text{btr})_2(\text{NCX})_2] \cdot \text{H}_2\text{O}$ ($\text{X}=\text{S}, \text{Se}$; $\text{btr}=4,4'$ -bis-1,2,4-triazole) are 2D SCO compounds [57, 58]. In these systems, the $\text{Fe}(\text{II})$ ions are surrounded by two thiocyanate anions filling the apical positions of a compressed octahedron at 2.125(3) Å and four nitrogen atoms belonging to the triazole rings with $\text{Fe}-\text{N}$ distances at 2.180(3) Å and 2.188(2) Å, which are typical for HS $\text{Fe}(\text{II})$. Each iron ion is bridged by one $\text{N1}, \text{N1}'$ coordinating btr ligand defining an infinite stack of layered grids (Fig. 6). Non-coordinated water molecules are linked by hydrogen bonding to the peripheral nitrogen atoms of the triazole. The layers are connected by means of van der Waals forces and weak hydrogen bond bridges involving the water molecules [59].

$[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ undergoes a complete ST centred at ~ 134 K with a hysteresis loop of width ~ 21 K. This derivative represents the first example of a 2D ST compound and has become a model material in SCO research. The presence of a crystallographic phase transition to account for the observed hysteresis was first proposed since crystal cracking was regularly observed when the sample was cooled through the temperature region of the spin transition [59]. Recent X-ray data recorded at 95 K, where the com-

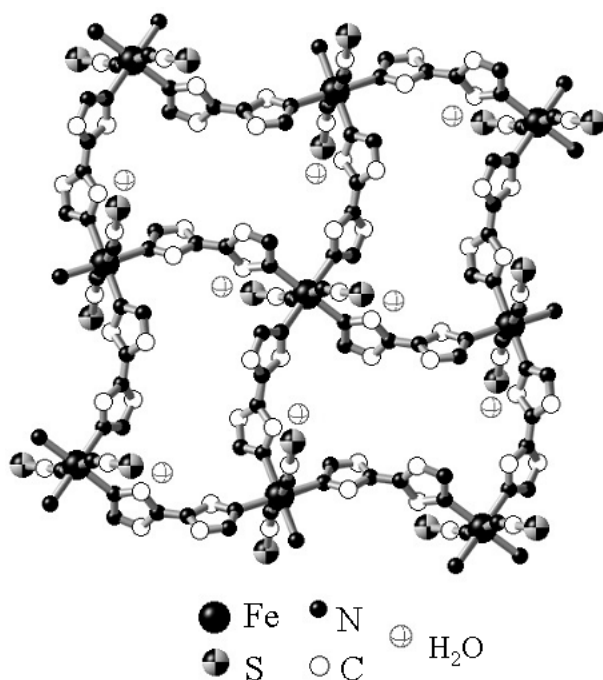


Fig. 6 Representative fragment of the layered structure of $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$

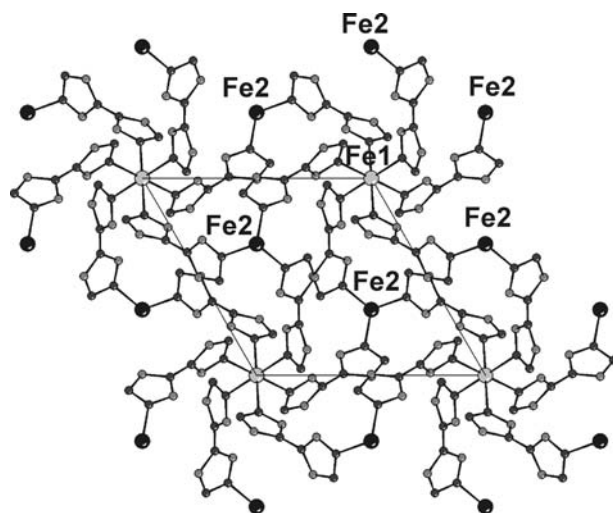


Fig. 7 Projection of the crystal structure of $[\text{Fe}(\text{btr})_3](\text{ClO}_4)_2$ on the (ab) plane. The hydrogen atoms and the perchlorate anions are omitted for clarity

pound is in the LS state, proved however that the C2/c space group is retained in the HS and LS phases [60]. Thus, the origin of the broad thermal hysteresis loop can be attributed to strong elastic interactions maintained by the polymeric character of the compound. $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ has also been subjected to pressure studies [61–64]. Application of hydrostatic pressure (≤ 10.5 kbar) surprisingly results in stabilisation of the HS state [62], contrary to the normal expectation that pressure should stabilise the LS state due to its smaller volume. On release of the pressure, the HS state remains partially trapped. After thermal relaxation of the metastable HS state obtained by light switching at 10 K (LIESST effect), a pure LS state is observed in contrast to the pressure experiments. This different behaviour suggests that pressure leads to a structural modification that is presumably responsible of the pressure-induced HS state [62].

The ST is observed as expected at higher temperatures (~ 214 K) for $[\text{Fe}(\text{btr})_2(\text{NCSe})_2] \cdot \text{H}_2\text{O}$ but occurs with a narrower hysteresis (~ 6 K) [58].

$[\text{Fe}(\text{btr})_3](\text{ClO}_4)_2$ represents the first polymeric 3D ST compound [65]. Its crystal structure consists of $\text{Fe}(\text{II})$ ions located on a threefold symmetry axis and an inversion centre, which are connected in three dimensions via bis-monodentate btr ligands (Fig. 7). Non-coordinated perchlorate anions are located in the voids of the 3D architecture and are connected to the triazole rings through weak $\text{CH} \cdots \text{O}$ hydrogen bonding interactions. The magnetic properties recorded below room temperature reveal a spin conversion occurring in two steps with a plateau of width ~ 20 K (Fig. 8). The high-temperature step is gradual while the low-temperature step is abrupt and reveals a

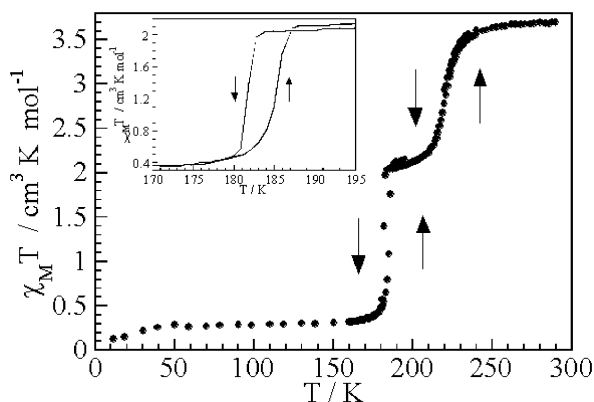


Fig. 8 $\chi_M T$ vs T plot for $[\text{Fe}(\text{btr})_3](\text{ClO}_4)_2$ in the 4.2–300 K range. The insert shows the hysteresis loop for the lower step of the spin conversion

hysteresis loop of width ~ 3 K (see insert of Fig. 8). Single-crystal X-ray analysis at 260 K, 190 K and 150 K together with temperature dependent ^{57}Fe Mössbauer spectroscopy have proved that this additional step is due to consecutive spin conversions occurring in two distinct Fe(II) sites [65]. No change of space group was observed between 260 K and 150 K. However, an interesting correlation between the variation of the dihedral angle between the two five-membered rings of the bistriazole moieties at one Fe(II) site and that at the other site, observed on cooling, and the steepness of the SCO behaviour has been noticed. The variation is $\sim 2^\circ$ between 260 K (77.35°) and 190 K (79.72°), and $\sim 7^\circ$ on cooling to 150 K (87.17°), which is close to the value found for the free btr (91.9°) [66]. Consequently, this suggests that the more drastic this variation, the more abrupt is the spin conversion for this Fe(II) compound.

Other Fe(II) btr coordination polymers with monovalent anions have been obtained [9, 67, 68]. $[\text{Fe}(\text{btr})_3](\text{CF}_3\text{SO}_3)_2$ is a HS compound. The stabilisation of the HS state is presumably due to the large size of the trifluoromethanesulfonate anion, which could increase the size of the cavities and, by mechanical influence, the Fe–N bond lengths, precluding the thermal spin crossover [9]. X-ray investigations should clarify this behaviour. Iron(II) btr compounds with BF_4^- and PF_6^- anions exhibit incomplete TSCO, with $T_{1/2} \sim 150$ K and 170 K, respectively. Interestingly, the 3D architecture of $[\text{Fe}(\text{btr})_3](\text{ClO}_4)_2$ is not retained in these derivatives as water molecules are detected in the coordination sphere of some Fe species [68].

3 Tetrazole Systems

$[\text{Fe}\{\text{N}(\text{entz})_3\}_2]\text{A}_2$ with $\text{A}=\text{BF}_4^-$, ClO_4^- with $\text{N}(\text{entz})_3=\text{tris}[(\text{tetrazol-1-yl})\text{-ethane}]$ amine, are polymeric Fe(II) ST complexes of a 1-substituted tetrazole derivative [69, 70].

The coordination to Fe(II) occurs through the N4 nitrogen atoms of the tetrazole rings which are provided by the tris-unidentate ligand $\text{N}(\text{entz})_3$ leading to a 2D grid for $[\text{Fe}\{\text{N}(\text{entz})_3\}_2](\text{BF}_4)_2$ (Fig. 9) [70]. An abrupt and complete ST with a thermal hysteresis loop of width ~ 9 K was observed ($T_{1/2\uparrow}=176$ K and $T_{1/2\downarrow}=167$ K). For the perchlorate derivative, a similar ST curve is observed, shifted to lower temperatures with $T_{1/2\uparrow}=168$ K and $T_{1/2\downarrow}=157$ K.

Following this discovery, a new family of Fe(II) coordination polymers was obtained by selecting ligands bearing two 1-R tetrazole groups separated by an alkyl chain of variable length. Their ST properties and structural aspects are described here. The reader is referred to Chap. 5 for further details. These compounds of formula $[\text{FeL}_3]\text{A}_2$ show a variety of SCO behaviour ranging from smooth to abrupt and even hysteretic [70–73]. $[\text{Fe}(\text{btzp})_3](\text{ClO}_4)_2$ (btzp=1,2-bis(tetrazol-1-yl)propane) is a Fe(II) polymeric compound exhibiting a gradual and incomplete spin conversion around 130 K [71]. The crystal structure consists of linear chains made up of Fe(II) ions linked by three $\text{N4}, \text{N4}'$ coordinating btzp ligands. The methyl substituents in the propane spacer are disordered over two positions (Fig. 10).

The relatively low cooperativity of this 1D system has been attributed to the flexibility of the btzp bridging ligand, which may act as a shock absorber against the elastic interactions between active SCO sites, as well as to the absence of a hydrogen bonding network. This compound undergoes the

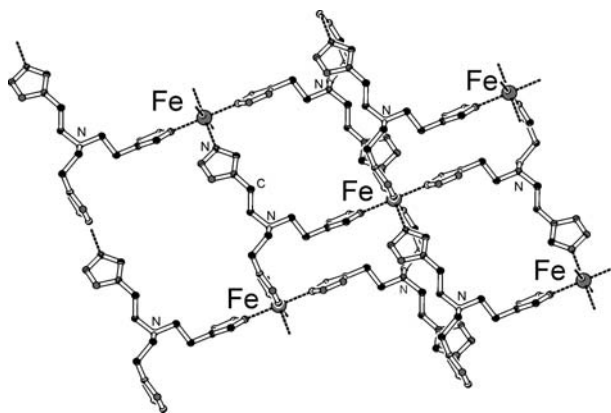


Fig. 9 Part of the crystal structure of $[\text{Fe}\{\text{N}(\text{entz})_3\}_2](\text{BF}_4)_2$ at 293 K. Counteranions and hydrogen atoms have been omitted for clarity

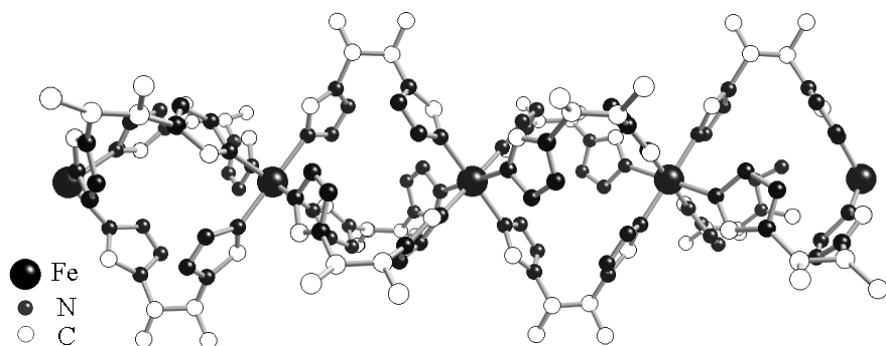


Fig. 10 View of the crystal structure of $[\text{Fe}(\text{btzp})_3](\text{ClO}_4)_2$ along the a axis. Perchlorate anions and hydrogen atoms have been omitted for clarity

LIESST effect at 5 K. The BF_4^- derivative displays a similar TSCO behaviour, shifted by 20 K towards higher temperatures. The 1D SCO compound $[\text{Fe}(\text{btze})_3](\text{BF}_4)_2$ (btze=1,4-bis(tetrazol-1-yl)ethane) with $T_{1/2} \sim 140$ K has also been reported [73].

$[\text{Fe}(\text{btzb})_3](\text{ClO}_4)_2$ (btzb=1,4-bis(tetrazol-1-yl)butane) undergoes a sharp thermal ST around 160 K with an hysteresis loop of width ~ 20 K, involving a limited fraction of Fe(II) ions as deduced from ^{57}Fe Mössbauer spectroscopy [72]. Irradiation with green light at 30 K leads to population of the metastable HS state for the thermally active Fe(II) ions. The ST is surprisingly highly cooperative with respect to the relatively small proportion of active sites involved in the switching process. Actually, a progressive loss of solvent molecules is presumably responsible for the disappearance of SCO properties. Thus, aged samples of $[\text{Fe}(\text{btzb})_3](\text{ClO}_4)_2$ are HS over the whole temperature range. This new phase can be switched to the LS state with red light. Interestingly, this experiment reveals a two step light-induced hysteresis [74].

4 Pyridine Type Systems

4.1

Two-Dimensional Pyridine-Type $[\text{FeL}_2(\text{NCS})_2]$ Compounds

The search for new coordination SCO polymers based on the assembling of iron(II) and bridging molecules other than 1,2,4-triazole- or 1-R-tetrazole-based ligands has afforded a series of frameworks closely related to the 2D system $[\text{Fe}(\text{btr})_2(\text{NCX})_2] \cdot \text{H}_2\text{O}$ ($\text{X}=\text{S}, \text{Se}$). This series of compounds formulated as $[\text{FeL}_2(\text{NCS})_2] \cdot n\text{Solv}$ can be considered as derived from the formal substitution of btr by bis-monodentate pyridine-like ligands such as bispyridylethylene (bpe, $n=1$, $\text{Solv}=\text{MeOH}$), *trans*-4,4'-azopyridine (azpy,

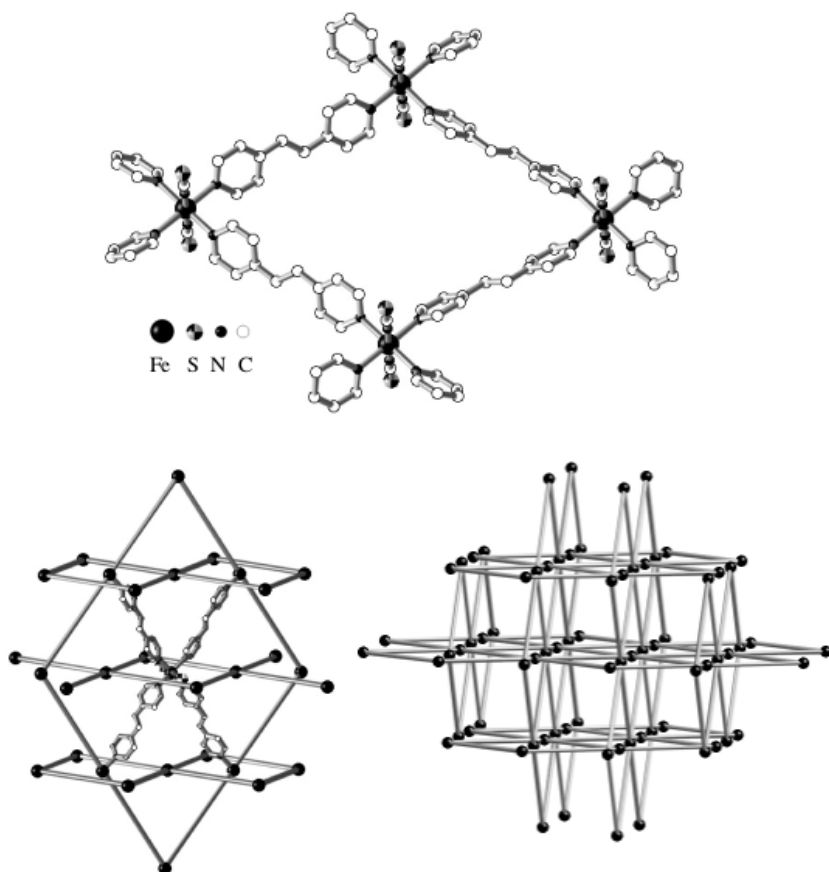


Fig. 11 (*Top*) Perspective view of an $[\text{Fe}]_4$ rhombus in the $[\text{Fe}(\text{bpe})_2(\text{NCS})_2] \cdot \text{CH}_3\text{OH}$ 2D polymer. (*Bottom*) Schematic representation of the interpenetration of a layer lying in the plane of the sheet and three orthogonal layers (left). Perspective view of the crossing of two independent net systems defining the rectangular channels (right). Balls and sticks represent iron atoms and bpe ligands, respectively

Solv=MeOH, EtOH and PrOH), and 1,4-bis(4-pyridyl-butadiyne) (bpb, $n=0.5$, Solv=MeOH). Like the btr derivative, compressed $[\text{FeN}_6]$ pseudo-octahedral sites define the knots of the square- or rhombus-shaped windows, which constitute the layered grid structure of the three compounds. Stacking of these layers in the crystal defines their most important structural differences, which are determined by the ligand size and crystal packing efficiency. In principle, the 2D grids are organised in a fashion similar to that described for the $[\text{Fe}(\text{btr})_2(\text{NCX})_2] \cdot \text{H}_2\text{O}$ system: the parallel layers are alternated so that the iron atoms of one layer lie vertically above and below the centres of the squares formed by the iron atoms of the adjacent layers.

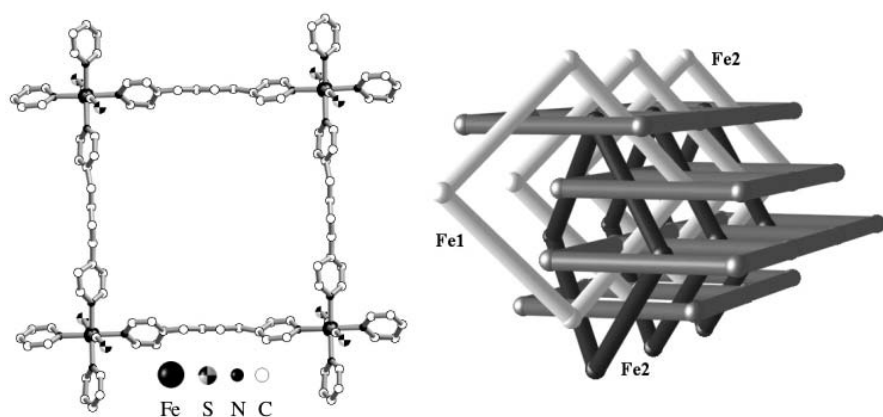


Fig. 12 (Left) Perspective view of a $[\text{Fe}]_4$ square fragment of the $[\text{Fe}(\text{bpb})_2(\text{NCS})_2] \cdot 0.5\text{CH}_3\text{OH}$ polymer. (Right) View of the interpenetrated array of three mutually orthogonal layers (rods represent the bpb ligands and balls the iron atoms)

However, the much larger window size defined by the bpe, and azpy ligands with respect to the btr ligand allows perpendicular interpenetration of two equivalent sets of layers, each one organised as in the $[\text{Fe}(\text{btr})_2(\text{NCX})_2] \cdot \text{H}_2\text{O}$ system. Intersection of both sets of layers defines large rectangular channels, where solvent molecules are located, conferring a porous character to the resulting framework (Fig. 11) [75]. The bpb ligand, even larger than bpe and azpy ligands, allows the formation of $[\text{Fe}(\text{bpb})_2(\text{NCS})_2] \cdot 0.5\text{MeOH}$, an unprecedented framework made up of three different arrays of mutually perpendicular interlocked 2D networks. Two crystallographically independent iron atoms, Fe1 and Fe2, define the knots of the layers. Fe1 defines a parallel array, stacked along the [001] direction and Fe2 defines, similarly to the bpe and azpy derivatives, two equivalent arrays of perpendicular interlocked layers running along [110] and $[-110]$ directions, respectively (Fig. 12) [76].

$[\text{Fe}(\text{bpe})_2(\text{NCS})_2] \cdot \text{MeOH}$ undergoes SCO behaviour whose extent and steepness are very sensitive to sample preparation and history showing different HS and LS residual fractions at low and high temperature, respectively. This behaviour was associated with the particular nature of the extended porous framework with large channels where crystalline defects and molecular inclusions exert, most likely, subtle structural and electronic effects with dramatic consequences on the SCO regime [75]. This question has been nicely clarified by Halder and coworkers who have reported the compound $[\text{Fe}(\text{azpy})_2(\text{NCS})_2] \cdot \text{Solv}$, a system having essentially the same structure as $[\text{Fe}(\text{bpe})_2(\text{NCS})_2] \cdot \text{MeOH}$ [77]. Full structural and magnetic characterisation of the solvated and unsolvated crystals of the $[\text{Fe}(\text{azpy})_2(\text{NCS})_2]$ framework shows reversible guest-dependence of both the structural and SCO behav-

ious. The fully solvated form undergoes SCO down to 150 K whereas the unsolvated form is HS over the whole range of temperature. Desorption of the solvent induces gradual disappearance of the crossover and replacement by the HS ground state. Conversely, exposure of the crystals to solvent molecules regenerates the original SCO behaviour [77]. This system is discussed further by Murray and Kepert in Chap. 8.

$[\text{Fe}(\text{bpb})_2(\text{NCS})_2] \cdot 0.5\text{MeOH}$ undergoes a continuous 50% spin conversion with $T_{1/2} \sim 139$ K. The occurrence of 50% conversion has been ascribed to the presence of two different iron sites. In this respect, it is worth noting that site Fe1 is more susceptible than site Fe2 to undergo SCO as the former displays shorter average Fe-N bond distances. This fact is presumably related to the strong interaction observed between solvent molecules and site Fe1 [76]. As in the previous examples, interaction of the solvent molecules with the Fe(II) centres has remarkable consequences for the SCO regime.

4.2

Two- and Three-Dimensional $\{\text{Fe}(\text{L})_x[\text{M}(\text{CN})_4]\}$ Hofmann-Like Cyanide Compounds

Hofmann clathrates [78, 79] belong to the well-known family of metal-cyanide complexes [80]. The formula of the original Hofmann clathrates is $\{\text{Ni}(\text{NH}_3)_2[\text{Ni}(\text{CN})_4]\} \cdot 2\text{G}$ (G = a guest molecule usually benzene, pyrrole, thiophene or furane). Their crystal structure was solved in the 1950s by Powell and Rayner [80–82]. It is constituted of two different nickel(II) ions, one belongs to the diamagnetic square-planar anion $[\text{Ni}(\text{CN})_4]^{2-}$ and the other is octahedrally coordinated by four nitrogen atoms of four $[\text{Ni}(\text{CN})_4]^{2-}$ groups, which define the equatorial plane, and two nitrogen atoms belonging to two ammonia molecules. Consequently, both kinds of nickel(II) atoms bridged by the cyanide groups define a 2D square-grid network. The layers stack along the *c* direction and are separated by ca. 8 Å, which allows inclusion of guest molecules (Fig. 13, left).

The first attempts to synthesise new series of Hofmann-like clathrates were reported by Baur and Schwarzenbach in 1960 [83], the goal was to replace the octahedrally coordinated nickel(II) ions by other divalent transition and post-transition metal ions like Cd(II), Cu(II) or Zn(II). However, it was in the 1980s that Iwamoto et al. gave an important impetus to this field [84, 85]. These authors synthesised the series of compounds $\{\text{M}(\text{NH}_3)_2[\text{M}'(\text{CN})_4]\} \cdot 2\text{G}$, where $\text{M} = \text{Mn(II)}$, Fe(II) , Co(II) , Ni(II) , Zn(II) , Cd(II) or Cu(II) ; $\text{M}' = \text{Ni(II)}$, Pd(II) or Pt(II) ; $\text{G} = \text{benzene}$, pyrrole, thiophene, dioxane, aniline or biphenyl. They also investigated the possibility of increasing the dimensionality from two to three by replacing the ammonia ligands by diamines like ethylenediamine or 1,4-diaminobutane (Fig. 13 right) or methanolamine [84], which may act as bis-monodentate bridging ligands.

Later, Kitazawa et al. synthesised the modified Hofmann 2D polymeric system $\{\text{Fe}(\text{py})_2[\text{Ni}(\text{CN})_4]\}$, where the ammonia ligands were replaced by

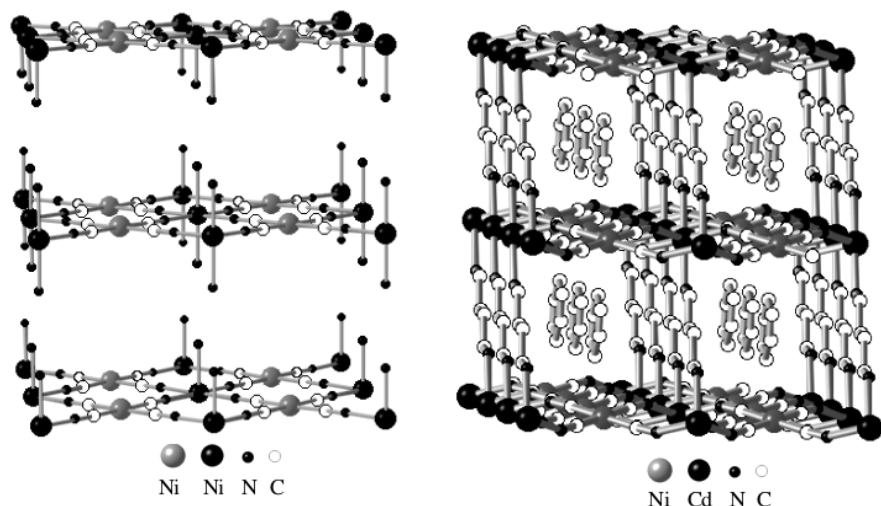


Fig. 13 (Left) Perspective view of the 2D Hofmann clathrate $\{\text{Ni}(\text{NH}_3)_2[\text{Ni}(\text{CN})_4]\} \cdot 2\text{G}$. (Right) Perspective view of the 3D Hofmann clathrate $\{\text{Cd}(\text{1,4-diaminobutane})[\text{Ni}(\text{CN})_4]\} \cdot \text{benzene}$

two pyridine (py) rings [86]. The different size and shape of both ligands has a dramatic effect on the crystal packing of the metal-cyanide layers as they glide until reaching a more efficient crystal packing: the iron(II) atom of one particular layer is in the vertical of the Ni(II) atoms of the layers immediately below and above (Fig. 14). This is the reason why the small effective void generated between the layers makes the inclusion of guest molecules more difficult. The thermal dependence of χ_{MT} for $\{\text{Fe}(\text{py})_2[\text{Ni}(\text{CN})_4]\}$ (Fig. 15, left) shows the occurrence of a cooperative ST with a hysteresis loop ca. 10 K wide, $T_{1/2\downarrow} \approx 186$ K and $T_{1/2\uparrow} \approx 196$ K. More recently, Niel et al. have observed similar behaviour for the Pd and Pt homologues [87]. These also display cooperative spin transitions with the following transition temperatures, $T_{1/2\downarrow} \approx 208, 208$ K and $T_{1/2\uparrow} \approx 213, 216$ K for the Pd and Pt derivatives, respectively. For all three systems $\{\text{Fe}(\text{py})_2[\text{M}(\text{CN})_4]\}$ (M=Ni, Pd, Pt) a dramatic change of colour upon spin conversion from white or pale yellow in the HS state to deep garnet in the LS state is observed.

These findings represent the first step towards a novel strategy to synthesise new polymeric SCO compounds. They also provide the possibility to change the dimensionality from two to three without inducing drastic modifications in the crystal structure, and to analyse any changes in the degree of cooperativity resulting from changes in the dimensionality of the network. In this regard, based on the $\{\text{Fe}(\text{py})_2[\text{M}'(\text{CN})_4]\}$ 2D system, a new series of 3D SCO compounds has been isolated. The straightforward replacement of the py ligand by a pyrazine (pz) ligand in the 2D system affords the new

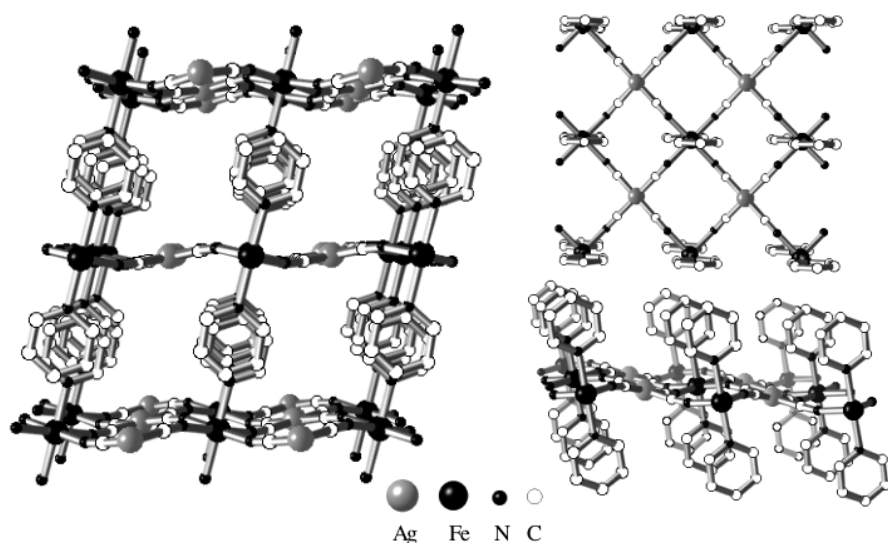


Fig. 14 Stacking of three consecutive layers (*left*) and two different perspectives of a layer (*right*) of the 2D $\{\text{Fe}(\text{py})_2[\text{Ni}(\text{CN})_4]\}$ system

family of 3D compounds $\{\text{Fe}(\text{pz}) [\text{M}'(\text{CN})_4]\} \cdot 2\text{H}_2\text{O}$ ($\text{M}=\text{Ni}$, Pd or Pt) [87]. In this structure the pz ligand bridges the iron(II) atoms of consecutive layers, achieving a pillaring of the 2D metal-cyanide sheets by vertical columns of the pz bridge to give the 3D structure (Fig. 16).

The magnetic properties of the py and pz compounds are compared in Fig. 15. The 3D derivatives undergo more strongly cooperative spin transitions than the corresponding 2D counterparts as indicated by the increase in width of the hysteresis loop (range 20–40 K). The significantly higher transition temperatures observed for the pz derivatives compared with their py counterparts cannot be explained in terms of the spectrochemical series

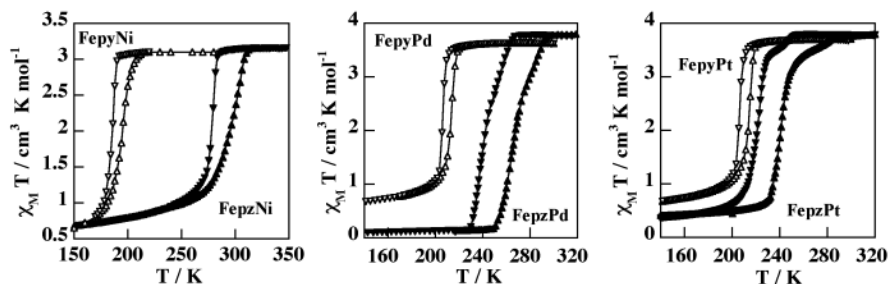


Fig. 15 $\chi_M T$ vs T plots for the 2D $\{\text{Fe}(\text{py})_2[\text{M}(\text{CN})_4]\}$ (white triangles) and 3D $\{\text{Fe}(\text{pz})[\text{M}(\text{CN})_4]\} \cdot 2\text{H}_2\text{O}$ (black triangles) coordination polymers with $\text{M}=\text{Ni}(\text{II})$, $\text{Pd}(\text{II})$, $\text{Pt}(\text{II})$

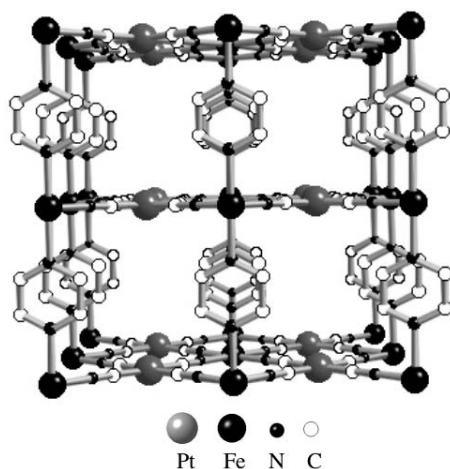


Fig. 16 Fragment of the $\{\text{Fe}(\text{pz})[\text{M}(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ ($\text{M}=\text{Ni}, \text{Pd}, \text{Pt}$) 3D coordination polymer

since py imparts a stronger ligand field than pz. Thus, the internal pressure originating in the more rigid 3D structures may be responsible for the effective stronger ligand field at iron(II) site. Both findings, broader hysteresis loops and higher $T_{1/2}$, can be considered to be a direct consequence of the difference in the dimensionality in two closely related structures.

4.3

Three-Dimensional Double Interpenetrated Structures $\{\text{Fe}(\text{L})_x[\text{Ag}(\text{CN})_2]\cdot \text{Guest}$

The important structural work done by Iwamoto et al. in the field of the heterobimetallic cyanide bridged compounds combined with the interest of $\{\text{Fe}(\text{L})_x[\text{M}'(\text{CN})_4]\cdot n\text{H}_2\text{O}$ ($\text{L}=\text{py}$, $x=2$, $n=0$; $\text{L}=\text{pz}$, $x=1$, $n=2$; $\text{M}'=\text{Ni}, \text{Pd}, \text{Pt}$) in the SCO field have motivated the search for new 3D SCO iron(II) polymers based on the capability of the diacyanoargentate anion, $[\text{Ag}(\text{CN})_2]^-$, and organic ligands like pz, 4,4'-bipy (4,4'-bipyridine) or bpe to induce polymerisation. The resulting systems $\{\text{Fe}(\text{L})_x[\text{Ag}(\text{CN})_2]_2\cdot \text{G}$, where L is pz ($x=1$, $\text{G}=\text{pz}$), 4,4'-bipyridine ($x=2$; 4,4'-bipy) and bpe ($x=2$), can be considered as a new kind of bimetallic doubly interpenetrated 3D coordination polymer [88]. As in the parent family of bimetallic SCO compounds, the iron atom and the $[\text{Ag}(\text{CN})_2]^-$ define a 2D network consisting of edge-shared $\{\text{Fe}_4[\text{Ag}(\text{CN})_2]_4\}$ rhombuses. All iron and silver atoms are coplanar and the layers alternate in such a way that the iron atoms in a particular layer are above and below, but slightly displaced from, the centres of the windows defined by the $\{\text{Fe}_4[\text{Ag}(\text{CN})_2]_4\}$ moieties belonging to the adjacent layers. The pz ligand connects two iron atoms of the adjacent layers and meshes the $\{\text{Fe}_4[\text{Ag}(\text{CN})_2]_4\}$ window of the contiguous layer defining two mutually inter-

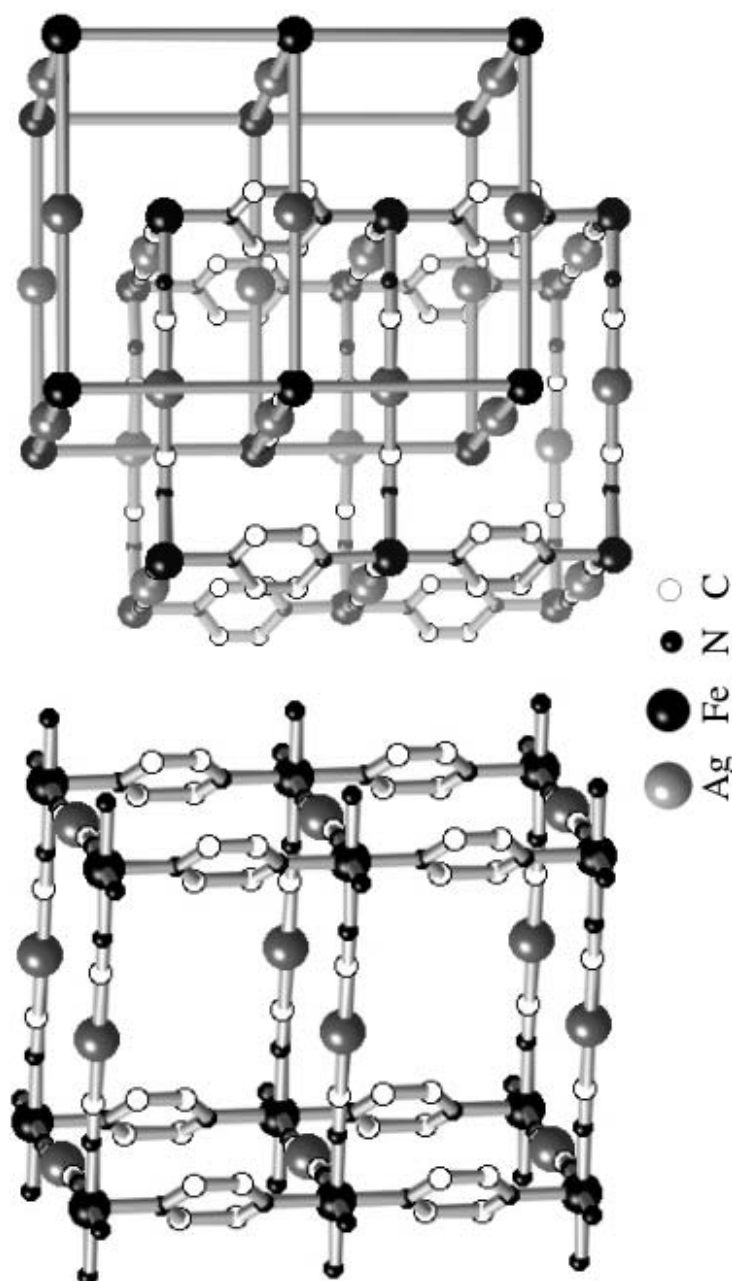


Fig. 17 (*Left*) Fragment of the 3D network of $[\text{Fe}(\text{pz})[\text{Ag}(\text{CN})_2]_2 \cdot \text{pz}]$. (*Right*) View of the double interpenetration of two identical nets

penetrated equivalent 3D networks (Fig. 17). The 2D networks stack in such a way that each pz ligand connects, through the axial positions of the iron(II) octahedron, two alternate layers so that interpenetration of two 3D identical subnets takes place. It is worth noting that no interpenetration is

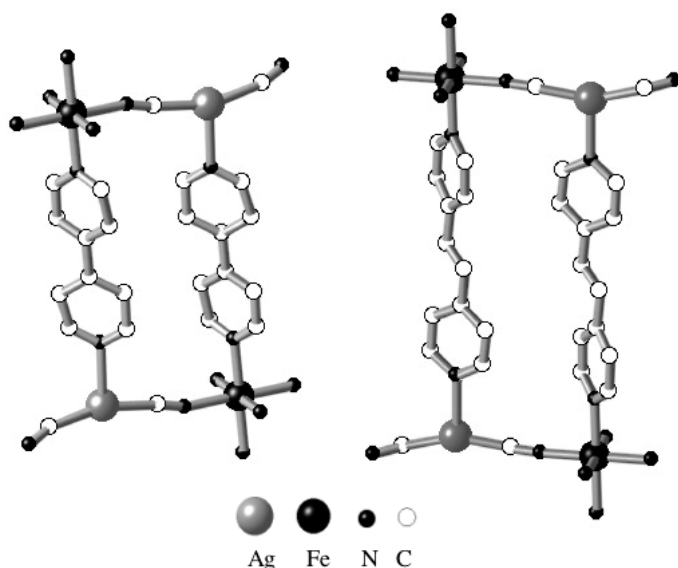


Fig. 18 Coordination scheme of the 3D $\{\text{Fe}(\text{L})_2[\text{Ag}(\text{CN})_2]_2\}$ ($\text{L}=4,4'$ -bipy (left) and bpe (right)) coordination polymers

observed for the $\{\text{Fe}(\text{pz})[\text{M}'(\text{CN})_4]\cdot 2\text{H}_2\text{O}\}$ compounds as the void defined by the tetradentate ligand $[\text{M}'(\text{CN})_4]^{2-}$ is four times smaller than the one in $\{\text{Fe}(\text{pz})[\text{Ag}(\text{CN})_2]_2\}\cdot \text{pz}$. The Fe-N(pz) bond distance observed for the former, 2.267(4) Å, is significantly longer than the one observed for the latter, 1.98(2) Å. This fact reflects the different ground state of these compounds since they are HS and LS at room temperature, respectively.

The 4,4'-bipy and bpe derivatives display a similar crystal structure to that of $\{\text{Cd}(4,4'\text{-bipy})_2[\text{Ag}(\text{CN})_2]_2\}$ reported by Iwamoto et al. [89]. It consists of the interpenetration of two identical 3D networks. The knots of the networks are defined by the iron(II) and silver(I) atoms. Each iron(II) atom located on an inversion centre defines an elongated octahedron whose axial positions are occupied by the nitrogen atoms of two 4,4'-bipy ligands. In addition, each 4,4'-bipy ligand binds a silver atom so that it is three-coordinated. This is the reason why the $[\text{Ag}(\text{CN})_2]^-$ group is bent (see Fig. 18).

The equatorial positions of the octahedron are occupied by the CN moieties of the $[\text{Ag}(\text{CN})_2]^-$ groups. As in the pz derivative, each $[\text{Ag}(\text{CN})_2]^-$ group connects two iron atoms defining the edges of a $\{\text{Fe}_4[\text{Ag}(\text{CN})_2]_4\}$ rhombus. However, the edge-shared rhombuses define 2D corrugated nets in contrast to the pz derivative, due to the three-coordination of the Ag atoms (see Fig. 19). A schematic view of one 3D network is depicted in Fig. 20.

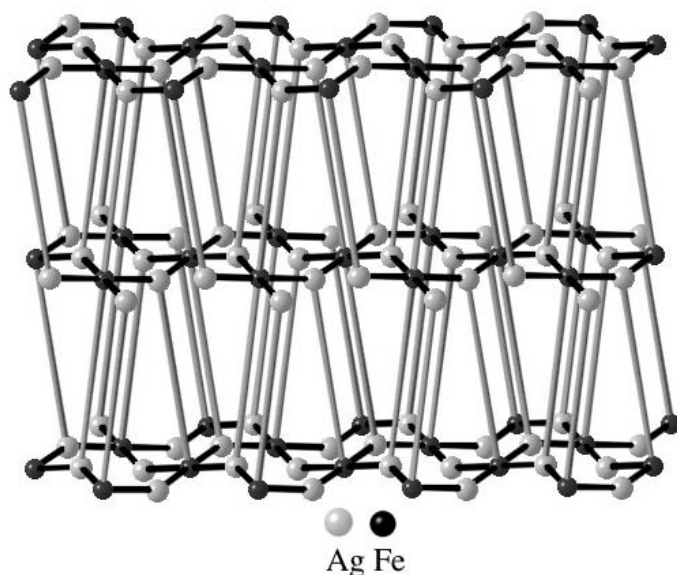


Fig. 19 Perspective view of three alternate 2D $\{Fe[Ag(CN)_2]_2\}_n$ corrugated layers connected by rods, which represent the organic ligand (4,4'-bipy and bpe). The void space in between these layers is occupied by an identical 3D network

Interpenetration takes place in a different way for the 4,4'-bipy and bpe derivatives. The axial positions of each iron atom are occupied by two organic ligands, but at variance with the pz derivative, these ligands link the Ag atoms belonging to alternate $\{Fe_4[Ag(CN)_2]_4\}_n$ sheets, so that each $\{Fe_4[Ag(CN)_2]_4\}$ window of a contiguous layer is threaded by two organic bridges.

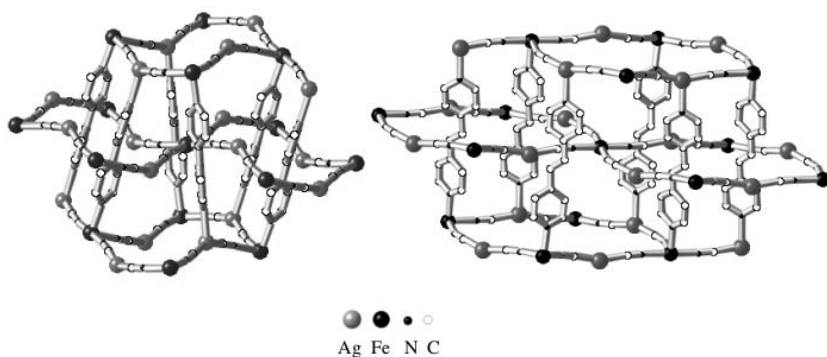


Fig. 20 View of the two interpenetrating networks in $\{Fe(L)_2[Ag(CN)_2]_2\}$ ($L=4,4'$ -bipy (left) and bpe (right))

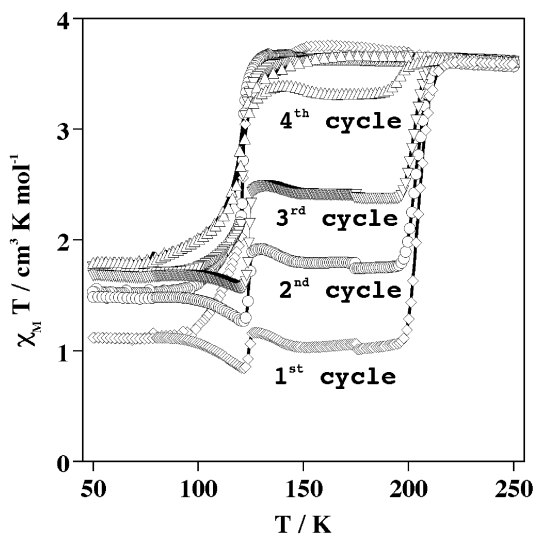


Fig. 21 $\chi_M T$ vs T plots for $\{\text{Fe}(\text{bpe})_2[\text{Ag}(\text{CN})_2]_2\}$. Different cooling-warming cycles show the loss of amplitude of the hysteresis loop

Despite the structural similarities of the bpe and 4,4'-bipy derivatives, the latter is HS in the whole range of temperature (the average Fe-N bond length is 0.011(9) Å greater for the 4,4'-bipy derivative), whereas the bpe derivative undergoes a very cooperative and single-step SCO at 1 bar. In fact, it shows one of the broadest thermal hysteresis loops observed for a SCO system, ca. 95 K wide, between 120 K and 215 K. Surprisingly, the ST becomes less complete after successive cooling and warming cycles, reaching ultimately 50% of conversion. The amplitude of the hysteresis loop decreases concomitantly in each cycle without affecting significantly its width (Fig. 21). Furthermore, the samples, constituted of single crystals, transform into a microcrystalline powder after five or more cycles. Single crystals and the microcrystalline powder display the same X-ray diffraction pattern indicating that no significant structural changes have been induced in the 3D polymer.

The 4,4'-bipy derivative undergoes incomplete, thermally induced SCO at 4.6 kbar and 4.8 kbar with estimated $T_{1/2}$ values ca. 100 K and 150 K, respectively. Interestingly, the system becomes essentially LS at room temperature at a pressure of 5.4 kbar. Similar behaviour is displayed by the bpe derivative. It is important to point out that 85% of the spin change takes place within the range of 2 kbar at room temperature suggesting that these 3D networks show strong cooperativity.

Photo-induced LS to HS spin conversion has been observed for the polycrystalline samples of the bpe derivative. Irradiation at 10 K with orange light (600 nm) induces a quantitative transformation of the LS ground state

into the HS metastable state. The system relaxes back to the ground state at ca. 80 K.

5 Concluding Remarks

We have reviewed SCO phenomena occurring in the most important series of Fe(II) polymeric complexes. Their structural aspects and topology have been discussed in the context of cooperative effects associated with the spin transitions. Some were found to exhibit large hysteresis effects, which can be of interest for possible application in memory devices and displays. The interplay between dimensionality and cooperativity of the SCO phenomenon in these polymeric species has also been addressed, and found to depend on many molecular parameters such as the type of linkage between active sites and supramolecular interactions. Such results are very important in the quest for a general relationship between dimensionality of the structures and cooperative effects of the spin transitions as, at this stage, it is still rather difficult to predict whether a specific crystal packing will lead to a given cooperative spin transition.

There is no doubt that further novel and fascinating polymeric species exhibiting SCO phenomena will be soon discovered. An Fe(II) system showing a reversible guest-dependent SCO has for instance recently been outlined, a finding that could have some implications in molecular sensing [77]. Indeed, the remarkable interest of this result is connected to the important expectation generated by the synthesis of zeolite-like metallo-organic porous networks with potential relevance to various fields such as catalysis, absorption and host-guest chemistry. In these systems the metal ion is considered usually as an assembling and templating tool for the construction of the supramolecular scaffolding. However, incorporation of electronically labile SCO centres may lead to a different kind of functionality, in addition to chemical reactivity, which may be important for developing sensors and information storage devices.

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Iron(III) Spin Crossover Compounds

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Abstract In this chapter, selected results obtained so far on Fe(III) spin crossover compounds are summarized and discussed. Fe(III) spin transition materials of ligands containing chalcogen donor atoms are considered with emphasis on those of *N,N*-disubstituted-dithiocarbamates, *N,N*-disubstituted-XY-carbamates (XY=SO, SSe, SeSe), X-xanthates (X=O, S), monothio- β -diketonates and X-semicarbazones (X=S, Se). In addition, attention is directed to Fe(III) spin crossover systems of multidentate Schiff base-type ligands. Examples of spin inter-conversion in Fe(III) compounds induced by light irradiation are given.

Keywords Spin crossover · Fe(III) · Dithiocarbamate · Thiosemicarbazone · Schiff base

List of Abbreviations

H ₂ thsa	Salicylaldehyde thiosemicarbazone
H ₂ Phthsa	Salicylaldehyde phenylthiosemicarbazone
H ₂ sesa	Salicylaldehyde selenosemicarbazone
H ₂ thpu	Pyruvic acid thiosemicarbazone
H ₂ sespu	Pyruvic acid selenosemicarbazone
H ₂ thpy	Pyridoxal 4- <i>R</i> -thiosemicarbazone
H-3-OEt-salAPA	Schiff base derived from 3-ethoxysalicylaldehyde and <i>N</i> -aminopropylaziridine
HsalAEA	Schiff base derived from salicylaldehyde and <i>N</i> -(2-aminoethyl)aziridine
Hsapa	<i>N</i> -Salicylidene-2-pyridylmethylamine
Hvapa	<i>N</i> -(3-Methoxysalicylidene)-2-pyridylmethylamine
H-3-CH ₃ OSPH	Schiff base derived from 3-methoxysalicylaldehyde and 2-pyridylhydrazine
H-X-salmeen	Schiff base derived from X-salicylaldehyde and <i>N</i> -methylethylenediamine
H-X-saleen	Schiff base derived from X-salicylaldehyde and <i>N</i> -ethylethylenediamine
H-X-salbzen	Schiff base derived from <i>N</i> -benzylethylenediamine and X-substituted salicylaldehyde
Hacea	Schiff base derived from 2,4-pentanedione and 1,2-diaminoethane
Hacpa	<i>N</i> -(1-Acetyl-2-propylidene)(2-pyridylmethyl)amine
Hbzpa	(1-Benzoylpropen-2-yl)(2-pyridylmethyl)amine
Hqsal	<i>N</i> -(8-Quinolyl)-salicylaldimine
Hpap	2-Hydroxyphenyl-(2-pyridyl)-methaneimine
cyclam	1,4,8,11-Tetraazacyclotetradecane
tcyclam	1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane
H ₂ amben	Schiff base derived from 2-aminobenzaldehyde and ethylenediamine
H ₂ salen	<i>N,N'</i> -Ethylenebis(salicylideneamine)
H ₂ salphen	<i>N,N'</i> - <i>o</i> -Phenylenebis(salicylideneamine)
Him	Imidazole
H ₂ -3-OCH ₃ -salpen	<i>N,N'</i> -1,2-Propylenebis(3-methoxysalicylideneamine)

H ₂ -3-OC ₂ H ₅ -sal-CH ₃ -phen	N,N'-3,4-Toluenebis(3-ethoxysalicylideneamine)
H ₂ acen	N,N'-Ethylenebis(acetylacetylidenamine)
H ₂ bzacen	N,N'-Ethylenebis(benzoylacetylidenamine)
H ₂ salacen	Ethylene(<i>N</i> -acetylacetylidenimine) (<i>N'</i> - α -methylsalicylideneimine)
H ₂ salten	N,N'-Bis[(2-hydroxy-phenyl)methylene]-4-azaheptane-1,7-diamine
H ₂ bpN	N,N'-Bis[(2-hydroxy-phenyl)phenylmethylene]-4-azaheptane-1,7-diamine
H ₂ mbpN	N,N'-Bis[(2-hydroxy-5-methyl-phenyl)phenylmethylene]-4-azaheptane-1,7-diamine
H ₂ sal ₂ trien	Schiff base obtained from the 1:2 condensation of triethylenetetramine with salicylaldehyde
H ₂ acac ₂ trien	Schiff base obtained from the 1:2 condensation of triethylenetetramine with acetylacetone
H ₂ bzac ₂ trien	Schiff base obtained from the 1:2 condensation of triethylenetetramine with benzoylacetone
H ₂ tfac ₂ trien	Schiff base obtained from the 1:2 condensation of triethylenetetramine with trifluoroacetylacetone
Mepepy	1-(Pyridin-4-yl)-2-(<i>N</i> -methylpyrrol-2-yl)-ethene

1

Introduction

1.1

The Discovery of the Spin Crossover Phenomenon for Iron(III) Compounds

Iron(III) occupies a unique position in the development of the spin crossover area since it was for derivatives of this ion that the phenomenon was first discovered. In 1931 Cambi and Szegő reported the unusual temperature dependence of the magnetic susceptibility of various tris(*N,N*-dialkyl-dithiocarbamato)iron(III) compounds [1, 2]. Their initial interpretation of this was in terms of two different magnetic isomers. At higher temperatures, an isomer having five electrons arranged in the d-orbitals according to Hund's rule ($S=5/2$) was proposed to account for the relatively high magnetic moment. The lower magnetic response observed at lower temperatures was attributed to a second isomer in which the d-orbitals are occupied by nine electrons, five of these originating from the 3d⁵ iron(III) ion supplemented with four electrons from the ligands, resulting in a total spin of $S=1/2$ [2]. This explanation was based on two different dipole moments present in the isomers, and a thermal equilibrium between these two species with different dipole moments was proposed. Although their assumption of dipole mo-

ments being involved in this phenomenon was later shown to be erroneous, their interesting results certainly attracted the attention of other researchers. This led to the correct description of the Fe(III) spin crossover phenomenon in terms of the two arrangements of the five 3d electrons possible for octahedral complexes depending on the strength of the ligand field. The situation is very similar to that described in Chap. 2 by Hauser for Fe(II) ($3d^6$), the important difference being in the actual spin multiplicity of the low spin and high spin states, for iron(III) these being a doublet $^2T_2$ and a sextet $^6A_1$, respectively [3].

1.2

Scope of the Chapter

In the following sections an overview is given of the progress made in the Fe(III) spin crossover research field. Section 2 deals with Fe(III) spin transition materials containing ligands with chalcogen donor atoms, such as the dithiocarbamates, whereas Sect. 3 focuses on the use of multidentate Schiff base-type ligands to generate Fe(III) spin crossover. Concluding remarks may be found in Sect. 4.

2

Iron(III) Spin Crossover Systems with Chalcogen Donor Atoms

2.1

Tris(*N,N*-Disubstituted-Dithiocarbamato)Iron(III) Compounds

2.1.1

General Considerations

Since the appearance of the first reports by Cambi and Szegő [1, 2], the tris(*N,N*-dialkyl-dithiocarbamato)iron(III) compounds have been extensively studied and the later work has included detailed structural characterisation by X-ray diffraction methods. In addition, new dithiocarbamato-based Fe(III) spin crossover materials have been prepared, those having the alkyl substituents as part of a ring system being of particular note. A schematic representation of the structure of tris(*N,N*-disubstituted-dithiocarbamato)iron(III) is given in Fig. 1, and relevant crystallographic and magnetic data are compiled in Table 1.

These compounds are first characterised by their magnetic behaviour. The spin-only high spin value of Fe(III) is 5.92 B.M., while a normal range for its low spin values in cubic symmetry is 2.0–2.3 B.M. [24–26]. Among the compounds listed in Table 1, these extreme cases are met by the low spin tris(1-pyrrole-dithiocarbamato)iron(III) hemikis(dichloromethane)

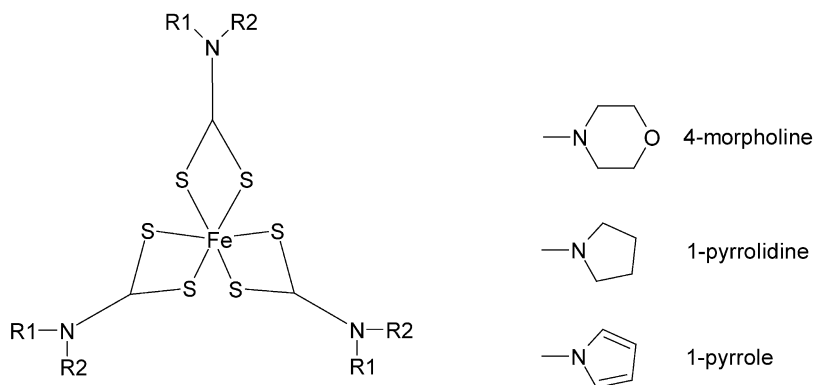


Fig. 1 Schematic drawing showing the structure of tris(*N,N*-disubstituted-dithiocarbamato)iron(III). Substituents R1 and R2 represent various types of alkyl groups including those being part of the ring systems morpholine, pyrrolidine or pyrrole (Table 1)

(μ_{eff} =2.19 B.M.) [23] and the high spin tris(1-pyrrolidine-dithiocarbamato)iron(III) (μ_{eff} =5.9 B.M.) [16].

If the energy difference between the two possible ground terms $^6A_1$ and $^2T_2$ of Fe(III) (assuming O_h symmetry of the FeS_6 core) is of the order of $k_B T$, a change in temperature results in a change in the relative occupancy of the sextet and doublet states, and thus a change in the effective magnetic moment. Generally, for this class of materials the change in the magnetic moment as a function of temperature proceeds very smoothly and the transitions are classified as *gradual* (Chap. 1). Therefore, the magnetic moments observed at the temperatures at which the crystal structures have been determined (Table 1) give an indication of the extent to which spin crossover has proceeded in the material.

2.1.2 Structural Aspects

The structures of these systems consist of an FeS_6 core, which is constrained by the four-membered chelate rings to approximate D_3 symmetry, being intermediate between octahedral and trigonal prismatic stereochemistries. Interestingly, this almost perfect threefold-symmetry only becomes evident from the structure (300 K) of the mainly high spin (μ_{eff} =4.72 B.M.) tris(*N*-methyl-*N*-*n*-butyl-dithiocarbamato)iron(III) [13]. This compound crystallises in the space group $P3_1/c$ revealing two crystallographically independent Fe(III) entities, each with C_3 symmetry.

The difference between the Fe–S bond lengths in the high spin and low spin states is about 0.15 Å, which is also in line with the Fe–S bond lengths for the low spin tris(1-pyrrole-dithiocarbamato)iron(III) hemikis(dichloro-

Table 1 Crystallographic and magnetic data of tris(*N,N*-disubstituted-dithiocarbamato)iron(III) compounds

Ligand	Lattice solvent	T (K)	Crystallographic data			S-Fe-S ^b (°)	References	Magnetic data	
			Space group	Fe-S ^a (Å)				$\mu_{\text{eff}}^{\text{c}}$ (B.M.)	References
<i>N,N</i> -Dimethyl-		400	Pbca	2.415			[4]	4.83	[4]
		295	Pbca	2.43		73.6	[5]	4.2	[5]
		150	Pbca	2.32		74.9	[5]	2.4	[5]
<i>N,N</i> -Diethyl-		25	Pbca	2.302			[4]	2.0	[4]
		297	P2 ₁ /c	2.357		74.3	[6]	4.3	[7]
		79	C2/n	2.306		75.9	[6]	2.2	[7]
<i>N,N</i> -Di(2-hydroxyethyl)-		295	P-1	2.39			[8]	4.2	[8]
		150	P-1	2.33			[8]	2.4	[8]
		210	P-1	2.308			[9]	3.19	[9]
<i>N,N</i> -Dipropionitrile-		295	P-1	2.324			[9]	3.94 ^d	[9]
		298	C2/c	2.416		72.8	[10]	5.32	[7, 11]
		295	Pncn	2.341		74.64	[12]	3.6	[12]
<i>N,N</i> -Di- <i>n</i> -butyl- <i>N</i> -Methyl- <i>N</i> - <i>n</i> -butyl-	C ₆ H ₆ solvate	300	P3 ₁ /c	A:2.406 ^e B:2.327 ^e		73.2	[13]	4.72	[13]
		300	P2 ₁ /a	2.31		75.1	[14]	3.0	[14]
		295	P2 ₁	2.34			[15]	3.45	[15]
<i>N,N</i> -Dibenzyl-		150	P2 ₁	2.31			[15]	2.47	[15]
		300	P2 ₁ /n	2.41		74.4	[14]	5.9	[14]
		295	P2 ₁ /n ^a	2.45		72.6	[16]	5.9 ^h	[16]
1-Pyrrolidine ^f		298	P2 ₁ /n	2.434		73.3	[17]	5.6	[17]
1-Pyrrolidine ^g	0.5 C ₆ H ₆ solvate	298	P-1	2.443		72.7	[18]	5.6	[18]
1-Pyrrolidine	H ₂ O solvate	298	P-1	2.44		72.5	[19]	5.1	[18, 19]
4-Morpholine	CH ₂ Cl ₂ solvate	293	P-1	2.427		72.7	[20]	5.60	[20]
	CH ₂ Cl ₂ solvate	178	P-1	2.401		73.4	[20]	5.05	[20]
	CH ₂ Cl ₂ solvate	110	P-1	2.371		74.0	[20]	4.45	[20]
	CH ₂ Cl ₂ solvate	20	P-1	2.358		74.2	[20]	3.80	[20]

Table 1 (continued)

Ligand	Lattice solvent	T (K)	Crystallographic data		Magnetic data	
			Space group	Fe-S ^a (Å)	S-Fe-S ^b (°)	References $\mu_{\text{eff}}^{\text{c}}$ (B.M.)
4-Morpholine	CHCl ₃ solvate	298	P-1	2.416	73.3	5.45 ⁱ [18]
4-Morpholine	2C ₆ H ₆ solvate	298	C2/c	2.317	75.7	3.5 [21]
4-Morpholine	C ₆ H ₅ NO ₂ solvate	298	P2 ₁ /c	2.353	74.5	[22]
1-Pyrrole	0.5 CH ₂ Cl ₂ solvate	298	P2 ₁ /c	2.297	75.6	2.19 ^j [23]

^a Averaged Fe–S bond distances for the FeS₆ core
^b S–Fe–S bite angle for a chelating dithiocarbamate ligand
^c The μ_{eff} value has been determined at the same temperature as the crystal structure determination (unless indicated otherwise)
^d μ_{eff} value determined at 297 K
^e The unit-cell contains two crystallographically independent entities A and B
^f Phase prepared from ethanol/chloroform solutions
^g Phase prepared from chloroform/toluene solutions
^h This compound remains in the high spin state at all temperatures
ⁱ μ_{eff} value determined at 280 K
^j This compound remains in the low spin state at all temperatures

methane) (Fe–S=2.297 Å (298 K)) [23] and the high spin tris(1-pyrrolidine-dithiocarbamato)iron(III) (Fe–S=2.45 Å (295 K)) [16]. The contraction in the Fe–S distance accompanying the HS→LS change results from the complete transfer of electrons in the antibonding e_g orbitals to the (almost) non-bonding t_{2g} orbitals. For Fe(III) dithiocarbamates, the spin transition extends over such large temperature intervals that it has not been possible to determine the Fe–S distances for the purely low spin and purely high spin state for the same material by X-ray diffraction methods. Thus data confined within the Fe(III) spin crossover region represent weighted averages for high spin and low spin sites. Only recently, an Fe K-edge XAFS study enabled the direct measurement of the separate Fe–S bond lengths for the high spin and low spin states and the spin state population in spin crossover systems at various temperatures [27]. These simultaneous measurements revealed identical results for tris(4-morpholine-dithiocarbamato)iron(III) and tris(*N*-ethyl-*N*-phenyl-dithiocarbamato)iron(III): in the high spin state the Fe–S distance is 2.44(2) Å, whereas it shortens by 0.14 Å to 2.30(2) Å in the low spin form. An examination of the crystallographic data supports a correlation between an increase in Fe–S distance and a restriction in S–Fe–S ligand bite angle, a common feature in four-membered chelates. Clearly, the Fe(III) spin crossover is accompanied by an important change in molecular volume, which has been confirmed by analyses of the change in the unit-cell volume within the spin crossover temperature range (125–295 K), carried out for tris(*N,N*-dimethyl-dithiocarbamato)iron(III) [5] and tris(*N,N*-dibenzyl-dithio carbamato)iron(III) [15].

Within the dithiocarbamate ligands the S_2CN system is usually conjugated. This is reflected in the generally good planarities of the S_2CNC_2 ligand fragments [14]. In this respect, it has been proposed that in the complexes, the partially filled d-orbitals of iron(III) may interact with empty ligand π -orbitals arising from the d-orbitals of sulfur [28, 29]. This back-donation, together with the inductive strength of the substituent R attached to the nitrogen atom, and the steric constraints involved when the substituent is part of a ring system, should result in partial double-bond character of the S–C and C–N bonds to varying extents [15]. Indeed, the S–C and C–N bonds appear to have partial double-bond character at both low and high values of the effective magnetic moment in all relevant Fe(III) tris(dithiocarbamate) systems investigated [5]. This partial double-bond character of the C–N linkage would normally prevent free rotation about this bond. Although this feature may be crucial, in that it may lead to the formation of different geometric isomers for the Fe(III) entity, it has not been considered in any of the investigations. In addition, there is some degree of Fe–S π -bonding depending on the spin state of Fe(III), for which further confirmation has been obtained from a ^{13}C NMR study indicating that the metal-ligand π -bonding increases as μ_{eff} decreases [29].

From the continuous nature of the spin transitions it may be expected that the crossover is not associated with any type of crystallographic phase transition. In the light of this, the structural details for tris(*N,N*-diethyldithiocarbamato)iron(III) appear to be very surprising. The space group of the compound changes from the monoclinic $P2_1/c$ at room temperature, where a significant high spin fraction is present ($\mu_{\text{eff}}=4.3$ B.M.), to $C2/n$ at 79 K, where the compound is mainly in the low spin state ($\mu_{\text{eff}}=2.2$ B.M.) [6]. Later, differential thermal analysis confirmed that a phase transition indeed takes place at 125 K [30]. It was postulated that this phase transition is not correlated with the spin crossover, but may be attributed to a minor modification of the ligand sphere configuration [30]. It is of note that, although the space group of the present crystal changes on cooling, the crystallographic monoclinic system remains essentially unaltered and the change in lattice constants is very small. The main differences between both structures are that at room temperature the Fe(III) ions are located on a pseudo-twofold axis, which becomes a true twofold axis in the low-temperature structure. Leipoldt and Coppens also proposed that the slight differences in the geometry of the ligand at the two temperatures are compatible with a mechanism by which the effect of the substituent on the crystal field is transmitted through the conjugated system of the ligand [6]. Although electronic and steric effects of substituents have frequently been found to affect the spin crossover behaviour within other classes of materials, their action is not very clear for this family of Fe(III) dithiocarbamates. Apart from the very gradual spin crossover behaviour, and the difficulty in obtaining detailed information on these systems by physical measurement methods (see below), a further complicating feature involves the occurrence of different polymorphs and/or solvates depending on the solvent used in the synthetic procedure [31]. Fe(III) dithiocarbamates are capable of interacting to varying degrees with a wide range of solvents. As a result, solvent molecules may either be incorporated in the crystal lattice by simple inclusion, or they may be involved in stronger hydrogen-bonding interactions. These solvates vary in their stability on exposure to the atmosphere, some persisting for long periods unchanged while others rapidly lose solvent, often crumbling to a powder, yielding a different phase [16]. For instance, H_2O [18], CH_2Cl_2 [18–20] or CHCl_3 [18] incorporated into tris(4-morpholine-dithiocarbamato)iron(III) favour the high spin state at room temperature [32]. These results have been interpreted in terms of interaction of the solvent molecules through hydrogen-bonding with ligand sulfur atoms, which must weaken the Fe–S bond slightly, and hence reduce the ligand field splitting ($10 Dq$) significantly ($10 Dq \propto (\text{Fe}–\text{S})^{-5}$) [22]. Benzene [21] and nitrobenzene [22] do not appear to be involved in any hydrogen-bonding interactions, and in this instance, the existing low spin $\leftrightarrow$ high spin equilibria have been found to be markedly shifted towards the low spin side [32]. Although this explanation appears to be reasonable in this case, the investigation of Albertsson and Os-

karsson, who compared tris(*N,N*-di(2-hydroxyethyl)-dithiocarbamato) iron(III) [8] with tris(*N,N*-dimethyl-dithiocarbamato)iron(III) [5] indicates that the expected effects may not always be observed. Their study may be regarded as an attempt to relate the differences in capability for hydrogen-bonding formation of the two ligands to the magnetic data for these compounds. As expected, the 2-hydroxyethyl-substituted ligand sets up an extensive hydrogen-bonding network [8], whereas the dimethyl-substituted derivative does not. However, the magnetic data recorded over the temperature range 80–300 K are about the same for both compounds. It is also noted that the magnetic behaviour is very similar to that observed for tris(*N,N*-diethyl-dithiocarbamato)iron(III) [7].

The situation may be further complicated by the presence of different polymorphs: for tris(1-pyrrolidine-dithiocarbamato)iron(III) two solvent-free modifications could be characterised. The first one has been crystallised from an ethanol/chloroform solution [14], whereas the second has been isolated from a chloroform/toluene mixture [16]. Both compounds differ in their structural parameters determined at room temperature, where they are both high spin. At lower temperatures the ethanol/chloroform product displays a gradual spin transition [14], whereas the chloroform/toluene form remains high spin down to very low temperature [33].

It was evident even at an early stage in the investigations on Fe(III) dithiocarbamate systems that there exists a correlation between the average Fe–S distance and the magnetic moment of these materials [6]. In their extended study, Ståhl and Ymén [34] attempted to relate ten different mean geometric parameters for 25 accurately determined structures to the effective magnetic moment. However, only the Fe–S distances or S–Fe–S ligand bite angles—both of course highly correlated—revealed a linear dependence on μ_{eff} .

2.1.3

Characterisation by Spectroscopic Techniques

Iron(III) dithiocarbamates have been widely studied by a variety of spectroscopic techniques. Unlike the normal situation in iron(II) and also in many other iron(III) systems, ^{57}Fe Mössbauer spectroscopy generally fails to give clear evidence of the simultaneous existence of the two electronic states. The ^{57}Fe Mössbauer spectra of the dithiocarbamate systems exhibit only a single quadrupole doublet with broad line widths within the temperature range of the spin crossover [35–50]. The rapid inter-conversion of spin states—faster or comparable to the lifetime of the ^{57}Fe nucleus ($\tau=1.4\times10^{-7}$ s)—in those materials prevents the observation of separate lines for high spin and low spin molecules. This feature allowed, on the other hand, the establishment of a linear correlation between the ^{57}Fe Mössbauer isomer shifts and the magnetic moments of solvated Fe(III) dithiocarbamates [40].

In addition, these Fe(III) spin crossover materials appear to be EPR active. The combined findings of EPR and ^{57}Fe Mössbauer spectroscopy has allowed the setting of limits for the relaxation times. Thus the relaxation time characteristic of a change from one state to the other is much shorter than the lifetime of the ^{57}Fe state with nuclear spin $I=3/2$ ($\tau=1.4\times 10^{-7}$ s) but longer than the Larmor precession time of the electron spin ($\tau\approx 10^{-10}$ s).

The EPR spectra demonstrate two kinds of signals associated with the $^6\text{A}_1$ and $^2\text{T}_2$ states [51–56], albeit some controversy still exists concerning the reliability of some of these data. This is motivated by the difficulties encountered in, for instance, the preparation of a pure sample, the possibility of sample decomposition and in the definitive assignment of the EPR signals [51, 55]. Hall and Hendrickson reported that it was only possible to observe EPR signals for the magnetically concentrated solids at temperatures approaching 4.2 K. However, the spin crossover could be followed for the complex in a CH_3Cl glass [51]. More accurate spectra could be obtained when doping 1% Fe(III) in tris(*N,N*-dimethyl-dithiocarbamato)cobalt(III), where at about 85 K a signal at $g=4.71$ attributed to high spin Fe(III) could be observed, while cooling to 12 K yielded additional signals at $g=3.27$ and 1.66, assigned to low spin Fe(III) [51].

The electronic spectra of these materials recorded in chloroform solution appear to be dominated by intense bands originating from internal ligand transitions, metal-ligand and ligand-metal charge-transfer bands, whose intensities change markedly with changes in the population of the two spin states [7].

Infrared spectroscopy has also been applied to monitor the Fe(III) spin crossover behaviour [30, 49–51, 57, 58]. For instance, for tris(*N,N*-diethyl-dithiocarbamato)iron(III) the temperature dependence (104–300 K) of the IR spectrum suggested that a band at 552 cm^{-1} might be assigned to a metal-ligand stretching mode in the $^2\text{T}_2$ state [30]. The intensity of this band increases with decreasing temperature at the cost of an iron-sulfur band at 355 cm^{-1} arising from the high spin state. This behaviour has been found to be in line with the temperature dependence of the magnetic susceptibility.

The effect of an applied external pressure on these Fe(III) spin crossover materials has not been extensively studied, although early experiments by Ewald et al. [7] indicated that the spin crossover may be induced when the pressure on ferric complexes in solution is increased at constant temperature. Later, the infrared spectrum of tris(*N*-ethyl-*N*-phenyl-dithiocarbamato)iron(III), a spin crossover system, was studied in the metal-ligand stretching region as a function of pressure (up to 35 kbar) and compared with non-spin crossover reference compounds [58]. It appeared that only the spin crossover system exhibits two metal-sulfur bands. The intensity of the band assigned to the low spin state increases relative to the high spin band with increasing pressure. This is in agreement with the normal desta-

bilisation of the more voluminous high spin form upon the application of external pressure.

2.2

Tris(*N,N*-Disubstituted-XY-Carbamato)iron(III) Compounds (XY=SO, SSe, SeSe)

In the course of the quest for new Fe(III) spin crossover compounds, systems related to *N,N*-disubstituted-dithiocarbamates have been explored. This section deals with oxygen and selenium derivatives of this parent ligand system, as displayed in Fig. 2.

In 1976 Nakajima et al. reported that tris(*N,N*-dimethyl-thiocarbamato)iron(III) contains high spin Fe(III) down to 2 K [59]. This was soon confirmed by an X-ray structure determination carried out at 298 K [60]. The [Fe(*N,N*-dimethyl-thiocarbamato)₃] entity has the facial conformation. This isomer possesses an approximate C₃ axis, with the plane of the three S atoms being virtually parallel to that of the three O atoms. The mean Fe–S bond distances are 2.413(5) Å, whereas the Fe–O distances are, as expected, considerably shorter, 2.073(7) Å. Shortly afterwards, another study appeared indicating that tris(*N,N*-disubstituted-monothiocarbamato)iron(III) compounds display, in fact, spin crossover behaviour [61]. Compounds with R=methyl, ethyl, *n*-propyl, 1-piperidine exhibit a decrease in magnetic moment with decreasing temperature, whereas the 1-pyrrolidine derivative remains in the high spin state (μ_{eff} =5.33 B.M. at 77 K). The room temperature magnetic moments for all spin crossover derivatives range from 5.73 to 6.04 B.M., thus approximating well the spin-only value for high spin Fe(III). The magnetic moments for compounds with R=methyl, ethyl, *n*-propyl determined at 77 K are 4.04 B.M. (corresponding to approximately 60% low spin Fe(III)), 3.61 B.M. (approximately 70% low spin) and 5.69 B.M. (approximately 10% low spin), severally [61]. These spin transitions are far from being complete at 77 K. This is in sharp contrast with the corresponding Fe(III) dithiocarbamates, which are more than 90% low spin at 77 K [51]. The contradictory findings for tris(*N,N*-dimethyl-thiocarbamato)iron(III) were later clarified by Perry et al. [62], who studied several materials obtained from different preparations. It appeared that two different modifications exist, one displaying spin crossover, whereas the other one is a purely high spin compound.

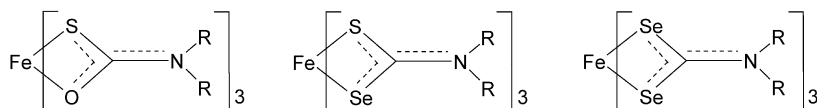


Fig. 2 Tris(*N,N*-disubstituted-monothiocarbamato)iron(III) (*left*), tris(*N,N*-disubstituted-thioselenocarbamato)iron(III) (*centre*) and tris(*N,N*-disubstituted-diselenocarbamato)iron(III) (*right*)

The increasing quadrupole splitting observed in the ^{57}Fe Mössbauer spectra for the methyl and ethyl Fe(III) spin crossover derivatives appears to parallel an increase in the low spin isomer population upon cooling [61]. In no case, however, could distinct doublets for the high spin and the low spin state be observed. Compared with the corresponding dithiocarbamates, the Fe(III) monothiocarbamates with an S_3O_3 donor atom set produce a significantly more positive isomer shift. A likely explanation for this feature involves increased d-electron shielding in the monothio complex resulting from reduced Fe-to-ligand back π -bonding.

Interestingly, tris(*N,N*-disubstituted-monothiocarbamato)iron(III) spin crossover compounds show visible thermochromism: their colour changes from red at room temperature to orange at 77 K [61].

The first studies of the magnetism of tris(*N,N*-disubstituted-diselenocarbamato)iron(III) compounds revealed magnetic moments ranging from 1.96 to 2.37 B.M. [63, 64]. Although the close relation with tris(dithiocarbamato)iron(III) spin crossover materials was already evident, these diselenium derivatives were at first wrongly classified as low spin compounds, probably as a result of the occurrence of diamagnetic non-iron-containing golden-yellow oxidation products of the ligands as by-products in the synthesis [65]. In fact, the Fe(III) materials are dark brown and their magnetic and ^{57}Fe Mössbauer spectroscopic data resemble those of the Fe(III) dithiocarbamates, i.e. both systems exhibit spin crossover [65].

Comparison of the experimental data of the $[\text{Fe}(\text{S}_2\text{CNR})_3]$ and $[\text{Fe}(\text{Se}_2\text{CNR})_3]$ series (R =1-piperidine, 1-morpholine, 1-thiomorpholine, dibutyl, diethyl, $(\text{PhCH}_2)_2$, $(\text{C}_6\text{H}_{13})_2$ and methylphenyl) revealed similar magnetic properties, although the spin transition is shifted slightly to higher temperatures in the diselenocarbamates compared to the corresponding dithiocarbamates [65]. This statement appears to be correct although the magnetic data reported for diselenocarbamates may be questionable in some cases, e.g. for the 1-morpholine derivative, the same authors have published three different values for the solid complex, ranging from 1.99 to 4.88 B.M. at about room temperature [65, 66]. The explanation of the usually lower magnetic moments of the diselenocarbamates has focussed on a greater nephelauxetic effect for Se compared to S, i.e. greater π -backbonding in the diselenocarbamates [66].

In contrast to the extensive literature on Fe(III) dithiocarbamates (Sect. 2.1) and to a lesser extent Fe(III) diselenocarbamates [62, 65, 67–73], the Fe(III) thioselenocarbamates [68–73] have not been widely studied. Certainly, one reason for this is the difficult preparation of the reagent carbon sulfideselenide (CSSe) [74]. This was later circumvented by an improved synthetic method for CSSe [75], allowing Dietzsch et al. [68–73] to report a large range of Fe(III) thioselenocarbamates. Although these studies have been carried out with care, the authors did not address the possibility of formation of different geometric isomers associated with the asymmetric na-

ture of the bidentate ligand. In their comparative study Dietzsch et al. reported various tris(diorganodichalcogencarbamato)iron(III) complexes of formula $[\text{Fe}(\text{XYCNR}_2)_3]$ ($\text{XY}=\text{OS}$, SS , SSe or SeSe ; $\text{R}=\text{organic substituent}$) [71]. It was concluded that the relative population of the high spin and low spin states depended on the coordinating chalcogen (O , S and/or Se), temperature, pressure, physical state (solution or solid, solvated or unsolvated), and the nature of the organic substituent. The $\text{Fe}(\text{III})$ compounds with FeS_3O_3 coordination sphere are high spin at room temperature, whereas the ones with FeS_6 , FeS_3Se_3 or FeSe_6 environment display different degrees of spin crossover at room temperature depending on the ligand substitution. The substituents, i.e. 1-pyrrolidine, 1-piperidine, 1-morpholine, dicyclohexyl, diethyl and dibenzyl, have been selected such that these cover the range from high spin to low spin $\text{Fe}(\text{III})$ compounds at room temperature.

The presence of selenium has been known to cause difficulties in the recording of ^{57}Fe Mössbauer spectra. Diselenocarbamates prepared with natural iron generally yielded very weak absorption peaks [62, 65, 67]. This feature is associated with the scattering of a large fraction of the incident γ -rays by the Se atoms. This has been overcome in part by preparing samples enriched up to 90% in ^{57}Fe [62, 65, 67]. In addition, it also appeared possible to obtain relatively accurate spectra by using collection times of about seven days for the $\text{Fe}(\text{III})$ diselenocarbamates and about three days for $\text{Fe}(\text{III})$ thioselenocarbamates [71]. The spectra exhibit a single, quadrupole-split absorption, comparable to those observed for $\text{Fe}(\text{III})$ dithiocarbamates. While a linear correlation between the ^{57}Fe Mössbauer isomer shifts and the magnetic moments of solvated $\text{Fe}(\text{III})$ dithiocarbamates could be established [40], no such correlation is clearly evident in the limited series of thioseleno- and diselenocarbamates studied by Dietzsch [71]. Although variations are noted for specific organic substituents, the general trend for the average isomer shifts is $^-\text{OSCNR}_2 < ^-\text{S}_2\text{CNR}_2 \approx ^-\text{SSeCNR}_2 \approx ^-\text{Se}_2\text{CNR}_2$. On the other hand, the quadrupole splittings tend to increase with selenium substitution: the typical order of the quadrupole splittings for a given ligand system is $^-\text{OSCNR}_2 < ^-\text{S}_2\text{CNR}_2 < ^-\text{SSeCNR}_2 < ^-\text{Se}_2\text{CNR}_2$. For the same organic substituent, the magnetic moments usually decrease in the order $^-\text{OSCNR}_2 > ^-\text{S}_2\text{CNR}_2 > ^-\text{SSeCNR}_2 > ^-\text{Se}_2\text{CNR}_2$, confirming that the selenium-containing ligands generally exert a slightly stronger ligand field towards $\text{Fe}(\text{III})$.

There have been conflicting interpretations of the EPR spectra of these selenium-containing complexes. For example, various X-band EPR spectra of $\text{Fe}(\text{III})$ diselenocarbamates recorded in chloroform solutions at 12 K tended to be broad and poorly resolved, except for a series of three resonances centred around $g=2$ [62]. They also appeared to be very similar to the spectra recorded for $\text{Mn}(\text{III})$ -doped $\text{Co}(\text{III})$ tris(dithiocarbamate) compounds [76] or $\text{Cu}(\text{II})$ di(diselenocarbamate) systems [77]. In another study of EPR spectra recorded for powdered $\text{Fe}(\text{III})$ thioselenocarbamates and diselenocarbamates at room temperature [69] broad, poorly resolved lines at $g \approx 4$

and a relatively narrow line around $g \approx 2$ were observed. It appears that the relatively narrow signal found in most spectra at $g \approx 2$ arises from low spin molecules. On the other hand, the broader lines at $g \approx 4$ (which narrow with decreasing temperature) and at $g \approx 2$ (that in some cases acquire a fine structure with decreasing temperature) may originate from high spin molecules [69]. The same authors later used information obtained from EPR spectra to propose a new resonance structure for the bonding of spin crossover Fe(III) dichalcogencarbamates. This low spin structure would involve an unpaired electron on the nitrogen atom of the dichalcogencarbamate and the transfer of an electron from the nitrogen to the Fe(III) ion [73]. Unfortunately, X-ray structures have not been reported for these selenium derivatives.

2.3

Tris(Substituted-X-Xanthato)Iron(III) Compounds (X=O, S)

Considerably less research has been directed towards Fe(III) compounds of substituted X-xanthates (X=O, S), as well as of the related dithiophosphates (Fig. 3), which can be thought of as being very closely related to the dithiocarbamates.

Iron(III) dithiophosphates are high spin compounds having magnetic moments of ca. 5.80 B.M. at room temperature [78, 79]. On the other hand, the Fe(III) thioxanthates exhibit thermal and pressure induced spin crossover, though the low spin form predominates for the O-xanthates and thioxanthates [80]. The structure of tris(*tert*-butyl-thioxanthato)iron(III) has been determined at room temperature and consists of an approximately octahedral FeS_6 entity with an average Fe–S distance of 2.297(7) Å and S–Fe–S bond angles of 75.2(2)° [81]. It was also concluded from the structural data that there is a significant amount (10–30%) of double bond character to the C–X bond for coordinated S_2CX (X=OR, SR) ligands, although appreciably less than for analogous dithiocarbamate (X=NR₂) compounds (40–50%) [81]. This was also confirmed for the predominantly low spin tris(O-ethyl-xanthato)iron(III), where the relatively short S₂C–O bond length (1.328(10) Å) is indicative of considerable double bond character [82]. Its structure has been determined at room temperature: the compound crys-

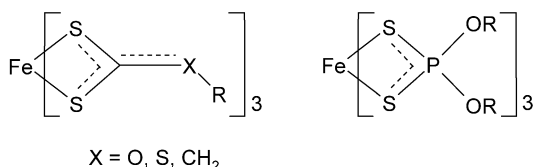


Fig. 3 Tris(O-substituted-xanthato)iron(III) (left; X=O), tris(substituted-thioxanthato)iron(III) (left; X=S), tris(substituted-dithioacetato)iron(III) (left; X=CH₂) and tris(disubstituted-dithiophosphato)iron(III) (right)

tallises in the rhombohedral space group R-3, and relevant bond distances and angles for the FeS_6 core are $\text{Fe-S}=2.31 \text{ \AA}$ and $\text{S-Fe-S}=75.5(5)^\circ$. Tris(*O*-ethyl-xanthato)iron(III) seems to form an exception in the Fe(III) *O*-xanthate series in that it exhibits spin crossover behaviour ($\mu_{\text{eff}}=2.19 \text{ B.M.}$ at 108 K and $\mu_{\text{eff}}=2.72 \text{ B.M.}$ at 296 K), whereas magnetic measurements recorded for other tris(*O*-xanthato) complexes of Fe(III) suggest that the xanthates are characteristically low spin with magnetic moments of ca. 2.45 B.M. at room temperature [78, 79].

Tris(dithioacetato)iron(III) compounds are purely low spin over the temperature range 93–293 K [83].

Taking the relative favouring of the low spin state for iron(III) as the criterion, the order of field strengths for this type of S_2 -ligand follows as: $\text{S}_2\text{P(OR)}_2 < \text{S}_2\text{CNR}_2 < \text{S}_2\text{CSR} < \text{S}_2\text{COR} < \text{S}_2\text{CCR}$ ($\text{R}=\text{alkyl}$).

2.4

Tris(Monothio- β -Diketonato)Iron(III) Compounds

In 1968 the first reports of spin crossover in iron(III) monothio- β -diketonates appeared [84, 85] and reviews on metal complexes of monothio- β -diketones were published shortly afterwards [86, 87]. The monothio- β -diketones can be considered as a ligand system intermediate between acetylacetone and dithioacetylacetone (Fig. 4).

The X-ray structure of $[\text{Fe}(\text{acetylacetonato})_3]$ has been known for almost 50 years and consists of an Fe(III) ion in a fairly regular octahedral environment of oxygen atoms with $\text{Fe-O}=1.95 \text{ \AA}$ [88]. For the unsubstituted complex and for various complexes in which the ligand is substituted at the 2-position ($\text{X}=\text{Cl, Br, I, CH}_3, \text{C}_6\text{H}_5, \text{NO}_2$) ^{57}Fe Mössbauer spectra and the magnetism indicate that they are purely high spin [89–92]. However, for the complex derived from 4,4,4-trifluoro-1-(3-pyridyl)-1,3-butane-dione the temperature dependence of the magnetic moment (3.69 B.M. at 293 K and 2.35 B.M. at 87 K) has been taken as evidence for spin crossover. This is the only system containing an Fe(III)O_6 chromophore known to show spin crossover behaviour [93]. On the other hand, tris(dithioacetylacetonato)iron(III) is purely low spin [94] with a mean Fe-S distance of $2.25 \text{ \AA}$, typical for low spin Fe(III) [95].

Monothio- β -diketones generate a ligand field strength intermediate between those exerted by acetylacetone and dithioacetylacetone, and yield

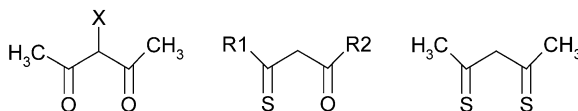


Fig. 4 2-Substituted-acetylacetone (*left*), 1,3-disubstituted-monothio- β -diketone (*middle*) and dithioacetylacetone (*right*)

Fe(III) compounds exhibiting spin crossover behaviour, its extent depending on the nature of the substituents R1 and R2 indicated in Fig. 4.

The structures of two of these mononuclear Fe(III) systems have been determined at room temperature. For the first compound R1=R2=C₆H₅, and for the second R1=C₆H₅ and R2=CF₃ [96]. [Fe(C₆H₅CS=CHCOC₆H₅)₃] is high spin at room temperature (μ_{eff} =5.50 B.M.), whereas [Fe(C₆H₅CS=CHCOCF₃)₃] is essentially low spin at this temperature (μ_{eff} =2.31 B.M.). Both compounds have a facial, distorted octahedral FeS₃O₃ geometry. The sulfur atoms lie at the corners of an almost equilateral triangle, which is parallel to a similar triangle formed by the oxygen atoms. The mean Fe–S distances are 2.368 and 2.239 Å, whereas the Fe–O distances are 1.988 and 1.942 Å for the high spin [Fe(C₆H₅CS=CHCOC₆H₅)₃] and the low spin [Fe(C₆H₅CS=CHCOCF₃)₃], respectively. Although a comparison of these high spin and low spin FeS₃O₃ coordination spheres belonging to different compounds may not be entirely valid in deriving the effects of the spin change on the metal-donor atom distances, it does appear that the Fe–S bond lengths are considerably more affected by the spin crossover than the Fe–O distances, the shortening being approximately 0.13 Å for the former and about 0.05 Å for the latter.

The magnetic data indicate that in all tris(monothio- β -diketonato)iron(III) systems investigated the spin crossover is gradual [84, 85, 87, 97–99], except for the complex with R1=R2=CH₃ which displays a rather abrupt spin transition at about 150 K [97]. Electron-withdrawing groups such as CF₃, phenyl and 4-substituted phenyl appear to be the most effective in increasing the population of the low spin configuration [84, 85]. Therefore a systematic study of the magnetic properties of nine iron(III) chelates of fluorinated monothio- β -ketones (R1C(SH)=CHCOCF₃ (R1=2-thienyl, β -naphthyl, phenyl, *p*-MeC₆H₄, *p*-FC₆H₄, *p*-ClC₆H₄, *m*-MeC₆H₄, *m*-ClC₆H₄, *m*-BrC₆H₄)) [99] contributed towards understanding the factors influencing the spin crossover behaviour. The magnetic moments vary from 5.49 to 2.16 B.M. at room temperature and are temperature dependent, falling as low as 1.82 B.M. at 83 K. The room temperature magnetic moments indicate that the order of the effective ligand fields is 2-thienyl < β -naphthyl < *p*-XC₆H₄ < phenyl < *m*-XC₆H₄ (X=CH₃, F, Cl or Br), i.e. the 2-thienyl substituent yields a predominantly high spin complex at room temperature, whereas the ligands with phenyl substituents yield essentially low spin materials [99]. The ⁵⁷Fe Mössbauer spectra of these Fe(III) compounds containing fluorinated monothio- β -ketones show only one doublet. The temperature dependence of the quadrupole splitting reflects the temperature dependence of the magnetic moment: μ_{eff} values lower than 2.5 B.M. correspond to quadrupole splitting values of ca. 1.75 mm s⁻¹, whereas μ_{eff} values larger than 4.9 B.M. correspond to quadrupole splittings of ca. 0.7 mm s⁻¹ [99].

It is noteworthy that these iron(III) chelates of fluorinated monothio- β -ketones are the only ones of this general family which show only a single

doublet in the ^{57}Fe Mössbauer spectra. All other studies reported well-resolved ^{57}Fe Mössbauer spectra for these spin crossover tris(monothio- β -diketonato)iron(III) compounds, in which contributions from both spin-isomers, with distinct quadrupole splittings, could be observed separately. In these cases, the quadrupole splittings are similar to those generally observed for low spin and high spin Fe(III) compounds [97, 98].

2.5

Bis(X-Semicarbazone)Iron(III) Compounds (X=S, Se)

In solution thiosemicarbazones or selenocarbazones probably consist of an equilibrium mixture of thione and thiol tautomers (Fig. 5) [100].

They may be condensed with suitable carbonyl compounds to yield tridentate chelating groups which generally coordinate in the anionic thiolate form. When the carbonyl compound is salicylaldehyde or a substituted salicylaldehyde, the tridentates coordinate as the di-anionic groups shown in Fig. 6. The salts of the (anionic) bis(ligand) iron(III) complexes of this class of Schiff base anion (typically (cation⁺)[Fe(ligand²⁻)₂·nH₂O]) frequently show spin crossover behaviour. A series of ligand systems of the X-semicarbazone type (X=S, Se) have been tested with the objective of determining the criteria for the occurrence of spin crossover in the Fe(III) derivatives.

The Fe(III) complexes of R-substituted salicylaldehyde thiosemicarbazone (R-thsa²⁻; Fig. 6) are among the most studied spin crossover materials of this family. The crystal structures of several of them have been determined at various temperatures. The iron-donor atom distances are compiled in Table 2. The Fe(III) ion is in a distorted FeS₂N₂O₂ octahedron formed by two thiosemicarbazone ligands, which are geometrically arranged in such a way that the S and O atoms are located in *cis* positions, whereas the N atoms occupy *trans* positions, i.e. each tridentate molecule coordinates in an equatorial plane [101].

The compound NH₄[Fe(5-Br-thsa)₂] could be crystallised in two forms, one existing as mica-like crystals and the other as tabular plates [102]. The

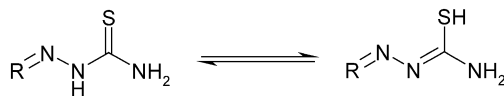


Fig. 5 Proposed equilibrium in solution for thiosemicarbazones between the thione (*left*) and thiol (*right*) tautomers

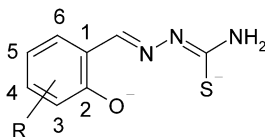


Fig. 6 The dianion of R-salicylaldehyde thiosemicarbazone (R-thsa²⁻)

Table 2 Fe–donor atom bond lengths for various (cation⁺)[Fe(ligand²⁻)₂] $\cdot$ nH₂O compounds of *R*-salicylaldehyde thiosemicarbazone (R-thsa²⁻) [101]

Compound	T (K)	Fe–S	Fe–N	Fe–O (Å)	Spin state ^b
Cs[Fe(thsa) ₂]	298	2.44	2.12	1.96	HS
	103	2.44	2.15	1.96	HS
NH ₄ [Fe(5-Cl-thsa) ₂]	298	2.24	1.95	1.93	LS
	135	2.23	1.96	1.94	LS
NH ₄ [Fe(5-Br-thsa) ₂] ^a	298	2.23	1.93	1.95	LS
NH ₄ [Fe(3,5-Cl-thsa) ₂] $\cdot$ 1.5H ₂ O	298	2.26	1.95	1.93 (site FeA)	LS
	298	2.40	2.06	1.97 (site FeB)	HS (sco)
	103	2.25	1.95	1.93 (site FeA)	LS
	103	2.31	1.95	1.94 (site FeB)	LS (sco)
	298	2.34	2.00	1.94 (site FeA)	LS/HS (sco)
K[Fe(3,5-Cl-thsa) ₂] $\cdot$ 1.5H ₂ O	298	2.42	2.05	1.94 (site FeB)	HS (sco)
	103	2.25	1.88	1.93 (site FeA)	LS (sco)
	103	2.30	1.92	1.93 (site FeB)	LS/HS (sco)
	103	2.30	1.92	1.93 (site FeB)	LS/HS (sco)

^a Determined for crystals of tabular form^b Predominant spin state (HS or LS) or mixture of both spin states (LS/HS) indicated. In case spin crossover (sco) occurs, this is mentioned in parentheses

mica-like crystals show spin crossover in the region around 200 K. The values for the magnetic moment— $\mu_{\text{eff}}=5.06$ B.M at 300 K and 2.29 B.M. at 77 K—indicate that the spin transition is substantially complete at both temperature extremes. The tabular crystalline form also exhibits spin crossover, albeit at a much higher temperature: the effective magnetic moment is 2.16 B.M. at 300 K, but at about 400 K it has almost reached the value for high spin iron(III). The X-ray structure has been determined for this tabular form at room temperature [102], and has been found to be isostructural with NH₄[Fe(5-Cl-thsa)₂] [103]. The main difference observed in the first coordination sphere of the Fe(III) ion in the Cl and Br derivatives is a slight increase in Fe–N distance and a decrease in Fe–O bond length in the chloro compound. In addition, the introduction of bromine instead of chlorine at the salicylaldehyde residue leads to a slight electronic rearrangement in the ligand.

The structure of NH₄[Fe(3,5-Cl-thsa)₂] $\cdot$ 1.5H₂O has been determined at 298 and 103 K [104]. There seems to be an inconsistency in the report. The authors [104] indicate that the magnetic properties of this material correspond to those reported for a compound without lattice water molecules [105]. Still, the structural features appear to be in line with the magnetic data reported for the solvent-free material, having a magnetic moment of 3.90 B.M. at room temperature, which gradually decreases to reach 2.57 B.M. at 80 K [105]. The asymmetric unit of NH₄[Fe(3,5-Cl-thsa)₂] $\cdot$ 1.5H₂O contains two crystallographically independent Fe(III) entities, denoted as sites FeA and FeB, respectively [104]. At room temperature, the Fe–ligand bond dis-

tances for FeA (Table 2) agree closely with these found for $\text{NH}_4[\text{Fe}(\text{5-Cl-thsa})_2]$ [103], and may be considered as the limiting values for the low spin Fe(III) configuration for systems such as these. At 103 K the configuration of FeA has not changed significantly. On the other hand, the structure at site FeB shows considerable temperature dependence. Upon spin crossover (298 K to 103 K), the FeB–S and FeB–N bond lengths decrease by about 0.1 Å, whereas the ligand bite angles S–FeB–O and S–FeB–N increase by about 6° and 3°, respectively. The geometry of FeB at 298 K is very close to that found for the iron atom in $\text{Cs}[\text{Fe}(\text{thsa})_2]$ [106], which contains a purely high spin Fe(III) chromophore.

The analysis of the magnetic and structural data reported by Ryabova revealed a linear correlation between the Fe–S bond distance and the effective magnetic moment [106].

Further attempts have been made to correlate the structural features of these systems with the spin state of Fe(III). The low spin $\text{NH}_4[\text{Fe}(\text{thsa})_2]$ complex [107] may be considered as the parent compound of this class of compounds. It was soon discovered that significant changes in the magnetic properties of the Fe(III) chelates may arise from (i) the replacement of the associated cation in the complex, (ii) the introduction of substituents into the benzene ring of the salicylaldehyde residue or (iii) the incorporation of substituents into the amido group of the thiosemicarbazide residue. In addition to these factors, the magnetic properties also appear to depend on heating of the solid compounds to 400 K prior to the magnetic measurements [105].

In the following, various Fe(III) compounds of R-substituted salicylaldehyde thiosemicarbazones will be discussed according to the criteria mentioned above, although it should be pointed out that a comparison of these materials may be rendered less meaningful due to the possible occurrence of different polymorphs. Moreover, upon variation of one substitution parameter, several other structural features may also be changed simultaneously. For instance, a change in outer-sphere cation or the introduction of a substituent at the salicylaldehyde moiety is frequently associated with increased hydration of the Fe(III) material.

The variation of the outer-sphere cation in Fe(III) compounds of the unsubstituted ligand yielded the low spin material $\text{NH}_4[\text{Fe}(\text{thsa})_2]$ [107], as well as the high spin compound $\text{Cs}[\text{Fe}(\text{thsa})_2]$ [106]. In addition $\text{Li}[\text{Fe}(\text{thsa})_2] \cdot 2\text{H}_2\text{O}$ is low spin whereas $\text{Na}[\text{Fe}(\text{thsa})_2] \cdot 3\text{H}_2\text{O}$ [108] shows spin crossover, the magnetic moment decreasing from 5.57 B.M. at 300 K to 5.10 B.M. at 80 K [108]. It is likely that the selected cation has an indirect influence on the spin state of Fe(III) by co-determining the crystal packing and/or the degree of hydration of the material. Moreover, ^{57}Fe Mössbauer spectroscopy results for $\text{pyridineH}[\text{Fe}(\text{thsa})_2] \cdot \text{H}_2\text{O}$ have revealed spin crossover behaviour, indicating 100% of low spin Fe(III) at 80 K, which decreases gradually to 19.2% at 280 K [109]. In addition, the magnetic susceptibility measurements

recorded on increasing temperature showed a sharp increase of the magnetic moment in the range 260–280 K.

The variation of the associated cation has also been investigated for 5-halo-salicylaldehyde thiosemicarbazone compounds [105]. The favouring of the low spin configuration for both (cation)[Fe(5-Br-thsa)₂] and (cation)[Fe(5-Cl-thsa)₂] follows the order of the associated cations: Na⁺>Li⁺>K⁺>NH₄⁺ even though the effect of variation of the monovalent cation is not very pronounced. Overall the low spin state is favoured to the greater extent in the salts of the 5-chloro derivative. On the other hand, the Zn²⁺ salt of this derivative, which crystallises as a sesqui hydrate, shows a more extended transition in the range 80–300 K [105].

Spin transitions have also been reported for Al_{0.33}[Fe(5-Cl-thsa)₂] [110] and H[Fe(5-Cl-thsa)₂] [109, 110]. For both compounds, a relatively abrupt and almost complete spin crossover occurs with T_{1/2}=228 K for the Al derivative, and 226 K for the H derivative. Transition temperatures determined by variable temperature heat capacity measurements are in agreement with those obtained from the magnetic susceptibility measurements.

It has been proposed that the introduction of substituents into the benzene ring of salicylaldehyde alters the ligand field strength, since the transfer of the polar properties of the substituent through the benzene ring is facilitated by the π -delocalisation in the ring [108]. Zelentsov et al. concluded that introduction of an NO₂ group into the benzene ring results in an increase in Dq/B [105]. Thus NH₄[Fe(thsa)₂] is a purely low spin compound, whereas a slight increase in magnetic moment for NH₄[Fe(5-NO₂-thsa)₂]·0.5H₂O and NH₄[Fe(3-NO₂-thsa)₂] between 80 and 300 K may indicate Fe(III) spin crossover behaviour. A similar effect was observed for a 5-CH₃ substituent [105] but a more significant increase in the magnetic moment has been observed on replacement of H by 5-Cl or 5-Br. At 300 K the 5-Cl and 5-Br derivatives have intermediate values for the magnetic moment, i.e. 3.26 B.M. and 4.04 B.M., respectively, but after a heating treatment at 130 °C almost high spin values, i.e. 5.23 B.M. and 5.54 B.M., respectively, are reached at 300 K [105]. For the systems H[Fe(5-Cl-thsa)₂] [109, 110] and H[Fe(5-Br-thsa)₂]·0.5H₂O [109] there seems to be a more distinct favouring of the low spin state in the chloro than in the bromo derivative. Thus, the substituents studied have been classified in the following sequence according to the extent of favouring the low spin state: NO₂>H>CH₃>Cl>Br.

Zelentsov et al. also observed that the high spin fraction in virtually all samples increased to varying extents after the samples were heated [105]. The origin of this effect is not clear since the complexes were mostly unsolvated and thus loss of solvate molecules, the most common cause of such a change, was not applicable. Nevertheless, the importance of the inclusion of lattice water molecules in co-determining the spin crossover properties is evident in the different magnetic properties of Li[Fe(5-Br-thsa)₂] [105] and Li[Fe(5-Br-thsa)₂]·H₂O [111]. For the unsolvated compound μ_{eff} =1.93 B.M.

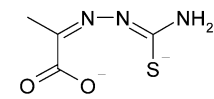


Fig. 7 The dianion of pyruvic acid thiosemicarbazone (thpu²⁻)

at 80 K and 3.97 B.M. at 300 K [105]. On the other hand the hydrate undergoes a spin transition associated with an asymmetric thermal hysteresis loop of width of 39 K with $T_{1/2\uparrow}=333$ K and $T_{1/2\downarrow}=294$ K [111]. A powder X-ray diffraction study at various temperatures demonstrates the occurrence of a first order crystallographic phase transition in the lattice coupled to the spin transition. This phase transformation might originate from a modification of the extended hydrogen-bonding network [111].

Finally, the effect of substitution of a phenyl group at the thioamido group of the thiosemicarbazide residue has been explored [108]. $\text{NH}_4[\text{Fe}(\text{Phthsa})_2] \cdot 0.5\text{H}_2\text{O}$ (H_2Phthsa =salicylaldehyde phenylthiosemicarbazone) is low spin [108], like $\text{NH}_4[\text{Fe}(\text{thsa})_2]$ [107]. Thus it appears that the ligand field and hence the spin state of Fe(III) is relatively insensitive to substitution at the NH_2 group, which is assumed to be involved neither in conjugation nor coordination.

The effect of the replacement of the sulfur atom in the ligand by selenium has also been briefly examined. ^{57}Fe Mössbauer spectral and magnetic susceptibility measurements show that $\text{NH}_4[\text{Fe}(\text{sesa})_2]$ (H_2sesa = salicylaldehyde selenosemicarbazone) displays spin crossover behaviour [108, 112]. In this salt there is a slight destabilisation of the doublet state for iron(III), relative to the corresponding derivative of the thiosemicarbazone [107], contrary to the trend observed in the dithio- and diseleno-carbamates. A further, and more significant, difference in the semicarbazone and carbamate series of ligands is seen in the Mössbauer spectra; those of the iron(III) complexes of the thiosemicarbazones and selenosemicarbazones, show separate doublets characteristic of the low spin and high spin forms [108].

The Fe(III) complexes of the dianion of pyruvic acid thiosemicarbazone (thpu²⁻; Fig. 7), (cation⁺)[Fe(thpu)₂] $\cdot n\text{H}_2\text{O}$, are very similar to those of the salicylaldehyde derivatives (Fig. 6) discussed above. The spin state properties are quite sensitive to changes in the counter-cation (typically an alkali-metal cation or a protonated nitrogenous base) and the lattice water content of the material. The parent compound, $\text{NH}_4[\text{Fe}(\text{thpu})_2]$, is low spin at room temperature [113]. $\text{Li}[\text{Fe}(\text{thpu})_2] \cdot 3\text{H}_2\text{O}$ is also low spin but $\text{K}[\text{Fe}(\text{thpu})_2] \cdot 2\text{H}_2\text{O}$ shows almost complete spin crossover between 80 and 300 K [108].

In contrast to the salicylaldehyde X-semicarbazone (X=S, Se) Fe(III) derivatives where replacement of sulfur by selenium results in an apparent slight de-stabilisation of the low spin state, $\text{NH}_4[\text{Fe}(\text{sespu})_2]$ (sespu²⁻=the dianion of pyruvic acid selenosemicarbazone) is low spin at room temperature [114], like the sulfur derivative $\text{NH}_4[\text{Fe}(\text{thpu})_2]$ [113].

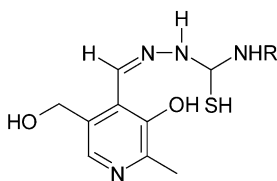


Fig. 8 Pyridoxal 4-*R*-thiosemicarbazone (R=alkyl; H₂thpy)

Timken et al. have reported the magnetic and spectroscopic characterisation of the spin crossover complex [Fe(Hthpu)(thpu)], where Hthpu[−] and thpu^{2−} are the singly and doubly deprotonated forms of pyruvic acid thiosemicarbazone, respectively [115]. This compound shows an abrupt transition with associated thermal hysteresis ($T_{1/2\downarrow}$ =225 K and $T_{1/2\uparrow}$ =235 K). Sample grinding leads to a more gradual and less complete spin transition. Again for this system distinct ⁵⁷Fe Mössbauer spectral features are observed separately for the low spin and high spin states. The structure of [Cr(Hthpu)(thpu)]·H₂O has been determined, which can be considered as a model for the low spin [Fe(Hthpu)(thpu)]·H₂O (μ_{eff} =2.48 B.M. at 299 K) [115]. These structural data, as well as those reported for other thiosemicarbazone Ni(II) [116] and Zn(II) [117] compounds, indicate that intermolecular hydrogen-bonding interactions are significant and result in a relatively strong coupling of the monomeric units in the solid state. It is quite likely, then, that for [Fe(Hthpu)(thpu)] the highly cooperative nature of the spin transition is due to the extended interaction of the complex centres through intermolecular hydrogen bonds.

The singly deprotonated form of pyridoxal 4-*R*-thiosemicarbazone (R=alkyl; H₂thpy; Fig. 8) has also been found to generate Fe(III) spin crossover [118, 119]. It has been proposed that the tridentate ligand coordinates to Fe(III) through the mercapto group, the azomethine nitrogen atom and the phenolic oxygen with the loss of a proton. For [Fe(Hthpy)₂]Cl [118] an abrupt and essentially complete spin transition (μ_{eff} =5.75 B.M. at 299 K; 2.01 B.M. at 78 K) is associated with thermal hysteresis ($T_{1/2\uparrow}$ =256 K; $T_{1/2\downarrow}$ =245 K; $\Delta T_{1/2}$ =11 K). It is most likely that the cooperative (first order) nature of this spin transition is due to an extended intermolecular hydrogen-bonding network. In fact, there seems to be an analogy with [Fe(Hthpu)(thpu)] [115] mentioned above, which also shows an abrupt transition. In both cases, the monohydrates are purely low spin compounds.

Substitution with R=methyl or ethyl yielded solvent-free compounds, which appeared to be in the low spin state (μ_{eff} =ca. 2.12 B.M. over the temperature range 78–320 K) [119]. However, the phenyl derivative shows an abrupt and almost complete transition, but now centred near room temperature ($T_{1/2\uparrow}$ =299 K and $T_{1/2\downarrow}$ =290 K) [119].

These complexes of thiosemicarbazones and related systems are of obvious general interest because of the involvement of hydrogen bonding and, in some instances, the association of the transitions with hysteresis. Since the pioneering work of the Russian school they have received relatively little attention but interest in them has been re-kindled [111] and can be expected to grow.

2.6

Other Complexes with Sulfur Donor Atoms

Various other Fe(III) systems containing sulfur atoms in the coordination sphere have been reported. Selected examples are discussed in this section.

An FeN_3S_3 chromophore is present in (1,4,7-tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane)iron(III) (Fig. 9 shows the ligand structure) [120, 121]. The complex displays a gradual transition extending over a very broad temperature range, μ_{eff} increasing from 2.4 B.M. at 77 K to 4.36 B.M. at 500 K [120]. The room temperature structure (where μ_{eff} is 2.9 B.M.) showed Fe(III) in a pseudooctahedral environment consisting of three nitrogen atoms of the macrocycle and three thiophenolato sulfur atoms in a facial stereochemistry. The average Fe–S and Fe–N distances are 2.28 Å and 2.08 Å, respectively [120]. In the ^{57}Fe Mössbauer spectra (1.2–450 K) only one quadrupole doublet could be observed, characteristic for compounds where the relaxation time between the high spin and the low spin configurations is shorter than the quadrupole precession time [121]. Interestingly, the temperature dependence of the quadrupole splitting indicates a phase transition at approximately 100 K. This feature has been further investigated by X-ray structure analysis on single-crystals at room temperature, as well as by temperature-dependent EXAFS investigations (30–200 K) on powdered

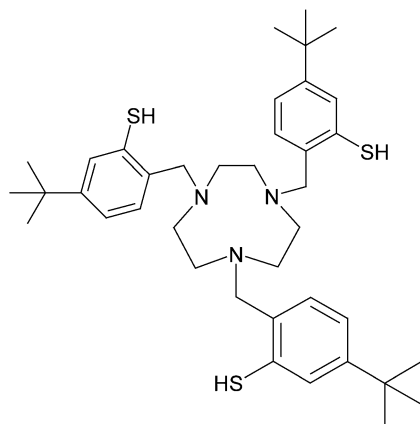


Fig. 9 1,4,7-Tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane

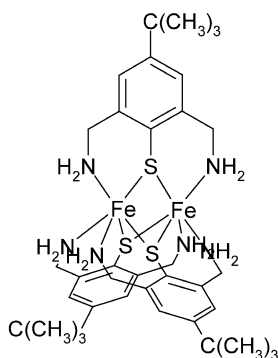


Fig. 10 Schematic representation of $[\text{Fe}_2(2,6\text{-di(aminomethyl)-4-tert-butyl-thiophenol})_3]^{3+}$

samples, from which it could be concluded that the observed phase transition induces changes of bond angles only, while the spin crossover would additionally be expected to result in changes of metal-donor atom distances [121].

When three 2-mercaptopropyl substituents instead of 4-*tert*-butyl-2-mercaptobenzyl are incorporated into the cyclononane ring shown in Fig. 9, a predominantly high spin material has been obtained [120]. On the other hand, disubstitution of the cyclononane ring by 2-pyridylmethyl groups resulted in $[\text{Fe}(1,4\text{-bis}(2\text{-pyridylmethyl})\text{-1,4,7-triazacyclononane})\text{Cl}](\text{PF}_6)_2 \cdot \text{MeOH}$ containing an FeN_5Cl chromophore [122]. For this material, a gradual transition with $\gamma_{\text{HS}}=0.3$ at 77 K and $\gamma_{\text{HS}}=0.5$ at 298 K was observed. In this instance, the ^{57}Fe Mössbauer spectra show three lines, i.e. a singlet attributed to high spin Fe(III) superimposed on an asymmetric quadrupole doublet assigned to low spin Fe(III).

A triply thiolate-bridged dinuclear Fe(III) compound exhibiting spin crossover behaviour has been reported by Kersting et al. [123]. The material has been obtained using the deprotonated form of 2,6-di(aminomethyl)-4-*tert*-butyl-thiophenol as tridentate ligand, yielding two connected FeN_3S_3 spin crossover chromophores (Fig. 10). The compound $[\text{Fe}_2\text{L}_3](\text{ClO}_4)_3$ is diamagnetic at room temperature due to the presence of an almost equimolar mixture of low spin-low spin Fe(III) dimers together with strongly antiferromagnetically coupled high spin-high spin species. The ^{57}Fe Mössbauer spectra show distinctly different features at 293, 180 and 77 K involving well resolved quadrupole doublets for low spin and high spin Fe(III) ions, indicating that both high spin Fe(III) ions within a dinuclear entity undergo a transition to the low spin state with decreasing temperature.

The synergy between magnetic interaction and spin crossover has been explored in five-coordinate Fe(III) complexes containing two bidentate *cis*-1,2-dicyano-1,2-ethylenedithiolates together with a monodentate coordinat-

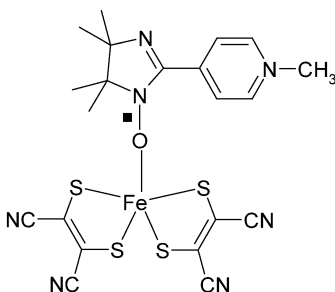


Fig. 11 Schematic representation of bis(*cis*-1,2-dicyano-1,2-ethylenedithiolato)[2-(*para*-*N*-methylpyridinium)-4,4,5,5-tetramethylimidazolin-1-oxyl]iron(III) [124]

ed organic radical [124, 125]. The X-ray structure of bis(*cis*-1,2-dicyano-1,2-ethylenedithiolato)[2-(*para*-*N*-methylpyridinium)-4,4,5,5-tetramethylimidazolin-1-oxyl]iron(III) (Fig. 11) determined at 293 K shows that the two bidentate thiolate ligands form the basal plane of an OS_4 square-pyramid about the Fe(III) ion (mean Fe–S=2.24 Å), whereas the radical cation occupies the apical position (Fe–O=2.056(5) Å) [124]. The magnetic data could be interpreted by assuming that the non-exchange-coupled radical spin ($S_{\text{radical}}=1/2$) and the quartet spin state of Fe(III) ($S_{\text{Fe}}=3/2$) were responsible for the χT value of $2.33 \text{ cm}^3 \text{ K mol}^{-1}$ determined between 100 and 300 K. Below 100 K, the χT value steadily decreases and tends towards zero at very low temperature. This behaviour may originate from the antiferromagnetic interaction between the radical spin ($S_{\text{radical}}=1/2$) and the doublet state of Fe(III) ($S_{\text{Fe}}=1/2$), resulting in a higher energetic $S=1$ molecular state, which is depopulated at decreasing temperature, while the lower lying $S=0$ molecular state is simultaneously populated. Obviously, this explanation involves an intermediate spin to low spin transition centred on the Fe(III) ion. Unfortunately, this phenomenon has not been further investigated by ^{57}Fe Mössbauer spectroscopy.

Changing the radical cation yielded the related material bis(*cis*-1,2-dicyano-1,2-ethylenedithiolato)[2-(*p*-pyridyl)-4,4,5,5-tetramethyl-imidazolium]iron(III)·2DMF [125]. The crystallographic data collected at 293 K again reveal two bidentate thiolate ligands in the basal plane (mean Fe–S=2.23 Å), but in this instance, the apical site is occupied by the N-donor radical cation (Fe–N=2.192(3) Å). The Fe(III) ion has an intermediate spin ($S_{\text{Fe}}=3/2$), but below 4 K the ^{57}Fe Mössbauer spectra show a second doublet with larger quadrupole splitting and a higher isomer shift, which has been ascribed to the low spin state ($S_{\text{Fe}}=1/2$).

A low spin $\leftrightarrow$ intermediate spin transition has also been found for a unique Fe(III) compound having an octahedral FeN_4S_2 environment [126]. In this compound the Fe(III) ion is surrounded by the tetradentate N-donating macrocycle *N,N'*-dimethyl-2,11-diaza[3.3](2,6)pyridinophane together with

the bidentate S-donating 1,2-benzenedithiolate, which occupies the *cis* positions in the equatorial plane. Magnetic measurements indicate a gradual spin crossover with $\gamma_{\text{HS}}=0.4$ at 150 K and $\gamma_{\text{HS}}=0.85$ at 298 K. The mean bond distances determined are (at 293 K, 150 K): Fe–N(pyridine)=2.020 Å, 1.979 Å, Fe–N(amine)=2.222 Å, 2.144 Å and Fe–S=2.197 Å, 2.206 Å. It has been proposed that the slight increase in Fe–S bond length may be related to the stronger π -donor interactions that occur in a compound containing an Fe(III) ion in an intermediate spin state than in one with a low spin Fe(III) ion. It has also been proposed that the highly distorted *cis* octahedral N₄S₂ geometry is responsible for the occurrence of this rather unusual intermediate spin state for a six-coordinate Fe(III) ion.

3

Iron(III) Spin Crossover Systems of Multidentate Schiff Base-Type Ligands

Schiff base-type systems are the second most widespread class of ligands which have been used to obtain Fe(III) spin crossover materials. These ligands may be classified according to the number of donor atoms available for coordination to the Fe(III) ion. In Sects. 3.1 to 3.4 attention is drawn to tri-, tetra-, penta- and hexadentate Schiff base-type ligands, severally. Section 3.5 focuses on spin crossover in iron(III) induced by light irradiation, whereas Sect. 3.6 is devoted to recent developments in the field of materials science with the objective of incorporation of Fe(III) spin crossover materials in devices.

Section 2 already demonstrated that ⁵⁷Fe Mössbauer spectroscopy provides a very powerful experimental technique to assess the spin state of Fe(III). High spin compounds show a quadrupole doublet with isomer shift δ values in the range 0.25–0.37 mm s^{−1} and quadrupole splitting ΔE_Q values below 1.3 mm^{−1}. On the other hand, low spin Fe(III) compounds have δ values in the range 0.05–0.20 mm s^{−1} together with relatively large ΔE_Q values (1.9–3.0 mm s^{−1}). It became evident that the spin states of compounds of dithio-, monothio-, and diselenocarbamates interconvert faster than the reciprocal of the lifetime, τ_N , of the ⁵⁷Fe Mössbauer nuclear level (10^{−7} s). However, for the complexes of Schiff base ligands the spin-interconversion rates have been found to depend on subtle solid-state effects such as variation in the counter ion and ligand substitution effects. This may give rise to distinctly different ⁵⁷Fe Mössbauer spectra even for systems which are chemically very similar. When the spin-interconversion is slower than the reciprocal of τ_N , two sets of quadrupole doublets corresponding to the high spin and low spin states are observed. On the other hand, spin crossover systems with much faster spin-interconversion than τ_N^{-1} show only one quadrupole doublet with quadrupole splitting and isomer shift parameters related to the fraction of each spin state. In the intermediate case, i.e. the spin-interconver-

sion rate being comparable to τ_N^{-1} , the spectra show broadened quadrupole doublet lines, so-called relaxation spectra or time-averaged spectra. Examples of each type of behaviour can be found in the present section.

3.1

Complexes of Tridentate N₂O-Donating Ligands

Among the Schiff base derivatives, the ones providing a tridentate N₂O donor set for Fe(III) have been studied the most extensively. Several ligand systems have been used; these are shown in Fig. 12. The compounds have the general molecular formula $[\text{Fe}(\text{ligand}^-)_2](\text{anion}^-)\cdot\text{solvent}$. The anionic nature of the ligand arises from deprotonation of the hydroxy group which is present in all examples. In addition, incorporation of solvent molecules has frequently been observed and this can have a decisive effect on the spin crossover properties. Clearly, a major difference among the ligand systems depicted in Fig. 12 is that these may form chelate rings of different sizes: the coordination involving the N and O atoms of the salicylidene moiety leads in all instances to a six-membered chelate, whereas the N,N coordination yields a six-membered chelate for 3-OEt-salAPA, and a five-membered chelate for all other ligand systems. Moreover, structural studies of these Fe(III) materials containing an FeN_4O_2 environment (Table 3), have revealed that the Fe–O distances are always shorter than the Fe–N bond lengths. These features result in a distortion of the FeN_4O_2 octahedron. Consequently, the

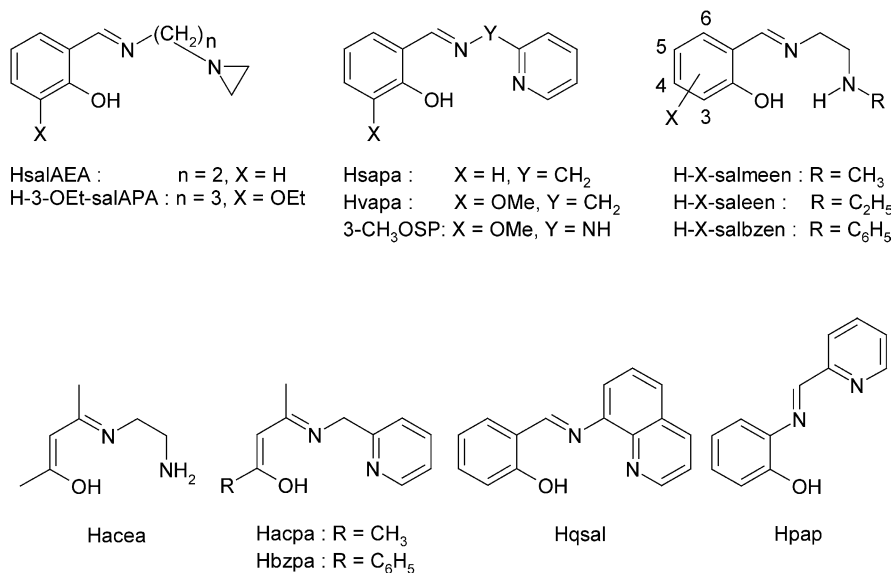


Fig. 12 Tridentate N₂O-donating Schiff base ligands

Table 3 Average Fe–donor atom bond lengths for Fe(III) compounds of tetradentate N_2O_2 -donating Schiff base ligands^{a,b,c,d}

Compound	T (K)	Fe—O	Fe—N _{central}	Fe—N _{outer} (Å)	Spin state	References
[Fe(3-OEt-salAPA) ₂][ClO ₄ ·C ₆ H ₆]	20	1.864 (8)	1.95 (1)	2.098 (9)	LS	[127]
		1.845 (8)	1.95 (1)	2.037 (9)	LS	
	128	1.864 (4)	1.954 (5)	2.023 (5)	LS	
		1.850 (4)	1.961 (5)	2.032 (5)	LS	
	175	1.884 (5)	1.994 (6)	2.071 (6)	LS/HS	
[Fe(3-OEt-salAPA) ₂][ClO ₄ ·C ₆ H ₅ Cl]		1.877 (5)	2.028 (6)	2.095 (6)	LS/HS	[128]
	298	1.923 (5)	2.085 (7)	2.173 (8)	HS	
	300	1.921 (2)	2.085 (3)	2.176 (3)	HS	
	158	1.860 (5)	1.968 (6)	2.040 (6)	LS	
		1.866 (5)	1.969 (6)	2.046 (6)	LS	
[Fe(3-OEt-salAPA) ₂][ClO ₄ ·C ₆ H ₅ Br]	296	1.914 (6)	2.095 (6)	2.185 (6)	HS	[128]
	163	1.900 (7)	2.027 (8)	2.115 (7)	LS	
		1.882 (7)	1.974 (7)	2.060 (7)	LS	
	296	1.917 (10)	2.091 (11)	2.179 (9)	HS	
	296	1.925 (3)	2.081 (4)	2.198 (6)	HS	
[Fe(3-OEt-salAPA) ₂][ClO ₄ ·C ₆ H ₄ Cl ₂]	292	1.913 (2)	2.092 (3)	2.224 (3)	HS	[129]
		1.915 (2)	2.108 (3)	2.194 (3)	LS ^e	
	292	1.880 (2)	1.933 (3)	2.053 (3)	LS ^e	
		1.877 (2)	1.934 (3)	2.067 (3)	LS ^e	
	292	1.886 (1)	1.944 (1)	2.046 (1)	67%LS	
[Fe(5-NO ₂ -salmeen) ₂][PF ₆]	298	1.941 (4)	1.976 (5)	2.148 (5)	(Fe1)	[130]
		1.852 (5)	1.989 (5)	2.094 (5)	(Fe1)	
		1.864 (4)	1.949 (4)	2.031 (4)	(Fe2)	
		1.903 (4)	1.924 (4)	2.063 (4)	(Fe2)	
	293	1.932 (2)	2.090 (2)	2.184 (2)	HS	
[Fe(3-allyl-salben) ₂][NO ₃]		1.937 (3)	2.085 (2)	2.182 (4)	LS	[131]
		1.889 (2)	1.941 (2)	1.989 (2)	LS	
	120	1.914 (2)	2.010 (2)	2.070 (2)	LS/HS	
	205	1.939 (2)	2.081 (2)	2.153 (2)	HS	
	290	1.939 (2)	2.081 (2)	2.153 (2)	HS	
[Fe(3-allyl-salben) ₂][PF ₆]	298	1.939 (2)	2.081 (2)	2.153 (2)	HS	[133]

Table 3 (continued)

Compound	T (K)	Fe—O	Fe—N _{central}	Fe—N _{outer} (Å)	Spin state	References
[Fe(acpa) ₂][BPh ₄]	120	1.902 (3)	1.937 (3)	1.976 (3)	LS	[132]
		1.889 (3)	1.938 (3)	1.987 (3)		
	202	1.896 (2)	1.941 (2)	1.979 (2)	LS	
		1.891 (2)	1.939 (2)	1.990 (2)		
	247	1.913 (2)	1.971 (2)	2.022 (2)	LS/HS	
[Fe(bzpa) ₂][ClO ₄]	311	1.873 (2)	1.969 (2)	2.001 (2)	LS/HS	[134]
		1.920 (2)	2.027 (2)	2.082 (2)		
		1.913 (2)	2.029 (2)	2.093 (2)		
	140	1.896 (3)	1.94 (3)	1.964 (3)		
		1.919 (3)	1.926 (3)	1.988 (3)		
[Fe(qsal) ₂][NCSe·MeOH]	290	1.911 (3)	2.018 (4)	2.070 (4)	HS	[135]
		1.930 (3)	2.015 (4)	2.078 (4)		
	200	1.871 (6)	1.949 (7)	1.976 (7)	LS	
		1.869 (6)	1.941 (7)	1.971 (7)		
	230	1.879 (2)	1.944 (3)	1.985 (3)	LS	
[Fe(qsal) ₂][NCSe·CH ₂ Cl ₂]		1.875 (3)	1.953 (3)	1.991 (3)	LS	[136]
	90	1.875 (4)	1.936 (4)	1.975 (4)		
		1.874 (3)	1.938 (4)	1.961 (4)		
	298	1.932 (8)	2.105 (9)	2.202 (10)		
		1.931 (8)	2.136 (9)	2.138 (9)		
[Fe(pap) ₂][ClO ₄ ·H ₂ O]		1.883 (4)	1.911 (5)	1.994 (5)	HS	[137]
	90	1.883 (4)	1.911 (5)	1.994 (5)		
		1.882 (4)	1.915 (5)	1.993 (5)		
[Fe(pap) ₂][PF ₆ ·MeOH]					LS	[138]

^a For non-centrosymmetric Fe(III) entities the bond lengths involving the two crystallographically independent tridentate ligands are noted in line 1 and 2, respectively ^b For compounds containing two crystallographically independent Fe(III) cations, the details for sites Fe1 and Fe2 are noted in line 1 and 2, respectively ^c The ligands are shown in Fig. 12. Abbreviations used for the ligands can be found in the list of abbreviations ^d Predominant spin state (HS or LS) or mixture of both spin states (LS/HS) is indicated. All compounds exhibit spin cross-over unless indicated otherwise ^e Purely low spin compound

rigidity and distortion of the Fe(III) coordination octahedron may be varied depending on the ligand.

Iron(III) compounds of 3-OEt-salAPA have been widely studied [127, 128, 139–145]. Both the anion and the incorporated solvent molecule influence the spin crossover behaviour of the complex salts. Thus $T_{1/2}$ for $[\text{Fe}(\text{3-OEt-salAPA})_2]\text{ClO}_4$ is 295 K, whereas that for the dichloromethane solvate is 152 K [140]. The transition in $[\text{Fe}(\text{3-OEt-salAPA})_2]\text{ClO}_4$ and $[\text{Fe}(\text{3-OEt-salAPA})_2]\text{BPh}_4$ is more gradual and occurs at a somewhat higher temperature than that for the benzene solvate $[\text{Fe}(\text{3-OEt-salAPA})_2]\text{ClO}_4 \cdot \text{C}_6\text{H}_6$ [141].

Interestingly, various benzene derivatives may be incorporated in the crystal lattice yielding $[\text{Fe}(\text{3-OEt-salAPA})_2]\text{ClO}_4 \cdot \text{solvent}$ [128, 141, 142]. Below about 50 K the six complexes studied (no solvent, C_6H_6 , $\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_6\text{H}_5\text{Br}$, $\text{C}_6\text{H}_5\text{I}$ or *o*- $\text{C}_6\text{H}_4\text{Cl}_2$) are low spin with a magnetic moment of 2.0 B.M. As the temperature is increased all six compounds exhibit spin crossover, which is the most gradual for the non-solvated material. The μ_{eff} value for this complex increases gradually from 2.24 B.M. at 99 K to 4.60 B.M. at 300 K. The degree of abruptness varies from one solvate to the other: the transition in the $\text{C}_6\text{H}_5\text{I}$ solvate is the least, and that in the $\text{C}_6\text{H}_5\text{Cl}$ is the most abrupt [128]. The transition temperature for the various $[\text{Fe}(\text{3-OEt-salAPA})_2]\text{ClO}_4 \cdot \text{solvent}$ systems was found to depend linearly on the molecular volume of the monohalogenated benzene derivative [142]. The only exception to this relation is the chlorobenzene analogue.

X-ray structures have been determined at various temperatures for $[\text{Fe}(\text{3-OEt-salAPA})_2]\text{ClO}_4 \cdot \text{solvent}$ containing solvated benzene or its halogenated derivatives (Table 3). Typically, within the FeN_4O_2 core the Fe–N(amine) bonds are longest, the Fe–O bonds shortest, and the Fe–N(imine) bonds intermediate. It appears that the Fe–N(amine) distances are most affected by the spin transition. Additional noteworthy structural features have been observed for some of these compounds. The space group determined for $[\text{Fe}(\text{3-OEt-salAPA})_2]\text{ClO}_4 \cdot \text{C}_6\text{H}_6$ is $\text{P}2_1/\text{c}$ at 20 K, 128 K and 175 K and $\text{C}2/\text{c}$ at room temperature [127]. In the $\text{C}2/\text{c}$ structures the Fe(III) entity is located on an inversion centre, whereas the perchlorate anion and the benzene molecule are situated on a twofold axis. The transformation to $\text{P}2_1/\text{c}$ brings about an inequality of the Fe(III) sites: in this instance, two crystallographically independent Fe(III) units are present, each located on a crystallographic inversion centre. However, the gradual, but complete spin crossover at $T_{1/2}=205$ K is not related to this change in space group, which can in fact be considered as an order-disorder transformation taking place at about 180 K [127]. The thermodynamic parameters associated with the phase and spin transitions in $[\text{Fe}(\text{3-OEt-salAPA})_2]\text{ClO}_4 \cdot \text{C}_6\text{H}_6$ have been determined from heat capacity measurements (see below) [144].

A change in space group has also been observed for $[\text{Fe}(\text{3-OEt-salAPA})_2]\text{ClO}_4 \cdot \text{C}_6\text{H}_5\text{X}$ ($\text{X}=\text{Cl}, \text{Br}$) [128]. The space group for the chlorobenzene derivative is $\text{P}2_1/\text{c}$ at 296 K and converts to $\text{P}2_1/\text{a}$ at 158 K. A similar trans-

formation has been observed for the bromobenzene compound: its space group is $P2_1/c$ at 296 K, whereas it is $P2_1/a$ at 163 K. In converting from $P2_1/c$ to $P2_1/a$ the Fe(III) cations and perchlorate anions remain in the same relative positions, however, half of the C_6H_5X solvate molecules experience a re-orientation. These structural phase transitions in $[Fe(3-OEt-salA-PA)_2]ClO_4 \cdot C_6H_5X$ ($X=Cl, Br$) have been investigated in detail [143, 145]. For the bromobenzene derivative there is little cooperativity between the structural phase transition at 288.3 K and the spin crossover, since the spin transition progresses essentially as an equilibrium process in the solid state. In contrast, for the chlorobenzene solvate, the 188.4 K phase transition cooperatively involves both the spin crossover and the structural change [143].

While both chelate rings in the complexes of 3-OEt-salAPA are six-membered, for salAEA a six-membered chelate ring involving N and O atoms and a five-membered N,N-chelate ring are formed. Only one compound of this ligand has been reported, $[Fe(salAEA)_2]ClO_4$, which is predominantly high spin; even at 20 K there is probably no more than 20% population of the low spin state [139].

Similar six-membered N,O- and five-membered N,N-chelate rings are formed in Fe(III) compounds of sapa and vapa. $[Fe(vapa)_2]PF_6$ appears to be high spin, whereas $[Fe(sapa)_2]NO_3 \cdot 1.5H_2O$ exhibits a very gradual and incomplete (at low temperature) spin transition [146]. The related 3- CH_3OSPH yielded the low spin compounds $[Fe(3-CH_3OSPH)_2]X$ ($X=Cl^-, NO_3^-$), as well as the spin crossover materials $[Fe(3-CH_3OSPH)_2]X$ ($X=PF_6^-, BPh_4^-$) [147]. Both the latter compounds exhibit gradual spin crossover, with the transition temperature for the PF_6^- salt being higher (45% of low spin Fe(III) ions at 298 K) than that of the BPh_4^- salt (fully high spin at 298 K) [147].

Another family of bis(ligand)Fe(III) spin crossover systems with the donor atom set N_4O_2 is that derived from Schiff bases obtained from the condensation of X-salicylaldehyde and N-R-ethylenediamine (X-salmeen ($R=CH_3$), X-saleen ($R=C_2H_5$), X-salbzen ($R=C_6H_5$); Fig. 12). Within the X-salmeen series crystal structures have been determined at 292 K for high spin $[Fe(5-OCH_3-salmeen)_2]PF_6$, as well as for the low spin materials $[Fe(3-OCH_3-salmeen)_2]PF_6$ and $[Fe(5-NO_2-salmeen)_2]PF_6$ [129] (Table 3). Apart from the observed differences in metal-donor atom bond lengths, the high spin compound is more distorted from octahedral than the low spin compounds [129]. Variation of the substituent X within $[Fe(X-salmeen)_2]PF_6$ yielded compounds showing substantial differences in their magnetic behaviour, but a general pattern for the influence of the substituent could not be established due to the overlying solid state effects involved [148]. The material containing unsubstituted salmeen ($X=H$) is purely high spin. Both the 5- OCH_3 -salmeen and 4- OCH_3 -salmeen complexes are essentially high spin at room temperature and exhibit gradual and incomplete transitions to low spin at low temperature [148]. The compounds with $X=3-NO_2$, 3- OCH_3 and 5- NO_2 show the onset of spin crossover at about 200 K, however, at room

temperature the magnetic moment is still below 3.0 B.M [148]. In acetone solutions, compounds that have been observed to be essentially low spin in the solid state exhibit spin crossover, and moreover, the spin transition becomes more pronounced for compounds that also show spin crossover in the solid state [148]. The percentage of the high spin isomer in acetone solution decreases according to the salicylaldimine ring substituent series: 3-OCH₃ (88% at 314 K) > 5-OCH₃ (82% at 314 K) > H (80% at 314 K) > 3-NO₂ (36% at 299 K) > 5-NO₂ (19% at 285 K). The variable-temperature studies confirm this to be the general pattern over the entire 200–300 K temperature range. The same sequence of field strengths, OCH₃ > H > NO₂, has also been observed for [Fe(X-sal₂trien)]PF₆ (X-sal₂trien=hexadentate N₄O₂ Schiff base obtained from the 1:2 condensation of triethylenetetramine with salicylaldehyde derivatives; see below) [149], but the actual values appear to be greater in the hexadentate systems [148]. The influence of the solvent on the spin crossover characteristics has been studied for the parent compound [Fe(salmeen)₂]PF₆ [148], with the order of favouring of the high spin state being acetone > CH₃CN > CH₃OH > CH₂Cl₂ > Me₂SO. There is no obvious correlation between this sequence and the strength of the [solvent...H–N] hydrogen bonding interaction as deduced from the position of the ν_{N–H} vibration in the IR spectra [148].

The dependence of the spin state of Fe(III) on the associated anion has been studied for solid-state [Fe(X-saleen)₂]Y (Y=BPh₄[–], NO₃[–], PF₆[–]) [150]. The tetraphenylborate salts [Fe(saleen)₂]BPh₄·0.5H₂O [150] and [Fe(3-OCH₃-saleen)₂]BPh₄ [151, 152] are high spin, whereas [Fe(3-OCH₃-saleen)₂]NO₃·0.5H₂O [150–152] and [Fe(5-OCH₃-saleen)₂]NO₃ are predominantly low spin [150, 151]. On the other hand, [Fe(saleen)₂]NO₃ exhibits an incomplete, gradual spin transition [150–152]. Interestingly, the mixed-anion species [Fe(5-OCH₃-saleen)₂](NO₃)_{0.5}(BPh₄)_{0.5} exhibits gradual spin crossover, the transition being complete at low temperature but incomplete at 286 K [150]. The hexafluorophosphate salts give rise to spin crossover in a number of instances [150–154]: [Fe(saleen)₂]PF₆ undergoes a gradual, but complete spin transition [151]. However, [Fe(3-OCH₃-saleen)₂]PF₆ exhibits an extremely abrupt spin crossover at about 159 K, associated with a thermal hysteresis loop of width 2–4 K [150–152]. The effect of grinding of the sample on the spin crossover characteristics is to render the transition less abrupt and less complete as well as to lower the transition temperature [151, 152]. It was suggested that this results from an increase in defects and stress points in the crystal [151]. Interestingly, a sample of [Fe(3-OCH₃-saleen)₂]PF₆ that had been subjected to an external pressure of about 1.4 kbar for a period of 5 min shows similar features [152]. The effect of grinding has been found to be much greater for a sample doped with Cr(III) ions, [Fe_{0.5}Cr_{0.5}(3-OCH₃-saleen)₂]PF₆, which shows a gradual, complete transition. After the sample has been ground in a ball mill, the spin transition has been found to be suppressed [151]. Experiments on [Fe_xM_{1–x}(3-OCH₃-saleen)₂]PF₆ doped with

M(III)=Cr or Co show that doping leads not only to more gradual spin transitions but also a displacement of the transition temperature to lower values for Cr(III) and to higher for Co(III) [152]. These features can be related to the difference in ionic radius for high spin Fe(III) (0.65 Å) compared to Cr(III) (0.62 Å) or low spin Co(III) (0.53 Å) [152]. Later the dilution effect of Co(III) on the spin transition of Fe(III) was described in terms of (i) the lattice contraction due to the Co(III) ions, which favours the low spin state of Fe(III) and (ii) the contribution due to the spin transition [154]. The lattice contraction induced by the Co(III) results in the iron centres experiencing an increase in pressure, the so-called "image-pressure" with a concomitant increase in the transition temperature [154]. Since Cr(III) and high spin Fe(III) have comparable ion radii, this lattice contraction is not operative in this instance. Using the model of Sasaki and Kambara [154], the spin transition curves for compounds having varying Co(III) or Cr(III) dopant concentrations could be reproduced.

With X-salbzen the essentially high spin compounds $[\text{Fe}(\text{3-OEt-salbzen})_2]\text{X}$ ($\text{X}=\text{Cl}^-$, NO_3^-) have been obtained [130]. On the other hand, $[\text{Fe}(\text{3-OEt-salbzen})_2]\text{BPh}_4\cdot\text{CH}_3\text{CN}$ shows a gradual, relatively complete spin crossover with a high spin mole fraction of 0.93 at room temperature, which decreases to 0.03 at 10 K [130]. The structure of $[\text{Fe}(\text{3-allyl-salbzen})_2]\text{NO}_3$ has been determined at room temperature [130]. The unit cell contains two centrosymmetric, crystallographically independent cations. The metal-donor atom bond lengths (Table 3) are consistent with Fe2 being in the low spin state, whereas Fe1 may be considered as an average of 67% low spin and 33% high spin Fe1 sites, in agreement with the magnetic data. $[\text{Fe}(\text{3-allyl-salbzen})_2]\text{NO}_3$ exhibits a partial, gradual spin transition, reaching the low spin state ($\mu_{\text{eff}}=1.88$ B.M.) at 4.2 K [130].

The complex $[\text{Fe}(\text{acea})_2]\text{BPh}_4$ exhibits a gradual, almost complete spin crossover [131]. The Fe-donor atom bond lengths (Table 3) are consistent with high spin Fe(III) at room temperature.

Complexes of *acpa* and *bzpa* have been extensively studied. Crystal structures have been determined for $[\text{Fe}(\text{acpa})_2]\text{PF}_6$ at 120, 290 [132] and 298 K [133] and for $[\text{Fe}(\text{acpa})_2]\text{BPh}_4$ at 120, 202, 247 and 311 K [132]. Both compounds exhibit incomplete, gradual spin crossover behaviour. The transition temperature is higher for the tetraphenylborate salt than for the hexafluorophosphate [132, 133, 155]. The metal-donor atom bond lengths observed for $[\text{Fe}(\text{acpa})_2]\text{BPh}_4$ (Table 3) correspond with the extent to which the spin crossover has progressed at 120 K (low spin Fe(III) percentage=96.7%) and at 311 K (high spin Fe(III) percentage=80.9%). The transition temperature for $[\text{Fe}(\text{acpa})_2]\text{NO}_3$ is higher than that of both the BPh_4^- and PF_6^- derivatives [155].

The ^{57}Fe Mössbauer spectra for $[\text{Fe}_x\text{Co}_{1-x}(\text{acpa})_2]\text{BPh}_4$ ($x=0.035$ and 0.074) show that the transition has been displaced to a higher temperature than that for the pure Fe(III) compound [156]. This may again be related to

the difference in ionic radii for low spin Co(III) compared to high spin Fe(III) (see below). The EPR spectra for these diluted complexes have been measured at various temperatures. Signals attributed to low spin Fe(III) have been observed at $g=1.965$, 2.219 and 2.291 . This observation suggests that the geometry about the Fe(III) ion is more distorted in the diluted complex than in the neat compound. A signal observed at $g=4$ is characteristic for a high spin ferric complex in a rhombically distorted environment [156].

Fast electronic relaxation within $[\text{Fe}(\text{acpa})_2]\text{PF}_6$ has been thought to be responsible for the observation of a single doublet in the ^{57}Fe Mössbauer spectra throughout the transition with strongly temperature dependent values for the quadrupole splitting and isomer shift [133]. It has been proposed that the spin-interconversion of $[\text{Fe}(\text{acpa})_2]\text{BPh}_4$ is faster than that of the PF_6^- salt [132]. X-ray crystallographic studies carried out for both compounds at different temperatures revealed smaller changes in metal-donor atom bond length for the BPh_4^- salt. It was therefore concluded that the activation energy for the spin change in the BPh_4^- salt is smaller than that in the PF_6^- salt, which would imply faster spin-interconversion for the former [132].

The thermodynamic parameters associated with the spin transition in $[\text{Fe}(\text{acpa})_2]\text{PF}_6$ have been determined by calorimetry [157]. The unusual heat capacity anomaly observed for this material was typical for neither a first-order nor a second-order phase transition. It has therefore been assumed that it might originate from a higher order phase transition that is characterised by weak cooperativity [157]. The entropy associated with the low spin $\rightarrow$ high spin transition in $[\text{Fe}(\text{acpa})_2]\text{PF}_6$ ($\Delta S=36.19 \text{ J K}^{-1} \text{ mol}^{-1}$) has been found to be comparable with values for other Fe(III) spin transition materials of tridentate N_2O Schiff base ligands, i.e. $[\text{Fe}(\text{3-OMe-salen})_2]\text{PF}_6$ ($\Delta S=36.74 \text{ J K}^{-1} \text{ mol}^{-1}$) [157], $[\text{Fe}(\text{3-OEt-salAPA})_2]\text{ClO}_4 \cdot \text{C}_6\text{H}_6$ ($\Delta S=38.4 \text{ J K}^{-1} \text{ mol}^{-1}$) [144] and $[\text{Fe}(\text{3-OEt-salAPA})_2]\text{ClO}_4 \cdot \text{C}_6\text{H}_5\text{Cl}$ ($\Delta S=37.2 \text{ J K}^{-1} \text{ mol}^{-1}$) [145]. It is, however, significantly smaller than the values determined for Fe(II) spin crossover complexes, e.g. $[\text{Fe}(\text{1,10-phenanthroline})_2(\text{NCS})_2]$ ($\Delta S=48.78 \text{ J K}^{-1} \text{ mol}^{-1}$) [158, 159], and $[\text{Fe}(\text{2-picolyamine})_3]\text{Cl}_2 \cdot \text{EtOH}$ ($\Delta S=50.59 \text{ J K}^{-1} \text{ mol}^{-1}$) [160]. The observed entropy change associated with the spin crossover of $[\text{Fe}(\text{acpa})_2]\text{PF}_6$ could be explained by the sum of the contributions due to the change in the spin manifold ($9.13 \text{ J K}^{-1} \text{ mol}^{-1}$) and the skeletal vibrational changes accompanying the spin transition ($28.56 \text{ J K}^{-1} \text{ mol}^{-1}$). In fact, the temperature dependence of the IR and Raman spectra revealed drastic changes, which could be assigned to skeletal vibration modes of the six-coordinate Fe(III) core [157]. The enthalpy change associated with the low spin $\rightarrow$ high spin transition in $[\text{Fe}(\text{acpa})_2]\text{PF}_6$ has been estimated to be 7025 J mol^{-1} [157].

The structure of $[\text{Fe}(\text{bzpa})_2]\text{ClO}_4$ has been determined for the low spin form at 140 K , as well as for the high spin form at 290 K (Table 3) [134]. The gradual spin transition is complete as has been confirmed by the time-aver-

aged ^{57}Fe Mössbauer spectra [134]. The transition in $[\text{Fe}(\text{bzpa})_2]\text{PF}_6$, on the other hand, is incomplete over the range 80–300 K [155, 161].

Both $[\text{Fe}(\text{acpa})_2]\text{X}$ and $[\text{Fe}(\text{bzpa})_2]\text{X}$ ($\text{X}=\text{PF}_6^-$, BPh_4^- , NO_3^-) show reversible thermochromism in acetone solutions, which is typical for a change in electronic ground state of the $\text{Fe}(\text{III})$ ion. The electronic spectra show a temperature dependence of the intensities of the metal-charge transfer bands ascribed to the high spin (550 nm) and low spin state (700 nm) [155].

Early investigations on $\text{Fe}(\text{III})$ complexes of qsal provided evidence for spin crossover behaviour, its extent depending on the associated anion and the degree of hydration [162, 163]. The slight change in magnetic moment with change in temperature observed in 1969 for $[\text{Fe}(\text{qsal})_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ [162], was, on the basis of ^{57}Fe Mössbauer spectral data, later ascribed to a spin transition [163]. The solvent-free iodide salt is purely low spin, whereas the bromide monohydrate is high spin. On the other hand, the solvent-free thiocyanate salt again showed spin crossover behaviour: the magnetic moment gradually decreases from 5.63 B.M. at 299 K to 2.37 B.M. at 24 K [163]. The nature of the transition observed in this instance depends markedly on the temperature at which the material has been synthesised, i.e. either at 298 K or below 280 K [164]. For a sample prepared from a methanolic solution at 298 K the transition is associated with an asymmetric hysteresis loop of width 70 K. There are two steps—at about 220 K and 270 K—in the heating branch, which may suggest the existence of another phase or another isomer with a different transition temperature. In contrast, $[\text{Fe}(\text{qsal})_2]\text{NCS}$ freshly recrystallised from methanol below 280 K is predominantly low spin. However, the magnetic moment determined at room temperature increases with time. Ten days after preparation the sample shows spin crossover with a pronounced hysteresis loop ($\Delta T_{1/2}=70$ K) centred at 286 K. These interesting spin crossover features prompted the study of the selenocyanate salts [135, 136]. $[\text{Fe}(\text{qsal})_2]\text{NCSe}\cdot\text{MeOH}$ [135], $[\text{Fe}(\text{qsal})_2]\text{NCSe}\cdot\text{CH}_2\text{Cl}_2$ [135] and $[\text{Fe}(\text{qsal})_2]\text{NCSe}\cdot 2\text{DMSO}$ [136] are low spin at room temperature. However, these all lose solvent molecules on heating, converting to the non-solvated high spin analogues which display spin crossover below room temperature. The non-solvated materials derived from the methanol and dichloromethane compounds show identical magnetic properties involving a reproducible two-step spin crossover. The high spin to low spin transition takes place at $T_{1/2\downarrow}=212$ K, while the low spin to high spin transition exhibits two pronounced steps at 215 K and 282 K, resulting in thermal hysteresis loops of widths 3 K and 70 K for these successive transitions, respectively. This unusual hysteresis loop involving a two-step spin crossover in the warming mode and a one-step transition in the cooling mode could be simulated theoretically [135]. Solvent removal from $[\text{Fe}(\text{qsal})_2]\text{NCSe}\cdot 2\text{DMSO}$ leads to a transition with an hysteresis loop of width 76 K ($T_{1/2\uparrow}=285$ K, $T_{1/2\downarrow}=209$ K), which is one of the broadest hysteresis effects reported so far for spin crossover compounds [136]. Structures were determined for low spin $[\text{Fe}$

(qsal)₂]NCSe·MeOH (200 K) [135], [Fe(qsal)₂]NCSe·CH₂Cl₂ (230 K) [135] and [Fe(qsal)₂]NCSe·2DMSO (90 K) [136] (Table 3). These revealed intermolecular π -interactions between quinoline and phenyl rings resulting in a two-dimensional network. It is very likely that the cooperativity operating in these selenocyanate systems arises mainly from this structural feature.

Very interesting Fe(III) spin crossover characteristics have been found for compounds of pap. Solvent-free [Fe(pap)₂](anion) compounds have been investigated: the nitrate and tetraphenylborate materials are high spin, whereas the hexafluorophosphate derivative is low spin [164]. The freshly prepared perchlorate compound exhibits spin crossover behaviour associated with an asymmetric thermal hysteresis loop ($T_{1/2\uparrow}$ =262 K and $T_{1/2\downarrow}$ =242 K) [164]; however, the transition temperature decreases as the compound ages, and reaches 150 K one week after preparation [165]. The authors do not indicate whether the hysteresis is retained. A further notable feature of this "aged" sample is that high spin Fe(III) ions can be frozen in by rapid quenching to 80 K [165]. The monohydrate, [Fe(pap)₂]ClO₄·H₂O, exhibits abrupt transitions in the heating ($T_{1/2\uparrow}$ =180 K) and cooling mode ($T_{1/2\downarrow}$ =165 K) [137]. [Fe(pap)₂]PF₆·MeOH also shows a relatively abrupt transition at $T_{1/2}$ =288 K, albeit without thermal hysteresis [138]. X-ray structures could be determined for high spin [Fe(pap)₂]ClO₄·H₂O (298 K) [137] and low spin [Fe(pap)₂]PF₆·MeOH (90 K) [138] (Table 3). Both compounds crystallise in the space group P-1 and their structures are similar. It is noteworthy that the changes in metal-donor atom bond lengths are larger than normally observed in Fe(III) spin crossover compounds. In addition, the changes in the Fe–N bond lengths are much greater than those for the *cis*-arranged Fe–O bonds. Thus the Fe(III) spin crossover is accompanied by an asymmetric stretching of the Fe-ligand bonds involving a scissor-like opening of the pap ligands. Strong intermolecular π -stacking occurs between the aromatic rings of pap ligands originating from different [Fe(pap)₂]⁺ units and resulting in the formation of wrapped sheets. This structural feature appears to be responsible for the high cooperativity as well as the occurrence of Light-Induced Excited Spin State Trapping (LIESST) for this system (see below) [137, 138].

3.2

Complexes of Tetradentate Ligands

3.2.1

General Considerations

Spin crossover behaviour generated by Schiff base ligands predominantly occurs when the Fe(III) ion is coordinated by an N₄O₂ donor set. This donor set is also found with N₂O₂-donating tetradentate Schiff base systems together with two appropriate N-donating heterocyclic bases as co-ligands. In ad-

dition, the N-donating nitrosyl anion may also be incorporated as co-ligand, in this instance resulting in FeN_3O_2 spin crossover entities. Interestingly, the use of N_4 -donating ligands has also lead to the generation of spin transition materials, in this case comprising FeN_4Br_2 , FeN_5 or FeN_4X ($\text{X}=\text{Cl}^-$, Br^-) moieties. These various systems are considered below.

3.2.2

Complexes of Tetradentate N_4 -Donating Ligands

Spin crossover in iron(III) has been generated using the N_4 -donating macrocyclic ligands 1,4,8,11-tetraazacyclotetradecane (cyclam) and its tetramethylated derivative (tmcyclam), as well as with the Schiff base system H_2amben (Fig. 13).

A series of mononuclear Fe(III) cyclam compounds has been reported in which monodentate, monovalent anionic groups occupy the axial positions [166]. The cyclam system acts as a neutral ligand and thus an additional non-coordinating anion is required for charge compensation. Both the magnetism and EPR spectra indicate that $[\text{Fe}(\text{cyclam})\text{Cl}_2](\text{ClO}_4)$ and $[\text{Fe}(\text{cyclam})(\text{NCS})_2](\text{NCS})$ are purely low spin compounds, but a transition is observed in $[\text{Fe}(\text{cyclam})\text{Br}_2](\text{ClO}_4)$ for which two sets of EPR signals are observed with relative intensities that are temperature dependent [166].

Using tmcyclam a five-coordinate compound has been obtained [167]. The X-ray structure of $[\text{Fe}(\text{tmcyclam})(\text{NO})](\text{BF}_4)_2$ has been determined at room temperature, revealing an Fe(III) ion in a distorted tetragonal pyramid consisting of the four nitrogen atoms of the macrocycle (average $\text{Fe}-\text{N}=2.165 \text{ \AA}$) together with a nitrosyl anion in the apical position. The $\text{Fe}-\text{N}-\text{O}$ bond angle is essentially linear ($177.5(5)^\circ$) with $\text{Fe}-\text{NO}$ and $\text{FeN}-\text{O}$ interatomic distances of $1.737(6)$ and $1.137(6) \text{ \AA}$, respectively. The axially oriented *N*-methyl groups are all on the same side of the $\text{Fe}(\text{tmcyclam})$ moiety as the nitrosyl group. The magnetic moment is 2.66 B.M. at 4.2 K, but gradually increases with increasing temperature, levelling off at about 150 K and remaining virtually constant at 3.62 B.M. to 286 K, characteristic for an $\text{S}=1/2 \leftrightarrow \text{S}=3/2$ transition, which has also been supported by EPR and ^{57}Fe Mössbauer spectral studies. In addition, the change in the appearance of the NO

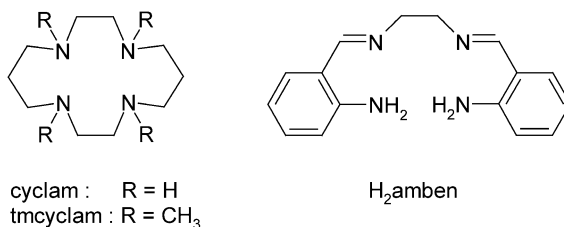


Fig. 13 Tetradentate N_4 -donating ligands

stretching vibration in the IR spectra with decreasing temperature is consistent with electrons pairing up in a lower lying molecular orbital that contains a contribution from the π^* orbitals of the nitrosyl entity [167]. Related five-coordinate FeN_3O_2 spin crossover systems involving the nitrosyl anion and N,N' -ethylenebis(salicylideneimine) have also been described (see below).

Five-coordinate FeN_4X ($\text{X}=\text{Cl}^-$, Br^-) spin transition entities have been obtained using H_2amben (Fig. 13) [168]. The magnetic moments of $[\text{Fe}(\text{amben})\text{Cl}]$ and $[\text{Fe}(\text{amben})\text{Br}]\cdot\text{H}_2\text{O}$ are similar (3.85 and 3.62 B.M., respectively at 295 K) and only slightly temperature dependent. However, the occurrence of spin crossover in these compounds has been confirmed by variable temperature ^{57}Fe Mössbauer spectroscopy, as well as by EPR spectroscopy carried out at 77 K. The ^{57}Fe Mössbauer spectra recorded at 77 and 295 K for the chloro compound reveal two quadrupole doublets indicating the existence of two different spin components at both temperatures and with relative intensities that are temperature dependent. The EPR spectrum recorded for the bromide material in dilute ethanol solution shows a sharp three line pattern characteristic of low spin Fe(III) at $g=2.10$, 2.05 and 1.93, and a broader band attributed to the high spin component at $g=4.9$ [168].

3.2.3

Five-Coordinate Complexes of Tetradentate N_2O_2 -Donating Schiff Base Ligands

The use of appropriate tetradentate N_2O_2 -donating Schiff base ligands (Fig. 14) together with the incorporation of the N-donating nitrosyl anion has resulted in the formation of a unique series of five-coordinate Fe(III) spin crossover materials containing FeN_3O_2 chromophores.

The first and most extensively studied compound of this class is $[\text{Fe}(\text{salen})(\text{NO})]$, which exhibits an abrupt $S=1/2 \leftrightarrow S=3/2$ spin transition with associated hysteresis centred at $T=175$ K and virtually complete over a temperature interval of a few degrees [169–171]. Such features are relatively uncommon for iron(III). In contrast, $[\text{Fe}(\text{5-Cl-salen})(\text{NO})]$ is in the $S=3/2$ state

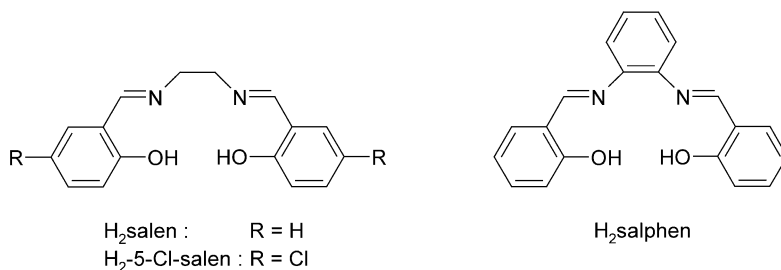


Fig. 14 Tetradentate N_2O_2 -donating Schiff base ligands. The use of NO as co-ligand yields FeN_3O_2 chromophores

(μ_{eff} =3.8 B.M.) at temperatures above 50 K. The magnetic moment decreases at lower temperatures, reaching a value of only 0.5 B.M. at 4.2 K, indicative of antiferromagnetic interactions [169].

The structure of [Fe(salen)(NO)] has been determined at 98 and 296 K [172]. Notwithstanding the abrupt nature of the spin transition and its association with thermal hysteresis, the space group $Pna2_1$ is retained at both temperatures. With decreasing temperature a significant shortening in metal-donor atom bond lengths involving the salen ligand has been observed: the mean Fe–O distance very slightly decreases from 1.908 Å at 296 K to 1.899 Å at 98 K, whereas more substantial changes are detected in the mean Fe–N bond length (2.075 Å at 296 K and 1.974 Å at 98 K). The Fe–N(nitrosyl) distance is 1.783 Å at 296 K, whereas at 98 K, where the NO group is disordered over two sites, an average distance of 1.80 Å was determined. The most important changes occurring with decreasing temperature, i.e. upon the $S=3/2 \rightarrow S=1/2$ spin crossover are (i) a decrease of almost 0.1 Å in Fe–N(salen) bond lengths, (ii) a smaller displacement of the Fe(III) ion from the salen coordination plane (0.47 Å at 296 K compared to 0.36 Å at 98 K), which is consistent with the smaller volume for the Fe(III) ion in the doublet state, and (iii) a closer approach to coplanarity of the salicylideneiminato moieties of the salen ligand. Interestingly, there are some noteworthy differences with respect to the structure of [Fe(tmcyclam)(NO)](BF₄)₂ (see above) [167]. In the tmcyclam compound the Fe–N–O sequence has been found to be essentially linear, and the coordination geometry about the Fe(III) centre can be regarded as distorted toward a trigonal bipyramid. In contrast, the salen material has a strongly bent Fe–N–O moiety, and the Fe(III) geometry is essentially tetragonal pyramidal at both temperatures [172].

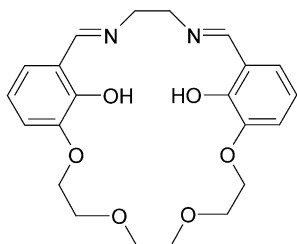
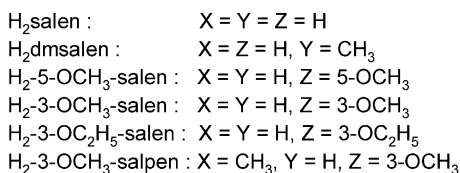
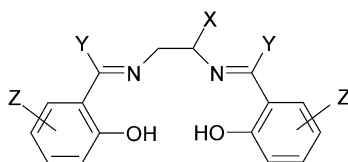
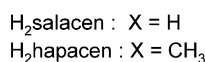
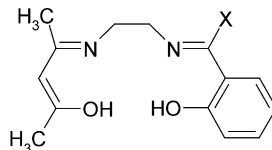
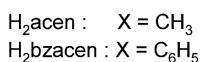
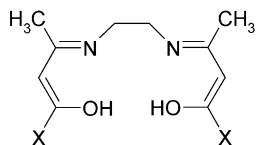
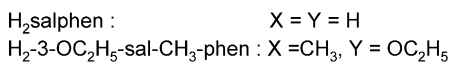
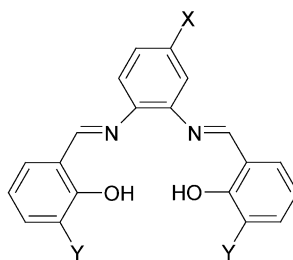
The spin transition in [Fe(salen)(NO)] has been studied by IR [171, 172], ⁵⁷Fe Mössbauer [169, 173] and EPR spectroscopy [169]. IR spectra have also been recorded at room temperature for various pressures ranging from ambient up to 37 kbar. At 37 kbar conversion to the $S=1/2$ state is complete [172]. The quartet state is re-populated on relaxation of the pressure.

A spin transition between the $S=1/2$ and intermediate $S=3/2$ spin state has also been observed for [Fe(salphen)(NO)], albeit the spin crossover is gradual in this instance [174, 175]. This material shows ⁵⁷Fe Mössbauer parameters comparable to those of the salen derivative. However, the relaxation between the spin states is fast relative to the ⁵⁷Fe Mössbauer time scale for the salphen compound, whereas it is slow for the salen compound [175]. Interestingly, the quadrupole splittings obtained from the ⁵⁷Fe Mössbauer spectra of [Fe(salphen)(NO)] have been found to decrease linearly with the magnetic susceptibility determined with increasing temperature [175].

3.2.4

Six-Coordinate Complexes of Tetradentate N_2O_2 -Donating Schiff Base Ligands

Three main families of N_2O_2 -donating Schiff base ligands have been used to obtain six-coordinate systems: (i) N,N' -ethylenebis(salicylideneimine) and its substituted derivatives, (ii) N,N' -ethylenebis(acetylacetonylideneimine)-type systems and (iii) ligand systems consisting of a salicylideneimine and an acetylacetonylideneimine moiety (Fig. 15). N -donating heterocyclic bases in axial positions complete the FeN_4O_2 coordination environment.

 $H_2cr-salen$ **Fig. 15** Tetradentate N_2O_2 -donating Schiff base ligands

The $[\text{Fe}(\text{salen})(\text{base})_2](\text{anion})$ systems have been most extensively studied and several X-ray structures have been determined. Table 4 compiles the Fe-donor atom bond lengths, as well as the spin state for these materials. $[\text{Fe}(\text{salen})(\text{Him})_2]\text{ClO}_4$ (Him=imidazole) is the only compound within this series for which the structure has been determined in both the low spin (120 K) and high spin states (295 K) [176, 177]. It appears that the average Fe–O bond distances are rather insensitive to the spin state of the Fe(III) ion (1.903 Å at 120 K and 1.901 Å at 295 K), whereas the mean Fe–N(salen) (1.913 Å at 120 K and 2.067 Å at 295 K) and Fe–N(Him) (1.992 Å at 120 K and 2.146 Å at 295 K) bond distances show a major dependence on the spin state [176, 177]. On the basis of bonding orbital considerations Nishida et al. have rationalised the different sensitivities of these bond lengths to changes in the spin state of the metal atom [178].

The compounds $[\text{Fe}(\text{salen})(\text{Him})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ [178], $[\text{Fe}(\text{salen})(\text{Him})_2]\text{X}$ ($\text{X}=\text{PF}_6^-$ [176], BPh_4^- [176, 185]), $[\text{Fe}(\text{salen})(4\text{-methyl-imidazole})_2]\text{Cl}$ [179], $[\text{Fe}(\text{salen})(\text{base})_2]\text{ClO}_4$ (base=N-methyl-imidazole [176], 5-Cl-N-methyl-imidazole [176]) and $[\text{Fe}(\text{salen})(\text{pyrazole})_2]\text{BPh}_4 \cdot \text{MeOH}$ [176] are purely high spin, whereas $\text{Na}[\text{Fe}(\text{salen})(\text{CN})_2] \cdot \text{CH}_3\text{OH}$ is purely low spin [185]. On the other hand, $[\text{Fe}(\text{salen})(\text{Him})_2]\text{X}$ ($\text{X}=\text{ClO}_4^-, \text{BF}_4^-$) and $[\text{Fe}(\text{salen})(\text{pyrazole})_2]\text{X} \cdot \text{H}_2\text{O}$ ($\text{X}=\text{ClO}_4^-, \text{BF}_4^-$) exhibit gradual spin transitions [176]. Both the magnetism and the ^{57}Fe Mössbauer spectra indicate that unsolvated $[\text{Fe}(\text{salen})(\text{Him})_2]\text{ClO}_4$ undergoes an almost complete transition between 90 K and 295 K [176], whereas the transitions for $[\text{Fe}(\text{salen})(\text{Him})_2]\text{BF}_4$ and $[\text{Fe}(\text{salen})(\text{pyrazole})_2]\text{X} \cdot \text{H}_2\text{O}$ ($\text{X}=\text{ClO}_4^-, \text{BF}_4^-$) proceed to varying extents over the temperature range 80 K to 295 K [176]. Interestingly, although there are differences in solvation of the materials, the spin crossover behaviour within both the imidazole and pyrazole series reveals a similar anion dependence [176]. In contrast, there does not appear to be a clear dependence of the spin state of Fe(III) on the selected N-donating heterocyclic base: neither their basicity nor position in the spectrochemical series is followed. This suggests that the spin state of Fe(III) in this series depends on the structural features of the particular material.

Comparison of the structures of $[\text{Fe}(\text{salen})(\text{Him})_2]\text{X}$ ($\text{X}=\text{ClO}_4^-, \text{BF}_4^-, \text{PF}_6^-$) revealed subtle structural differences, such as (i) the orientation of the imidazole ligands, (ii) equatorial ligand-imidazole C–H interactions, and (iii) conformations of the FeN_2C_2 chelate ring involving the ethylene backbone of salen. It has been proposed that these three parameters contribute to the spin state differences [176]. In particular, the FeN_2C_2 conformation has been thought to be substantially related to the spin state of Fe(III). The *envelope* conformation of this entity has been found in the spin crossover perchlorate and tetrafluoroborate salts, whereas it is in the *meso* configuration in the high spin hexafluorophosphate salt. It has been suggested that this *meso* configuration results in constraints of the planar ligand to the extent that it may not be able to adapt to incipient spin state change, i.e. the

Table 4 Average Fe-donor atom bond lengths for Fe(III) compounds of tetradentate N₂O₂-donating Schiff base ligands^{a,b}

Compound	T (K)	Fe-O	Fe-N	Fe-N _{base} (Å)	Spin state ^c	References
[Fe(salen)(Him) ₂][ClO ₄]	120	1.903	1.913	1.992	LS (sco)	[176, 177]
	295	1.901	2.067	2.146	HS (sco)	[176, 177]
[Fe(salen)(Him) ₂][BF ₄]	295	1.902	2.072	2.123	HS (sco)	[176]
[Fe(salen)(Him) ₂][PF ₆]	295	1.904	2.136	2.153	HS	[176]
[Fe(salen)(Him) ₂][ClO ₄ ·H ₂ O]	295	1.917	2.108	2.143	HS	[178]
[Fe(salen)(4-mim) ₂][Cl] ^d	293	1.909 (3)	2.111 (3)	2.159 (3)	HS	[179]
[Fe(salen)(tdim)][ClO ₄] ^e	295	1.896	2.120	2.157	HS (sco)	[180]
[Fe(5-OCH ₃ -salen)(Him) ₂][ClO ₄]	295	1.896	2.113	2.18	HS	[181]
[Fe(5-OCH ₃ -salen)(Him) ₂][Cl]	295	1.914	2.134	2.122	HS	[181]
[Fe(3-OCH ₃ -sapien)(Him) ₂][ClO ₄]	293	1.919	2.090	2.123	HS (sco)	[182]
[Fe(salphen)(Him) ₂][BPh ₄]	295	1.896	2.125	2.165	HS	[178]
[Fe(3-OC ₂ H ₅ -sal-CH ₃ -phen)(Him) ₂][ClO ₄]	293	1.899	2.105	2.148	HS	[182]
[Fe(acen)(Him) ₂][BPh ₄]	295	1.920	1.899	1.990	LS	[178]
[Fe(acen)(dmpy) ₂][BPh ₄]	120	1.906	1.918	2.036	LS (sco)	[183]
	290	1.930	2.058	2.186	HS (sco)	[183]
[Fe(salacen)(Him) ₂][PF ₆]	293	1.895	1.924	2.017	83% LS	[184]

^a The ligands are shown in Fig. 15. Abbreviations used for the ligands can be found in the list of abbreviations^b Abbreviations used for the monodentate N-donating heterocyclic bases: Him=H-imidazole, 4-min=4-methylimidazole, tdim=1,1'-tetraethylenedimidazole, dmpy=3,4-dimethylpyridine^c Spin state (predominant spin state or exact percentage) at the temperature of the crystal structure determination is mentioned. In case spin crossover (sco) occurs, this is mentioned in parentheses^d Centrosymmetric^e Zigzag chain

complex remains locked in the high spin form [176]. The geometry of the salen ligand was later compared to the environment created by the heme system in metalloproteins; both ligand systems are conformationally flexible and may adopt an overall *stepped*, *umbrella* or *planar* conformation [181]. Analysis of structural data for a large variety of Fe(III) compounds of N₂O₂-donating Schiff base ligands—involving most of the materials listed in Table 4—leads to the assumption that the molecule is fixed in a high spin-type *umbrella* or *planar* geometry due to crystal packing effects or intermolecular interactions. It is significant that some of the materials that have been found to be purely high spin in the solid state exhibit spin crossover in solution (see below) where the conformational restraints are relaxed [181]. Another analogy with related porphyrin systems has been considered [178] based on findings that the relative orientation of the imidazole rings is the controlling factor for the spin state of those systems [186]. It is proposed that the relative orientations of the imidazole rings control the metal-to-imidazole π -back-bonding and consequently the efficiency of stabilisation of the low spin state of Fe(III). Efficient $d\pi$ - $p\pi$ overlap—and stabilisation of the low spin state of Fe(III)—is achieved when the two planes defined by the imidazole rings are orthogonal and oriented along the two approximately diagonal N-Fe-O axes of the equatorial coordination frame [182]. However, since other small structural changes—for instance the other parameters mentioned above—may be involved, a dependence of the dihedral angles between the axially coordinated imidazole groups on the spin state could only be established in one comparative study [182].

Spin transitions have also been observed for derivatives of substituted salen-type ligands. [Fe(dmsalen)(Him)₂]BPh₄·2CH₃OH, in which salen is substituted at the methane C atoms, undergoes a gradual and incomplete transition (experimental range 78–298 K) [187]. The effect of substitution at the 3- or 5-positions of the salicylidene moiety has been more widely investigated. The structures of the purely high spin (in the solid state) [Fe(5-OCH₃-salen)(Him)₂]X (X=ClO₄⁻, Cl⁻) have been determined at 295 K [181]. For both compounds, the five-membered FeN₂C₂ ring of the ligand has the *meso* conformation, which further confirms the relation of this constrained form to the high spin state of the Fe(III) ion. However, spin crossover of these compounds in methanolic solutions has been observed by variable temperature EPR spectroscopy [181]. [Fe(3-CH₃O-salen)(*N*-methyl-imidazole)₂]X (X=ClO₄⁻, BPh₄⁻) and [Fe(3-CH₃O-salen)(5-Cl-*N*-methyl-imidazole)₂]ClO₄ are also purely high spin materials in the solid state [176], whereas [Fe(3-CH₃O-salen)(Him)₂]BPh₄ displays gradual spin crossover behaviour [176, 185]. The gradual spin transition in the latter complex involves only half of the Fe(III) ions [176, 185, 188].

While [Fe(3-OCH₃-salpen)(Him)₂]BPh₄·H₂O is purely high spin in the solid state, the analogous anhydrous perchlorate salt, which was structurally characterised at 293 K, undergoes gradual spin crossover with T_{1/2}=91 K

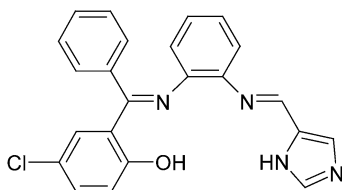


Fig. 16 5-o-[(5-Chloro-2-hydroxyphenyl)phenylmethyleneamino]phenyliminomethylimidazole

[182]. From an analysis of the magnetic properties according to the model of Slichter and Drickamer the thermodynamic parameters for the spin transition of $[\text{Fe}(\text{3-OCH}_3\text{-salpen})(\text{Him})_2]\text{ClO}_4$ were evaluated as $\Delta H = 5.46 \text{ kJ mol}^{-1}$ and $\Delta S = 60 \text{ J mol}^{-1} \text{ K}^{-1}$ [182]. These values are close to those found for other iron(III) systems.

The synthesis of dinuclear [189] and linear chain [180] materials based on $[\text{Fe}(\text{salen})]^+$ entities has been reported. The structure of dinuclear $[\text{Fe}_2(\text{salen})_2(\text{trans-4,4'-vinylenebis(pyridine)})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot (\text{trans-4,4'-vinylenebis(pyridine)}) \cdot \text{H}_2\text{O}$ has been reported but this compound is purely high spin [189]. On the other hand, $[\text{Fe}(\text{salen})(1,1'\text{-tetramethylenediimidazole})]\text{ClO}_4$ shows incomplete spin crossover, principally in the temperature range 70–100 K. It is suggested that the large residual high spin fraction (~ 0.7) may be related to the presence of two different orientations of the imidazole moieties with occupation factors 0.65 and 0.35. The complex has a zigzag chain structure (Table 4) [180].

Two strategies have been applied in order to obtain hetero-dinuclear compounds. In the first example, the incorporation of a spin-inactive cation to modulate the Fe(III) spin crossover has been attempted, exploiting the cyclic ligand cr-salen (Fig. 15) which contains a salen-type N_2O_2 cavity together with a polyether cavity [190]. However, both $[\text{Fe}(\text{cr-salen})(\text{pyridine})_2]\text{ClO}_4$ and $[\text{BaFe}(\text{cr-salen})(\text{pyridine})_2](\text{ClO}_4)_3$ are purely high spin.

In addition, heterodinuclear Fe(III)Ni(II) compounds have been prepared starting from high spin $[\text{FeCl}(\text{salen})]$ and NiL with L being the di-anion of the N_3O ligand depicted in Fig. 16 [191]. The imidazole-bridged $[\text{FeCl}(\text{salen})\text{NiL}]$ [191] and also $[\text{FeCl}(\text{5-OCH}_3\text{-salen})\text{NiL}]$ both exhibit Fe(III) spin crossover [192].

The purely high spin nature of $[\text{Fe}(\text{salphen})(\text{Him})_2]\text{BPh}_4$ [178, 185] and $[\text{Fe}(\text{3-OC}_2\text{H}_5\text{-sal-CH}_3\text{-phen})(\text{Him})_2]\text{ClO}_4$ [182] has been confirmed by magnetic measurements and structure determinations. On the other hand, $[\text{Fe}(\text{acen})(\text{Him})_2]\text{BPh}_4$ [185] is low spin while $[\text{Fe}(\text{acen})(3,4\text{-dimethylpyridine})_2]\text{BPh}_4$ [193] exhibits gradual spin crossover. The structure of the former low spin complex [178] as well as that of the latter in both high spin and low spin states [183] has been determined.

A large variety of heterocyclic bases and anionic groups have been incorporated within the $[\text{Fe}(\text{acen})]^+$ system. $[\text{Fe}(\text{acen})(\text{Him})_2]\text{BPh}_4$ [185] and $[\text{Fe}(\text{acen})(4\text{-aminopyridine})_2]\text{ClO}_4$ [185] are low spin, as is the one-dimensional polynuclear $[\text{Fe}(\text{acen})(1,1'\text{-tetramethylenediimidazole})]\text{ClO}_4$ [180]. Different degrees of gradual spin crossover behaviour have been observed for several members of this family: $[\text{Fe}(\text{acen})(\beta\text{-picoline})_2]\text{ClO}_4$ ($\mu_{\text{eff}} = 2.51$ B.M. (295 K), $\mu_{\text{eff}} = 1.93$ B.M. (80 K)) [185], $[\text{Fe}(\text{acen})(\text{pyridine})_2]\text{BPh}_4$ ($\mu_{\text{eff}} = 3.31$ B.M. (295 K), $\mu_{\text{eff}} = 2.30$ B.M. (80 K)) [185], $[\text{Fe}(\text{acen})(\gamma\text{-picoline})_2]\text{BPh}_4$ ($\mu_{\text{eff}} = 3.64$ B.M. (295 K), $\mu_{\text{eff}} = 2.04$ B.M. (80 K)) [185], whereas $[\text{Fe}(\text{acen})(\text{base})_2]\text{BPh}_4$ (base = *N*-methyl-imidazole [176], 1,3-di-4-pyridylpropane [193], 4-methylpyridine [193], 3,4-dimethylpyridine [193]) exhibit fairly complete, gradual spin transitions.

Derivatives of bzacen have been studied to a minor extent: $[\text{Fe}(\text{bzacen})(N\text{-methyl-imidazole})_2]\text{ClO}_4$ [176] and $[\text{Fe}(\text{bzacen})(\text{Him})(\text{CN})]\text{ClO}_4$ [185] are purely low spin, whereas $[\text{Fe}(\text{bzacen})(\text{Him})_2]\text{BPh}_4$ shows gradual spin crossover [185].

The di-anionic ligands derived from $\text{H}_2\text{salacen}$ and $\text{H}_2\text{hapacen}$ (Fig. 15) may be considered as providing a field strength intermediate between that of salen and acen. The structure of $[\text{Fe}(\text{salacen})(\text{Him})_2]\text{PF}_6$ has been determined at 293 K, where 83% of the Fe(III) ions are low spin [184]. Both the Fe–O (1.879(6) Å) and the Fe–N (1.912(7) Å) bond distances associated with the salicylideneimine residue are shorter than those associated with the acetylacetylonylideneimine residue (1.911(5) Å and 1.936(6) Å, respectively) [184]. $[\text{Fe}(\text{salacen})(\text{Him})_2]\text{PF}_6$ shows the onset of gradual spin crossover at about 200 K, reaching a magnetic moment of 2.83 B.M. at room temperature. In contrast, the *N*-methyl-imidazole derivative is high spin at room temperature but a gradual transition to the low spin state takes place between 300 and 200 K [184]. Both compounds exhibit striking thermochromism in organic solvents, being purple at room temperature and green at ca. 200 K. The absorption spectrum of $[\text{Fe}(\text{salacen})(\text{Him})_2]\text{PF}_6$ recorded at 289 K shows a strong band at 525 nm assigned to the high spin state, together with a shoulder at 680 nm attributed to the low spin state. From a study of the temperature dependence of the spectrum it was concluded that the transition occurs to a greater extent in solution than in the solid state [184]. Although EPR data indicate that $[\text{Fe}(\text{salacen})(\text{Him})_2]\text{BPh}_4 \cdot \text{CH}_3\text{OH}$ and $[\text{Fe}(\text{hapacen})(\text{Him})_2]\text{BPh}_4 \cdot 2\text{CH}_3\text{OH}$ are essentially low spin in the solid state they exhibit thermochromism similar to that described above and indicative of spin crossover in solution [187].

Solid $[\text{Fe}(\text{salacen})(1\text{-methyl-imidazole})_2]\text{ClO}_4$ displays a relatively complete, gradual spin crossover [180]. Measurements of both ^{57}Fe Mössbauer spectra and magnetism indicate that the transition observed in the one-dimensional polymeric system $[\text{Fe}(\text{salacen})(1,1'\text{-tetramethylenediimidazole})]\text{ClO}_4$ is also gradual but incomplete at both 290 K ($\mu_{\text{eff}} = 5.37$ B.M.) and 4.2 K ($\mu_{\text{eff}} = 3.37$ B.M.) [180].

3.3

Complexes of Pentadentate N₃O₂-Donating Ligands

In the only instances where spin crossover has been observed for a system involving a pentadentate ligand this has been an N₃O₂-donating Schiff base and the sixth coordination site has been occupied by a nitrogen donor, giving rise to an FeN₄O₂ coordination core. Most examples involve salten (Fig. 17).

When the sixth coordination site is occupied by an anionic group the derivatives are either purely low spin ([Fe(salten)CN]·1.5CH₃OH) or purely high spin ([Fe(salten)Cl]·CH₃OH and [Fe(salten)N₃]·0.5H₂O) [194]. It was soon discovered that upon using heterocyclic bases as co-ligand solvent-free spin crossover compounds could be prepared [194]. The mononuclear compounds [Fe(salten)(base)]BPh₄ (base=pyridine, 3-methyl-pyridine, 4-methyl-pyridine, 3,4-dimethyl-pyridine, 2-methyl-imidazole) exhibit spin crossover behaviour [194, 195], whereas derivatives with base=imidazole and *N*-methyl-imidazole are purely high spin [194]. The spin transitions are gradual, and are accompanied by thermochromism both in (dichloromethane) solution and in the solid state, changing from dark violet to blue-green with decreasing temperature.

The spin state of Fe(III) in this series depends directly on the ligand field strength exerted by the co-ligand X, as given by the spectrochemical series: CN[−] > pyridine or imidazole derivative > N₃[−] > Cl[−] [194].

The structure of [Fe(salten)(4-methyl-pyridine)]BPh₄ has been determined at 293 K [194]. The Fe(III) ion is in a pseudo-octahedral environment in which the basal plane is formed by two salicylideneimine entities (average Fe–O=1.885 Å, Fe–N=1.987 Å) oriented in *trans* geometry. The two axial positions are occupied by the secondary amine nitrogen atom of the di(3-aminopropyl) moiety of the ligand (Fe–N=2.035(7) Å) and the nitrogen

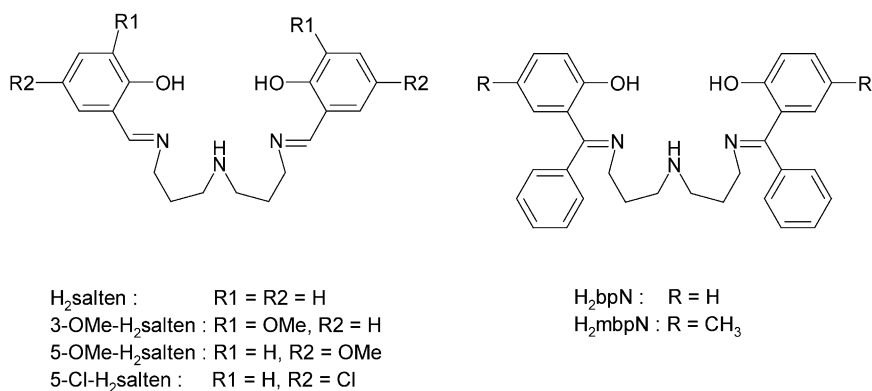


Fig. 17 Pentadentate N₃O₂-donating Schiff base ligands

atom of 4-methyl-pyridine ($\text{Fe-N}=2.010(6) \text{ \AA}$). The bond lengths observed are consistent with the magnetic data showing about 26% of high spin Fe(III) ions at 293 K.

More recently, $[\text{Fe}(\text{salten})(\text{base})]\text{BPh}_4$ compounds containing a potentially photo-isomerisable ligand have been reported [196, 197]. $[\text{Fe}(\text{salten})(1\text{-(pyridin-4-yl)-2-(N-methylpyrrol-2-yl)-ethene})]\text{BPh}_4$ having the nitrogenous base in the *trans* conformation exhibits a gradual Fe(III) spin crossover taking place between 150 and 320 K [196]. In addition, spin transition compounds of both isomers of 4-styrylpyridine could be obtained [197]. The transitions are gradual for $[\text{Fe}(\text{salten})(\text{trans-4-styrylpyridine})]\text{BPh}_4 \cdot (\text{CH}_3)_2\text{CO} \cdot 0.5\text{H}_2\text{O}$ and $[\text{Fe}(\text{salten})(\text{cis-4-styrylpyridine})]\text{BPh}_4$; however, the transition temperature for the *trans* derivative is 260 K, whereas it is almost 100 K higher for the *cis* compound. These features open interesting perspectives for testing the possibility of ligand-driven light-induced spin conversion (LD-LISC) for these materials (see below). This topic is treated in detail in Chap. 20. Confirmation of the conformation of the co-ligand has been obtained from crystal structures determined for both materials at 296 K [197].

The use of *N*-(4-picolyl)-aza-15-crown-5-ether as co-ligand enabled the encapsulation of alkali metal ions and the study of their effect on the Fe(III) spin transition within the series $[\text{Fe}(\text{salten})(\text{base})\text{M}]\text{ClO}_4$ (base=*N*-(4-picolyl)-aza-15-crown-5-ether; $\text{M}=\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+$) [198]. The magnetic moments determined for the non-alkali metal-containing $[\text{Fe}(\text{salten})(\text{base})]\text{ClO}_4$ in the solid state are 4.20 B.M. at 80 K and 4.85 B.M. at 300 K. Incorporation of the monovalent cations resulted in significant changes in the magnetic moment for the lithium derivative (2.29 B.M. at 80 K and 4.00 B.M. at 300 K), whereas only moderate changes were observed for sodium (4.21 B.M. at 80 K and 5.03 B.M. at 300 K), potassium (4.78 B.M. at 80 K and 5.82 B.M. at 300 K) and rubidium (4.52 B.M. at 80 K and 5.68 B.M. at 300 K). Since these compounds are thermochromic, the spin crossover could be monitored by recording the electronic spectra in acetonitrile solutions. Attempts at triggering the spin crossover in $[\text{Fe}(\text{salten})(\text{base})]\text{ClO}_4$ (base=*N*-(4-picolyl)-aza-15-crown-5-ether) in solution by ion-recognition have met with some success. On the addition of sodium perchlorate to a solution of the complex salt a change in the absorption spectrum was observed, suggesting that the high spin to low spin transition may be induced by the encapsulation of Na^+ ions [198].

Attaching the rather bulky methoxy substituent at the 3-position of the salicylaldehyde ring of salten does not appear to preclude formation of Fe(III) spin crossover materials. Using 3-OMe-salten yielded $[\text{Fe}(3\text{-OMe-salten})(\text{pyridine})]\text{BPh}_4$, which also displays spin crossover both in solution and in the solid state [199, 200]. On the other hand, the 5-Cl substituted salten derivative turns out to be a high spin compound [200].

Dinuclear materials of formula $[(\text{salten})\text{Fe}(\text{base})\text{Fe}(\text{salten})](\text{BPh}_4)_2$ have been obtained from *N,N'*-bridging heterocyclic ligands. The pyrazine deriva-

tive is low spin, but compounds containing 1,1'-tetramethylenebis(imidazole), 4,4'-bipyridine, 4,4'-ethylenebis(pyridine) or 4,4'-vinylenebis(pyridine) exhibit gradual and incomplete (at 300 K) transitions [201]. These materials are the first reported dinuclear Fe(III) spin crossover compounds. For $[(\text{salten})\text{Fe}(\text{base})\text{Fe}(\text{salten})](\text{BPh}_4)_2$ (base=azobis(4-pyridine), 4,4'-vinylenebis(pyridine)) in which the bridging system is potentially photo-isomerisable a gradual spin crossover characterised by $\mu_{\text{eff}}=\text{ca. } 2.2$ B.M. at 200 K and $\mu_{\text{eff}}=4.3$ B.M. at 350 K was observed for both systems [202]. The dinuclear nature of these complexes, in which both bridging moieties adopt the *trans* configuration, was confirmed by X-ray structure determinations carried out at 100 and 298 K [189, 203]. Magnetic measurements on single crystals under an external pressure of 8 kbar have revealed a suppression of the spin crossover: under these conditions both compounds are low spin at 350 K [203].

Dinuclear Fe(III) compounds were also obtained using substituted salten derivatives together with 4,4'-bipyridine as bridging ligand [200]. The 3-OMe-salten tetraphenylborate compound seems to show the onset of spin crossover at about 270 K, the 5-OMe-salten material is probably a purely high spin compound, whereas the 5-Cl-salten derivative exhibits gradual spin crossover behaviour.

Heterodinuclear Fe(III)Ni(II) imidazole-bridged compounds have been prepared starting from $[\text{Fe}(\text{salten})]^+$ and NiL with L being the N_3O ligand shown in Fig. 16 [191]. Gradual and incomplete spin crossover occurs in the range 80–295 K for $[\text{Fe}(\text{salten})\text{NiL}]\text{BPh}_4$. For the analogous complex containing a methyl group at the central nitrogen atom of the ligand a spin transition was also observed but only below 120 K [191].

The related ligands H_2bpN [205] and its 5-methyl-substituted derivative H_2mbpN (Fig. 17) [204, 205] have also been investigated. $[\text{Fe}(\text{bpN})(\text{pyridine})]\text{BPh}_4$ shows gradual and partial spin crossover between 78 and 300 K [205]. $[\text{Fe}(\text{mbpN})(\text{imidazole})]\text{BPh}_4$ is high spin ($\mu_{\text{eff}}=5.85$ B.M. at 298 K), whereas $[\text{Fe}(\text{mbpN})(3,4\text{-dimethylpyridine})]\text{BPh}_4$ exhibits a gradual spin transition ($\mu_{\text{eff}}=2.64$ B.M. at 78 K and 5.40 B.M. at 320 K) [205]. The structure of the latter material determined at 293 K confirmed that it is essentially high spin at this temperature [204].

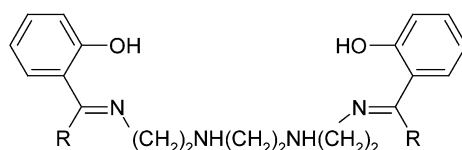
3.4

Complexes of Hexadentate N_4O_2 -Donating Ligands

3.4.1

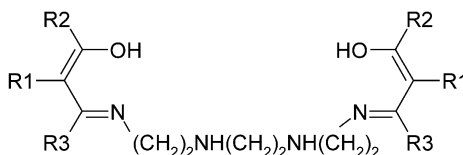
General Considerations

The N_4O_2 ligand systems depicted in Fig. 18 have been shown to generate spin crossover in Fe(III). Two families of Schiff base ligands have been obtained from the 1:2 condensation of triethylenetetramine with derivatives of



$\text{H}_2\text{sal}_2\text{trien}$: $\text{R} = \text{H}$

$\text{H}_2\text{bpk}_2\text{trien}$: $\text{R} = \text{C}_6\text{H}_5$



$\text{H}_2\text{acac}_2\text{trien}$: $\text{R1} = \text{H}, \text{R2} = \text{R3} = \text{CH}_3$

$\text{H}_2\text{acacCl}_2\text{trien}$: $\text{R1} = \text{Cl}, \text{R2} = \text{R3} = \text{CH}_3$

$\text{H}_2\text{bzac}_2\text{trien}$: $\text{R1} = \text{H}, \text{R2} = \text{C}_6\text{H}_5, \text{R3} = \text{CH}_3$

$\text{H}_2\text{bzacCl}_2\text{trien}$: $\text{R1} = \text{Cl}, \text{R2} = \text{C}_6\text{H}_5, \text{R3} = \text{CH}_3$

$\text{H}_2\text{tfac}_2\text{trien}$: $\text{R1} = \text{H}, \text{R2} = \text{CF}_3, \text{R3} = \text{CH}_3$

Fig. 18 Hexadentate N_4O_2 -donating Schiff base ligands

either salicylaldehyde or β -diketones. In addition, variation of the tetramine has been systematically explored within the salicylaldehyde series [206].

Several common structural features have been observed for iron(III) compounds of di-anionic hexadentate ligands containing a triethylenetetramine (abbreviated as trien) moiety. The stereochemical requirements of these ligands are such that hexadentate coordination towards the Fe(III) ion involves the formation of two six-membered chelate rings using the adjacent outer O and imine N donor atoms, together with three five-membered chelate rings containing the imine and amine N donor atoms of the central ligand moiety. X-ray structures have been determined for several compounds of this type, which revealed an identical general structure with the Fe(III) ion in a distorted octahedral N_4O_2 environment [206–209]. In each case the terminal oxygen atoms occupy *cis* positions and the remaining four nitrogen atoms (two *cis* amine and two *trans* imine) complete the coordination sphere.

3.4.2

Hexadentate N_4O_2 -Donating Ligands Derived from Salicylaldehyde Derivatives and Triethylenetetramine

Within the $[\text{Fe}(\text{sal}_2\text{trien})](\text{anion}) \cdot x(\text{solvent})$ family the magnetic moments determined at room temperature are anion and solvation dependent, span-

ning the range from essentially high spin Fe(III) ($\mu_{\text{eff}}=5.81$ B.M.) for anhydrous $[\text{Fe}(\text{sal}_2\text{trien})]\text{PF}_6$ to low spin Fe(III) ($\mu_{\text{eff}}=1.94$ B.M.) for $[\text{Fe}(\text{sal}_2\text{trien})]\text{Cl}\cdot 2\text{H}_2\text{O}$ [149]. It seems that the greater the extent of hydration the larger the population of the low spin state at room temperature. This may be illustrated by the following range of magnetic moments: 5.00 B.M. for the anhydrous PF_6^- and BPh_4^- salts, about 2.4 B.M. for the mono- and 1.5 hydrated I^- and NO_3^- salts, respectively, and 1.94 B.M. for the dihydrated Cl^- salt [149].

X-Ray structures have been reported for the purely low spin compounds $[\text{Fe}(\text{sal}_2\text{trien})]\text{Cl}\cdot 2\text{H}_2\text{O}$ [207], $[\text{Fe}(\text{sal}_2\text{trien})]\text{NO}_3\cdot \text{H}_2\text{O}$ [207] and $[\text{Fe}(\text{sal}_2\text{trien})]\text{Br}\cdot 2\text{H}_2\text{O}$ [208], as well as for the predominantly high spin material $[\text{Fe}(\text{sal}_2\text{trien})]\text{PF}_6$ [208] at room temperature. In addition, structures have been determined for $[\text{Fe}(\text{sal}_2\text{trien})]\text{BPh}_4$ [208] and $[\text{Fe}(\text{sal}_2\text{trien})]\text{BPh}_4\cdot \text{acetone}$ [209] at room temperature where significant fractions of both spin states are present. As expected, the average metal-donor atom distances observed for the low spin complexes are shorter by about 0.12–0.13 Å relative to those determined for the (predominantly) high spin materials. However, this difference is not uniform: the Fe–N bonds vary more ($\Delta r(\text{Fe}-\text{N}(\text{amine}))=\Delta r(\text{Fe}-\text{N}(\text{imine}))=0.17$ Å) than the Fe–O bonds ($\Delta r(\text{Fe}-\text{O})=0.04$ Å). In addition, the 12 angles subtended at the metal ion by adjacent donor atoms lie in the range 75–105° in the predominantly high spin materials, whereas these are closer to regular octahedral values (84–95°) in the low spin forms [208].

The role of the lattice water molecules in stabilising the low spin state for the Fe(III) ion could be clarified by analysis of the structures of the isomorphous low spin $[\text{Fe}(\text{sal}_2\text{trien})]\text{X}\cdot 2\text{H}_2\text{O}$ ($\text{X}=\text{Cl}^-$ [207], Br^- [208]) compounds. In these materials, the halogen anion is hydrogen bonded to the two water molecules, one of which is in turn hydrogen bonded to an amine donor atom. This hydrogen bonding network in the solid state is consistent with solution state studies on Fe(III) sal_2trien materials (see below) where strong $[\text{N}-\text{H}\cdots\text{solvent}]$ interactions were shown to favour the low spin state. The hydrogen bonding links the anions and cations in a polymeric chain. A similar hydrogen bonding scheme also exists in the low spin compound $[\text{Fe}(\text{sal}_2\text{trien})]\text{NO}_3\cdot \text{H}_2\text{O}$ [207].

$[\text{Fe}(\text{sal}_2\text{trien})]\text{PF}_6$ and $[\text{Fe}(\text{sal}_2\text{trien})]\text{BPh}_4$ exhibit gradual spin crossover behaviour, that for the latter being the more gradual and shifted to higher temperature [149, 207, 208]. The structure of $[\text{Fe}(\text{sal}_2\text{trien})]\text{BPh}_4$ determined at 293 K shows that the compound is essentially in the high spin state [208]. Interestingly, the asymmetric unit of $[\text{Fe}(\text{sal}_2\text{trien})]\text{PF}_6$ (293 K) contains two crystallographically independent and predominantly high spin Fe(III) ions, for which the bond lengths and angles involving the ligand donor atoms differ slightly [208]. The authors have ascribed the unusual variation of the magnetic moment with temperature to the occurrence of two separate and gradual transitions, one occurring at one of these Fe(III) sites between 200

and 100 K, and the other at the second Fe(III) site below 100 K. This hypothesis has not been confirmed by other experimental techniques, however, and it may be more likely that the slight decrease in magnetic moment starting at about 50 K with decreasing temperature is due to zero-field splitting associated with the remaining high spin Fe(III) ions.

Crystals of $[\text{Fe}(\text{sal}_2\text{trien})]\text{BPh}_4\cdot\text{acetone}$ could be obtained in two crystalline forms, i.e. monoclinic and twinned crystals [209]. Both forms have distinctly different X-ray powder patterns. The twinned crystals contain high spin Fe(III) over the temperature range 78–320 K, whereas the monoclinic form exhibits gradual spin crossover. The average Fe–donor atom bond lengths determined for a monoclinic crystal at 290 K (Fe–O=1.875 Å, Fe–N(imine)=1.988 Å, Fe–N(amine)=2.069 Å) are in good agreement with the extent to which the spin transition has proceeded at this temperature (40% high spin). The difference between these two modifications also becomes evident from the EPR spectral data, recorded for the monoclinic compound with decreasing temperature, which show that the low spin signals ($g_1=2.20$, $g_2=2.194$, $g_3=1.944$) increase in intensity at the expense of the high spin signals ($g=4$ and $g=2$). These high spin and low spin EPR signals are typical for ferric centres of this type. For the twinned crystals broad signals at $g=2.1$, 3.7 and 5.3 were observed at 296 K [209].

The ^{57}Fe Mössbauer spectra collected for the monoclinic form of $[\text{Fe}(\text{sal}_2\text{trien})]\text{BPh}_4\cdot\text{acetone}$ comprise a time-average of contributions from both electronic spin states [209]. The quadrupole splitting values decrease with increasing temperature, i.e. with increasing population of the high spin state. These features indicate that the lifetimes of the low spin and high spin states are as short as or less than the nuclear lifetime τ_N of ^{57}Fe (10^{-7} s); this has also been found in a subsequent and more extended study [210]. In contrast, the ^{57}Fe Mössbauer spectra for $[\text{Fe}(\text{sal}_2\text{trien})]\text{BPh}_4$ consist of a superposition of high spin and low spin signals [207] indicating longer lifetimes for the spin states in this instance [207]. In addition, the dynamics of the spin state interconversion of $[\text{Fe}(\text{sal}_2\text{trien})](\text{anion})\cdot x(\text{solvent})$ complexes have also been studied in detail for solutions by laser Raman temperature-jump kinetics [149, 211, 212], and the lifetimes estimated are consistent with the spectral data.

Tweedle and Wilson have carried out extensive studies on Fe(III) compounds of X-substituted sal_2trien derivatives in solution [149]. The compounds $[\text{Fe}(\text{X-sal}_2\text{trien})]\text{Y}$ (X=H, 3- NO_2 , 5- NO_2 , 3- OCH_3 , 4- OCH_3 , 5- OCH_3 ; Y= PF_6^- , NO_3^- , BPh_4^- , I^- , Cl^-) have been found to exhibit variable temperature magnetic susceptibility, ^1H NMR and electronic spectral properties indicative of spin crossover behaviour. The differences observed in the spin transition characteristics have been related to the hydrogen bonding capability of the particular solvent, the anion associated with the complex, and the nature and position of the substituent in the salten ligand. For the parent $[\text{Fe}(\text{sal}_2\text{trien})]\text{Y}$ series, the spin transition appears to be strongly solvent de-

pendent but essentially anion independent. The solvent dependency has been interpreted as arising mainly from a specific $[\text{Fe}(\text{sal}_2\text{trien})]^+$ -solvent hydrogen bonding interaction involving the N-H protons on the trien backbone, where the strongest [N-H...solvent] hydrogen bonding produces the largest population of the low spin isomer. Most elegantly, the N-H stretching frequency in the infrared spectra for the $[\text{Fe}(\text{sal}_2\text{trien})]\text{PF}_6$ parent compound has been measured in a variety of solvents and correlated with the magnetic behaviour of this compound in the same solvents at 295 K. Interestingly, the results indicate a nearly linear relationship between the splitting pattern of the $\nu_{\text{N-H}}$ vibration and the measured magnetic moment for a rather diverse series of nitrogen- and oxygen-containing solvents. The effect of substitution in the salicylaldehyde moiety has been studied [149] and at room temperature the measurement of the magnetism of $[\text{Fe}(\text{X-sal}_2\text{trien})]\text{PF}_6$ in acetone solution indicated that the percentage of high spin isomer depends on the salicylaldehyde ring substituent and decreases in the order: 4- OCH_3 (97%) > 5- OCH_3 (85%) > 3- OCH_3 (73%) > H (68%) > 3- NO_2 (49%) > 5- NO_2 (19%). Magnetic data recorded down to 180 K confirm that this order is followed over a wide temperature range. Obviously, the nature of this substituent effect must be electronic in origin since the spatial orientation of the two chelated salicylaldehyde rings indicates no specific intramolecular substituent steric interactions. For this X- sal_2trien series the more electronegative NO_2 groups favour the low spin state while OCH_3 favours the high spin form, with the unsubstituted parent compound exhibiting intermediate behaviour. It is of note that a similar substituent effect has also been found for tris(substituted-monothio- β -diketonato)iron(III) compounds in the solid state, where electronegative CF_3 substituents favoured the low spin state relative to the CH_3 groups (see above) [84]. For the $[\text{Fe}(\text{X-sal}_2\text{trien})]\text{PF}_6$ materials the location of the substituent seems to be almost as important as its nature in influencing the spin crossover in solution. In their analysis of the magnetic properties Tweedle and Wilson pointed out that for this range of substituents the different extents to which either spin state is favoured may be explained by the assumption that π -acceptance by the ligands is more important than the σ -donor capabilities in stabilising the low spin state [149].

The sal_2trien system has also been modified by incorporating a sulfonate group at the 5-position of the salicylaldehyde moiety and spin crossover is observed in the Fe(III) complex [213]. Substitution by phenyl groups at the imine carbon atom of the sal_2trien ligand has resulted in the purely high spin $[\text{Fe}(\text{bpk}_2\text{tet})]\text{ClO}_4\cdot\text{EtOH}$ [206].

In a systematic study of the effects of variation of the tetramine involved in formation of the hexadentate N_4O_2 donor Schiff base the linear 3,3,3-, 3,2,3-, 2,3,2- or 2,2,2-tetramines, where the numbers refer to the number of carbon atoms between the amine groups (note 2,2,2-tetramine is synonymous with the nomenclature trien used previously) have been condensed with salicylaldehyde, acetophenone or benzophenone [206]. Crystal struc-

tures have been determined at room temperature for a number of Fe(III) compounds of this series. However, none of these displayed spin crossover behaviour but their spin state seemed to depend on the arrangement of the N_4O_2 ligand donor atoms about the Fe(III). When the terminal oxygen atoms occupy *cis* positions the complexes have been found to be purely high spin, whereas when they are in *trans* positions the complexes are low spin.

3.4.3

Hexadentate N_4O_2 -Donating Ligands Derived from β -Diketones and Triethylenetetramine

Condensation of triethylenetetramine with two equivalents of acetylacetone or its substituted derivatives results in the formation of the second class of hexadentate N_4O_2 Schiff base-type ligands (Fig. 18) which can generate spin crossover in iron(III). Only two crystal structures are available for Fe(III) compounds belonging to this series. Those of $[\text{Fe}(\text{acac}_2\text{trien})]\text{PF}_6$ and $[\text{Fe}(\text{acacCl}_2\text{trien})]\text{PF}_6$ have been determined at room temperature where they are high spin [207]. The general structural features are similar to those of the Fe(III) sal_2trien series, involving a distorted octahedral *cis* FeN_4O_2 chromophore. The Fe-donor atom bond lengths are typical for high spin Fe(III). The average Fe–O distances are by far the shortest (1.930 Å for the acac derivative and 1.908 Å for the acacCl compound), the Fe–N(amine) distances are relatively long (2.174 Å), whereas the Fe–N(imine) bonds are intermediate (2.097 Å). Typically, the 12 angles subtended at the Fe(III) ion by adjacent donor atoms range from 76.7° to 102.1° implying a significant deviation from perfect octahedral symmetry.

While $[\text{Fe}(\text{acac}_2\text{trien})]\text{PF}_6$ is a purely high spin compound, $[\text{Fe}(\text{acacCl}_2\text{trien})]\text{PF}_6$ displays spin crossover to a moderate extent below 200 K [207]. In contrast, $[\text{Fe}(\text{acac}_2\text{trien})]\text{BPh}_4$ is essentially low spin at 77 K, but appears to show the onset of spin crossover above 200 K [207], its magnetic moment increasing to 3.04 B.M. at room temperature [211]. On the other hand, the trifluoroacetylacetone analogue, $[\text{Fe}(\text{tfac}_2\text{trien})]\text{PF}_6$, is predominantly high spin at room temperature ($\mu_{\text{eff}}=4.91$ B.M.) [211]. The ^{57}Fe Mössbauer spectra of these spin crossover compounds show separate signals attributable to the high spin and low spin states [207, 211].

Spin crossover for a series of Fe(III) compounds of several β -ketoimine ligands in solution has been confirmed [211]. The compounds $[\text{Fe}(\text{acac}_2\text{trien})]\text{Y}$ ($\text{Y}=\text{PF}_6^-$, BPh_4^- , Br^- , I^-) exhibit a striking reversible thermochromism associated with the spin crossover in acetone solutions. The solutions are red at room temperature and change to blue at -80°C , which parallels the thermochromism displayed by the $[\text{Fe}(\text{sal}_2\text{trien})]^+$ complexes [149]. The measurement of the temperature dependence of the electronic spectrum, coupled with that of the magnetic moment, has allowed characterisation of the spin crossover for $[\text{Fe}(\text{acac}_2\text{trien})]\text{PF}_6$ in methanol. The higher

energy bands at 520–540 nm were found to decrease steadily in intensity with decreasing temperature and magnetic moment, and thus could be assigned to the high spin form. Conversely, the intensity of lower energy bands at 610–640 nm increased steadily with decreasing temperature and magnetic moment, permitting assignment mainly to the low spin form. Although the spin crossover for the $[\text{Fe}(\text{acac}_2\text{trien})]\text{Y}$ [211] complexes is more gradual than that for the $[\text{Fe}(\text{sal}_2\text{trien})]\text{Y}$ series [149], there are strong similarities in the way this behaviour is influenced by solvent, anion and ligand substitution, but the effects are in fact generally more pronounced [149]. Although the influence of the anion seems to be greater for the $[\text{Fe}(\text{acac}_2\text{trien})]\text{Y}$ series, the same order is found for both series, at least in acetonitrile solution.

The effects of ligand substitution on the Fe(III) spin crossover properties have been examined for $[\text{Fe}(\text{Z}_2\text{trien})]\text{PF}_6$ ($\text{Z}=\text{acacCl}$, bzac , bzacCl , tfac ; Fig. 18). Comparisons of the low spin population in the spin crossover systems at a given temperature indicates a systematic effect of the R1, R2 and R3 chelate ring substituents on the Fe(III) spin state. Since the low spin isomer population for a given temperature increases according to the ligand series $\text{acacCl}_2\text{trien} > \text{bzac}_2\text{trien} > \text{acac}_2\text{trien}$, it appears that electron-withdrawing substituents (assuming $\text{C}_6\text{H}_5 > \text{CH}_3$) produce the strongest ligand fields and, thus, the largest low spin populations [211]. This general pattern parallels that found for the $[\text{Fe}(\text{sal}_2\text{trien})]\text{Y}$ complexes where the low spin form is favoured according to $\text{X}=\text{NO}_2 > \text{H} > \text{OCH}_3$ [149].

3.5

Iron(III) Spin Crossover Induced by Irradiation

The progress achieved in the detailed understanding of photophysical and photochemical processes that may be induced by light-irradiation in particular spin crossover systems has driven research efforts towards the development of materials that may be used for various technological applications. Only relatively recently, reports have appeared exploring this field for Fe(III) spin crossover materials.

Spin-interconversion by light-irradiation was first observed for Fe(II) spin crossover materials. In some of these Fe(II) compounds in the solid state, the thermally stable low spin state could be converted to a metastable high spin state by light-irradiation (Light-Induced Excited Spin State Trapping (LIESST)) (see Chap. 17). Since thermally-induced spin state relaxation processes may be operative favouring the reverse spin conversion, the lifetime of this metastable high spin form may be rather short and in most instances it may be observed only at very low temperatures. As a first approach it may be assumed that the lifetime increases when the structural differences relative to the initial low spin form become more pronounced. In Fe(II) and Fe(III) spin crossover compounds, major differences are observed between the metal-donor atom bond distances for the low spin and high

spin states. The average change in these bond distances is 0.18 Å for Fe(II), while a significantly smaller change (0.12 Å) is observed for Fe(III). Therefore, it may be presumed that the light-induced high spin form of Fe(III) will have a considerably shorter lifetime than that of the metastable high spin form of Fe(II), or alternatively, the back conversion from the metastable high spin to the low spin state requires a much smaller activation energy for Fe(III) compounds compared to the Fe(II) derivatives. The generation of metastable high spin species by light irradiation of Fe(III) compounds in solution was first reported by Lawthers and McGarvey [214] and later by Schenker and Hauser [215, 216]: irradiation into the spin-allowed ligand-to-metal charge transfer (LMCT) band results in the transient generation of high spin Fe(III) states. It has been estimated that the low-temperature tunnelling rate constant for the high spin to low spin relaxation is about seven orders of magnitude greater for Fe(III) than for Fe(II) compounds in solution [216].

Successful LIESST studies on Fe(III) spin crossover compounds in the solid state have been achieved by preventing the rapid relaxation from the metastable high spin to the low spin state through the introduction of strong intermolecular interactions [137, 138]. It has been proposed that the cooperativity resulting from the intermolecular interaction enhances the activation energy for the relaxation processes, enabling the observation of a relatively long-lived metastable state after irradiation [137]. In fact, strong intermolecular π -stacking interactions are responsible for the observation of the LIESST effect, as well as for the abrupt transition for $[\text{Fe}(\text{pap})_2]\text{ClO}_4\cdot\text{H}_2\text{O}$ (pap=the deprotonated bis(2-hydroxyphenyl)-(2-pyridyl)-methaneimine); $T_{1/2}\uparrow=180$ K, $T_{1/2}\downarrow=165$ K, $\Delta T_{1/2}=15$ K) [137] and the somewhat less abrupt spin transition without thermal hysteresis for $[\text{Fe}(\text{pap})_2]\text{PF}_6\cdot\text{MeOH}$ ($T_{1/2}=288$ K) [138]. The formation of high spin Fe(III) ions at 5 K upon irradiation ($\lambda=400\text{--}600$ nm) into the spin-allowed ligand-to-metal charge transfer (LMCT) band of $[\text{Fe}(\text{pap})_2]\text{ClO}_4\cdot\text{H}_2\text{O}$ has been confirmed by the increase of the magnetic moment, as well as by the ^{57}Fe Mössbauer spectra showing two well-separated quadrupole doublets typical for low spin and high spin Fe(III) ions [137]. Relaxation of this metastable high spin state sets in above about 70 K. The LIESST effect has also been observed for $[\text{Fe}(\text{pap})_2]\text{PF}_6\cdot\text{MeOH}$ at 5 K [138]. The critical temperature of the photo-induced high spin species for this complex ($T_c(\text{LIESST})=55$ K) is lower than that of the perchlorate derivative ($T_c(\text{LIESST})=105$ K), consistent with the lower degree of cooperativity for the transition in the former.

An alternative strategy towards photo-induced spin crossover behaviour was proposed several years ago by Roux et al. [217]. This ligand-driven light-induced spin conversion (LD-LISC) is a very promising process which could also enable photo-induced spin crossover at room temperature. The principle is based on ligands containing potentially photo-isomerisable groups. The first studies have taken advantage of the *cis-trans* photo-iso-

merisation of a C=C entity incorporated in a ligand coordinated to an Fe(II) active spin crossover centre [217–219]. The topic is treated in detail by Boilot, Zarembowitch and Sour in Chap. 20. Recently, this strategy has been applied to mononuclear Fe(III) compounds [196, 197]. For this purpose the Fe(III) N_4O_2 environment was provided by the pentadentate salen ligand (see above) together with the potentially photo-isomerisable ligand 1-(pyridin-4-yl)-2-(*N*-methylpyrrol-2-yl)-ethene (abbreviated as Mepepy) [196] or 4-styryl-pyridine [197]. Solid state $[Fe(salen)(Mepepy)]BPh_4$ with Mepepy in *trans* configuration, exhibits a gradual Fe(III) spin crossover taking place between 150 and 320 K. Irradiation experiments have been carried out in acetonitrile solutions with a wavelength of 405 ± 5 nm, at which the *trans* to *cis* isomerisation is expected to take place. The evolution of the magnetic data under irradiation has been followed by the Evans method. In this way, the ligand field strength is varied under the effect of electromagnetic radiation. Since the methylpyrrole moiety of Mepepy is a strong π -donor group, the *trans* to *cis* isomerisation results in a decrease of the π -donor character of the ligand and has been found to induce a partial high spin to low spin change even at room temperature [196]. Further experiments have been carried out on $[Fe(salen)(trans\text{-}4\text{-styrylpyridine})]BPh_4 \cdot (CH_3)_2CO \cdot 0.5H_2O$ and $[Fe(salen)(cis\text{-}4\text{-styrylpyridine})]BPh_4$, which both display gradual spin crossover behaviour in the solid state with $T_{1/2}$ being 260 K for the former, whereas it is almost 100 K higher for the latter [197]. Although irradiation ($\lambda=313$ nm) of the materials in acetonitrile solutions, as well as in the solid state, brought about changes in the UV spectra, conclusive evidence for an actual change in the spin state of Fe(III) could not be obtained.

The same approach has been applied to dinuclear Fe(III) spin crossover materials. In $[(salen)Fe(azobis(4\text{-pyridine}))Fe(salen)](BPh_4)_2$ the Fe(III) spin crossover centres are connected by the potentially photo-isomerisable azobis(4-pyridine) entity [202]. The solid compound undergoes a gradual temperature-induced spin transition ($\mu_{eff} = ca. 2.2$ B.M. at 200 K and 4.3 B.M. at 350 K). Since the material is thermochromic in acetonitrile solution, it has been possible to monitor the spin transition by recording the electronic spectra. These results could be compared to those obtained from irradiation measurements. Upon the thermal spin transition the absorption at 430 nm increases in intensity, whereas the absorption at 480 nm simultaneously decreases in intensity. The same changes in electronic spectra have been observed upon irradiation with a wavelength of 300 nm at room temperature. The experiments are consistent with a reversible photo-induced Fe(III) spin crossover taking place in solution. Interestingly, irradiation ($\lambda=300$ nm) of a KBr disc containing the complex at room temperature revealed that the *trans* to *cis* photo-isomerisation also occurs in the solid state, although the process is irreversible in this instance [202].

3.6

Developments in Materials Science

Several approaches to obtaining Fe(III) spin crossover materials in a form suitable for incorporation in devices for possible practical application have been reported.

Nakano et al. have demonstrated that Fe(III) spin crossover complexes adsorbed on the surface of silicon dioxide retain their spin crossover behaviour [220]. EPR and ^{57}Fe Mössbauer spectral data indicated that the spin transitions observed are similar to those of the neat solid materials used, i.e. $[\text{Fe}(\text{acpa})_2]\text{PF}_6$, $[\text{Fe}(\text{acpa})_2]\text{BPh}_4$ ($\text{Hacpa} = N$ -(1-acetyl-2-propylidene)(2-pyridylmethyl)amine) and $[\text{Fe}(\text{bzpa})_2]\text{PF}_6$ ($\text{Hbzpa} = (1\text{-benzoylpropen-2-yl})(2\text{-pyridylmethyl})\text{amine}$).

$[\text{Fe}(\text{salten})]^+$ entities (salten is a pentadentate Schiff base; see above) have been attached to polymer matrices providing the sixth N-donor atom through their pyridine or imidazole entities [221]. The polymers used are polymeric-4-vinylpyridine, the copolymer of octylmethacrylate and 4-vinylpyridine, and the copolymer of octylmethacrylate and 1-vinylimidazole. The resultant six-coordinate materials show spin crossover, confirmed by measurements of magnetic susceptibility, EPR and ^{57}Fe Mössbauer spectra, together with thermochromism. An alternative and more direct approach involved modified five-coordinate $[\text{Fe}(\text{salten})]^+$ or six-coordinate $[\text{Fe}(\text{sal}_2\text{trien})]^+$ -type entities containing appropriate polymerisable groups attached to the 5-position of the salicylideneimine moiety. These have been polymerised with 4-vinylpyridine to obtain spin crossover polymeric materials by a more direct synthetic route [221]. Despite the polymeric nature of these systems, the transitions are not strongly cooperative.

Recently, the preparation of liquid crystals displaying spin crossover has been achieved [222]. For this purpose the N_2O -tridentate Schiff base ligand obtained from the condensation of 4-(dodecyloxybenzoyloxy)-2-hydroxybenzaldehyde and N -ethylethylenediamine (H_2L) (analogous to those shown in Fig. 12) has been selected. Liquid crystal properties were confirmed for $[\text{FeL}_2]\text{PF}_6$ in the crystal state and meso phase by polarising optical microscopy, differential scanning calorimetry and X-ray scattering, from which it could be concluded that the compound consists of rod-like molecules; it exhibits the fan-shaped texture usually attributed to the smectic A mesophase in the temperature range 388–419 K [222]. Measurements of magnetism and ^{57}Fe Mössbauer spectra indicate an almost complete, gradual spin crossover over the range ca. 75 to 200 K.

4 Conclusions

The comparison of Fe(III) spin transition systems with those of other metal ions reveals the greater variety of chromophores for which spin crossover is observed in iron(III). This is reflected in a generally more diverse coordination environment as well as a far broader range of donor atom sets. For six-coordinate systems the spin crossover generally involves an $S=1/2 \leftrightarrow S=5/2$ change, whereas for five-coordinate materials an intermediate (quartet) spin state is involved in $S=1/2 \leftrightarrow S=3/2$ transitions. There is just one report of such a transition in a six-coordinate system and that is considerably distorted [126].

The donor atom sets for six-coordinate systems range from FeS_6 in the dithiocarbamate and X-xanthate ($X=\text{O}, \text{S}$) systems to FeS_3O_3 for monothiocarbamates and monothio- β -diketones, and FeS_3Se_3 or FeSe_6 for thioseleno- or diselenocarbamates, respectively. In addition, $\text{FeS}_2\text{N}_2\text{O}_2$ and $\text{FeSe}_2\text{N}_2\text{O}_2$ chromophores are formed from the important thiosemicarbazone or selenosemicarbazone-type ligands, respectively. FeN_3S_3 chromophores are known but are less common [120, 121, 123]. In addition, spin crossover FeN_5Cl and FeN_4Br_2 chromophores have been identified [122, 166]. In contrast to the FeS_6 systems which, particularly in the dithiocarbamates, represent the most widely studied group, there is only a single example for an FeO_6 spin crossover species [93]. Multidentate Schiff base-type ligands are widely suited to the generation of spin crossover in iron(III) but the range of donor atom sets for these is more limited than for the systems above. Two N_2O -donating tridentate ligands or a single hexadentate N_4O_2 ligand are remarkably effective in leading to spin transitions in six-coordinate FeN_4O_2 chromophores. Several N_3O_2^- or N_2O_2 -donating systems are also effective but require one or two appropriate additional N-donating heterocyclic bases to complete the pseudo-octahedral N_4O_2 coordination sphere.

The $S=1/2 \leftrightarrow S=3/2$ Fe(III) spin crossover in five-coordinate compounds is also found for a relatively large number of donor atom sets: FeOS_4 [124, 125], FeNS_4 [125], FeN_3O_2 [169–171, 174, 175], FeN_5 , and FeN_4X ($X=\text{Cl}^-, \text{Br}^-$) [168].

Apart from the wider range of donor atom sets, the transitions in iron(III) are distinguished from those in iron(II) in a number of other ways. Although for both metal ions the change in the total spin for the transitions in six-coordinate systems is $\Delta S=2$, the actual change in bond length (for the same donor atoms) accompanying the transitions is less for iron(III) than for iron(II). This is the origin of many of the important differences encountered in the nature of the spin crossover observed for the two metal ions. Perhaps the two most important characteristics resulting from this are the generally increased rate of inter-conversion of the spin states and the lower degree of cooperativity associated with the transitions in the solid state for iron(III).

The inter-conversion of the spin states in many instances is so rapid that the separate contributions to the ^{57}Fe Mössbauer spectra are not resolved. Thus this technique, which has proved so diagnostic in iron(II) systems, is frequently less suited to the derivation of spin transition curves for iron(III). A further corollary of the faster spin state inter-conversion is the rarity of the LIESST effect among iron(III) systems, in contrast to its ubiquitous occurrence in iron(II).

The great majority of transitions observed for iron(III) are gradual and the observation of thermal hysteresis associated with them is relatively rare. In the only instances where features indicative of significant cooperativity have been reported, extensive hydrogen-bonding networks (formed in some thiosemicarbazone compounds [111, 115, 118, 119]) or π - π stacking interactions (operative in several compounds of N_2O Schiff base systems [135–138, 164, 165]) have been invoked as the origin of the cooperativity.

Despite these differences, the similarities predominate and virtually all the features noted for spin crossover in iron(II) are also found for iron(III). Because of the great emphasis on the cooperative aspects of the spin crossover phenomenon, iron(II) systems have tended to dominate more recent research. However, there are very striking examples among the iron(III) systems which are of strong relevance to these aspects and there is certainly scope for future work in this area. This is evident in much of the very recent work where it can be seen that specific strategies to increase the cooperativity have been successful and have led, for example, to solid iron(III) systems which display the LIESST effect [137, 138]. The generation of polymeric species as a means of increasing cooperativity, an approach which has been widely adopted for iron(II), has received relatively little attention for iron(III) and this is an area which can be expected to be exploited further.

It is clear that spin crossover occurs widely for iron(III). The treatment given here has been confined in the main to typical synthetic systems but it needs to be stressed that among iron(III) naturally occurring porphyrin-type systems spin crossover is widespread and its presence in them is vital to their roles [223–227].

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