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Spin Crossover in Transition Metal Compounds II



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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 interdisciplinary 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 establishment 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 understand-

ing 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-State Transition in LaCoO_3 and Related Materials

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Abstract Of the several inorganic systems that exhibit spin-state transitions, LaCoO_3 and related cobaltates represent an important category of oxides exhibiting a transition from the low-spin (LS) state to a state of higher spin with increasing temperature. It was first considered that the transition was from the LS ($^1\text{A}_1$) to the high-spin (HS, $^5\text{T}_2$) state and a variety of investigations were performed on this transition by employing magnetic susceptibility, Mössbauer spectroscopy, NMR spectroscopy and other measurements. These studies not only showed the evolution of the high-spin state with temperature but also the ordering of the two spin states and other related phenomena. The spin-gap energy in LaCoO_3 is smaller than the charge-gap energy. The transition temperature varies depending on the rare earth ion in the LnCoO_3 series. In recent years, it has been demonstrated that the spin-state transition in LaCoO_3 occurs initially from the LS state to the intermediate spin (IS, $^3\text{T}_1$) state rather than to the HS state with increase in temperature. The intermediate spin-state Co^{3+} is a Jahn-Teller (JT) ion. The spin-state transition is therefore associated with lattice distortion, which is readily studied by infrared spectroscopy. Raman spectroscopy yields valuable information on the spin-state transition. Electronic structure calculations have been performed and the results verified experimentally by photon emission spectroscopy and other techniques. Recent studies indicate that it may be necessary to employ a three spin-state (LS-IS-HS) model rather than a two spin-state (LS-IS) model to fully explain the observed transition. Several theoretical models have been proposed to explain the spin-state transition in LaCoO_3 . These include the singlet-triplet transition model, the two-sublattice model, and the two-phonon model. The effect of hole doping on the spin-state transition has been examined in compounds like $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$. In this article, we discuss the various experimental and theoretical studies of LaCoO_3 and related cobaltates.

Keywords Spin-state transition · Low-spin Co^{3+} · Intermediate-spin Co^{3+} · High-spin Co^{3+} · Metal-insulator transition

1

Introduction

Perovskite oxides of the general formula ABO_3 , where A is a trivalent rare earth cation and B is a transition metal ion, exhibit fascinating electrical, magnetic and other properties [1]. Among these oxides, LaCoO_3 is an important member. The structure and properties of LaCoO_3 have been investigated for nearly four decades [2–5], but they have continued to attract attention up to the present. One of the important properties of LaCoO_3 , recognized early on, is the existence of a transition from the low-spin ($^1\text{A}_1; t_{2g}^6 e_g^0$) state of Co^{3+} to the high-spin ($^5\text{T}_2; t_{2g}^4 e_g^2$) state over the temperature range 0–650 K. Evolution of the magnetic and transport properties of LaCoO_3 with temperature has been discussed by several workers [2–7], but the details of the spin-state transition remain somewhat inconclusive. The description of the spin state transition has undergone several revisions over the last few years. For example, it was first considered that the spin-state transition occurring in the 30–100 K temperature range is from the low-spin to the high-spin state, but it was later suggested that the transition was to the intermediate-spin ($^3\text{T}_1; t_{2g}^5 e_g^1$) state [8]. While there is considerable experimental and theoretical evidence for the intermediate-spin state, more recent investigations suggest the need for a three spin-state model involving the low, the intermediate and the high-spin states to explain all the properties of LaCoO_3 in the 30–650 K regime. In this article, we discuss the spin-state transition in LaCoO_3 and its implications for the electronic structure and properties of this material. Substitution of La^{+3} by Sr^{+2} in LaCoO_3 brings about marked changes in the electronic and magnetic properties. While LaCoO_3 is a paramagnetic insulator at ordinary temperatures, $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ is a ferromagnetic metal when $x > 0.2$. We will examine the nature of the spin states of cobalt in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ as well.

2

Background

In Fig. 1, we show the temperature dependent molar magnetic susceptibility (χ_m) of the bulk samples of the composition $\text{LaCo}_{1-x}\text{O}_3$ ($-0.1 \leq x \leq 0.1$). The data show an increase in χ_m with increasing temperature (from 30 to 100 K), attaining a maximum value around 100 K. In this temperature range, the low-spin trivalent cobalt ion was considered to transform to the high-spin state. Above 100 K, the molar susceptibility decreases, eventually leading to

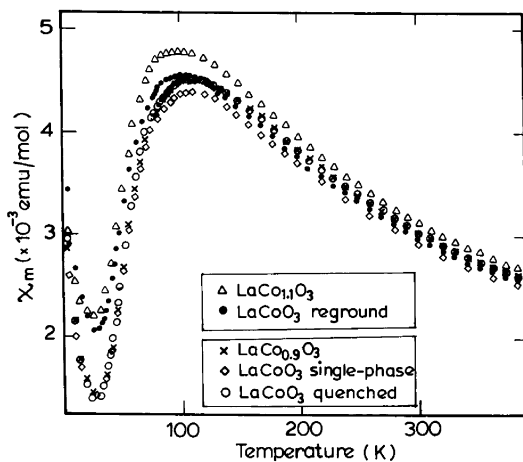


Fig. 1 Temperature dependence of the molar magnetic susceptibility of samples with nominal composition $\text{LaCo}_{1-x}\text{O}_3$ ($-0.1 \leq x \leq 0.1$) measured at $H=10$ kOe in the temperature interval $4.2 \text{ K} < T < 380 \text{ K}$ (from [7])

a plateau regime between 350 K and 650 K. The plateau regime (Fig. 2) was associated with the ordering of the different spin-states of cobalt accompanied by a change in symmetry from $R\bar{3}c$ to $R\bar{3}$. Two distinct Co–O distances were found above 523 K, with 50% occupation at 610 K, supporting such ordering [9]. This was soon followed by a gradual semiconductor-metal transi-

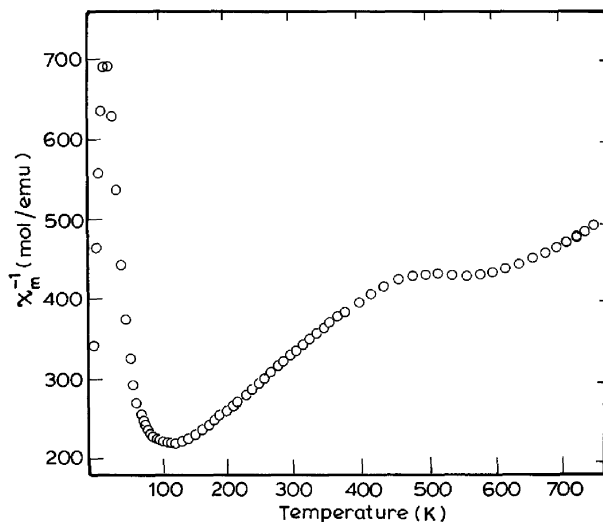


Fig. 2 Inverse molar magnetic susceptibility versus T plot of single phase LaCoO_3 in the temperature range $4.2 \text{ K} < T < 750 \text{ K}$ ($H=10$ kOe) (from [7])

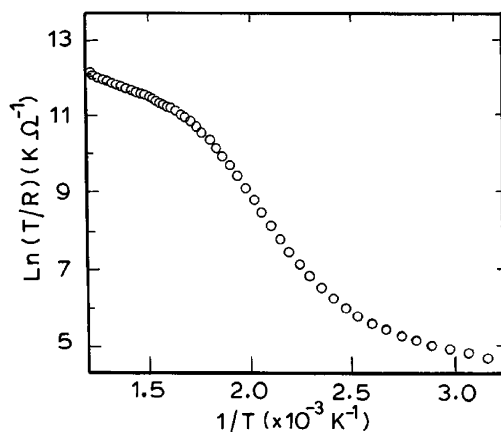


Fig. 3 Plots of $\ln(T/R)$ versus T^{-1} corresponding to the single phase LaCoO_3 material at the high temperature interval: $300 \text{ K} \leq T \leq 823 \text{ K}$ (from [7])

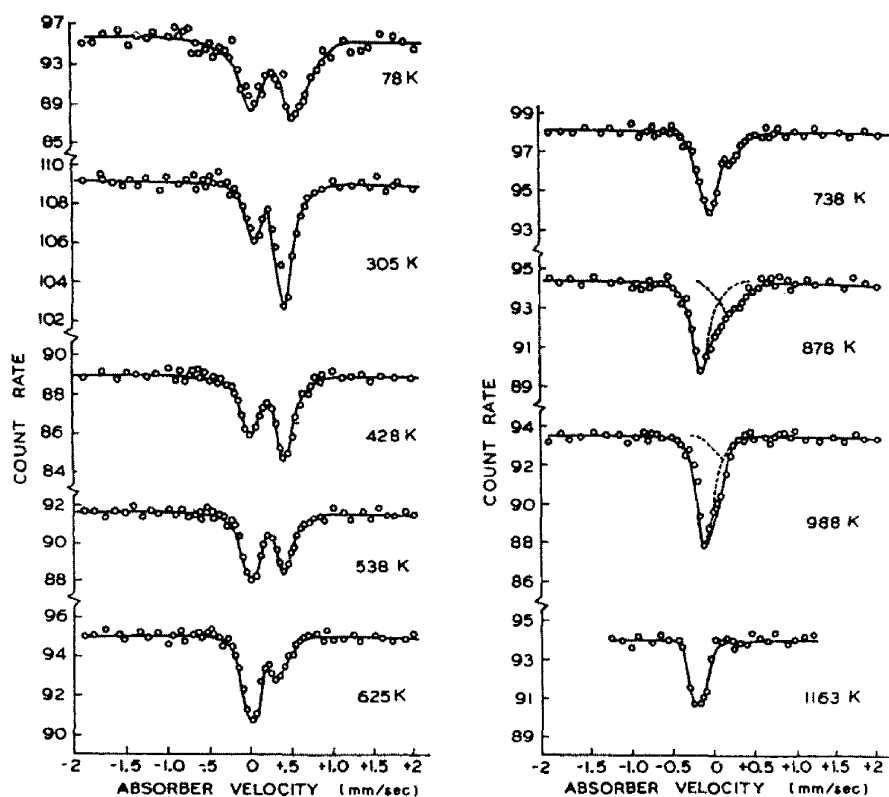


Fig. 4 Mössbauer spectra of LaCoO_3 : ^{57}Co matched against $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ single crystal showing the coexistence of low and high spin Fe^{3+} (from [5])

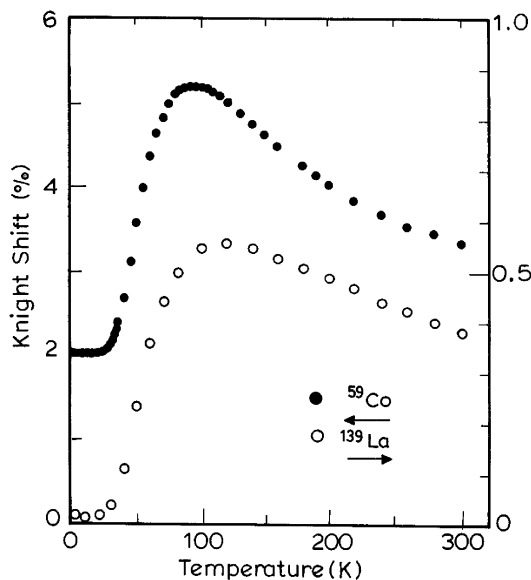


Fig. 5 Temperature-dependence of the ^{59}Co and ^{139}La Knight shifts in LaCoO_3 taken at 68.5 MHz and 40 MHz, respectively. The ^{139}La Knight shift is referred to the right vertical axis (from [14])

tion around 650 K (Fig. 3) [10]. Early emission Mössbauer studies gave direct evidence for the occurrence of a spin-state transition corresponding to the nucleogenic $^{57}\text{Fe}^{3+}$, as shown in Fig. 4 [5]. The possibility of disproportionation of Co^{3+} into Co^{2+} and Co^{4+} above 200 K was suggested on the basis of susceptibility and other measurements [5].

Properties of LaCoO_3 were reviewed by Señarís-Rodríguez and Goode-nough in 1995 [7]. Their main observations relating to the spin states of Co^{3+} are as follows. According to these authors, there is an evolution with temperature from an entirely low-spin Co^{3+} state to a 50% high-spin state up to 100 K. In the $100\text{ K} < T < 350\text{ K}$ range, there is dynamic ordering and the material remains semiconducting. In the $350\text{ K} < T < 650\text{ K}$ range, a smooth transition occurs from the semiconducting phase to a metallic phase. The metallic phase contains 50% high-spin (HS) and 50% intermediate-spin (IS) state ($t_{2g}^5 e_g^1$) cobalt ions. The metallic phase is characterized by two Co–O separations, possibly due to a quasi-static ordering of the high-spin and the intermediate-spin cobalt ions on two cobalt subarrays. Other rare earth cobaltates also show evidence for a spin state transition, the transition temperature increasing with a decrease in the size of the rare earth ion [11].

The spin gap energy in LaCoO_3 is only 30 meV, which is much smaller than the charge gap energy, which is about 0.1 eV as estimated by optical

spectroscopy [12]. Photoemission spectra of LaCoO_3 showed the existence of both of the spin-states at 100 K or below, with the proportion of the high-spin state remaining constant in the 100–420 K range, in agreement with inelastic neutron scattering measurements [13]. ^{59}Co and ^{139}La NMR measurements show the presence of a non-magnetic ground state at low temperatures [14]. The temperature dependence of the Knight shift and magnetic susceptibility could be rationalized in terms of a spin-state transition. Figure 5 shows the temperature-independent Knight shift of ^{59}Co ($2.088 \pm 0.01\%$) below ~ 30 K, which indicates the nonmagnetic ground state of the trivalent Co ion, ascribed to the Van Vleck orbital susceptibility of the low-spin ground state.

3

Recent Results on LaCoO_3

Early x-ray photoemission and x-ray absorption studies of LaCoO_3 were interpreted in terms of the spin crossover at the semiconductor to metal transition. The $\text{Co}^{3+} 2p$ line in the absorption spectra is that of the low-spin cobalt ion, which is not consistent with the transition at 100 K. Furthermore, the valence band spectrum at 300 K is quite different from that of the high-spin state. The early studies assumed an ionic and ligand-field like picture and ignored the possibility of the intermediate (IS) state and the associated lowering of local symmetry. In order to investigate the electronic structure of LaCoO_3 , Korotin et al. [8] employed the local density approximation (LDA + U) approach and showed the ground state to be a non-magnetic insulator with the cobalt ion in the low-spin state. At a slightly higher energy, they found two intermediate-spin (IS) states followed by the high-spin state at a much higher energy. The calculations indicated that the Co $3d$ states of t_{2g} symmetry form narrow bands which would be localized easily, while the e_g orbitals form a broad small σ^* band due to interaction with the O $2p$ states. With temperature variation, a transition occurs from the low-spin state to the intermediate-spin state. The intermediate-spin state with the electronic configuration $t_{2g}^5 e_g^1$ ($^3T_1$) can develop orbital ordering (Fig. 6). Such orbital ordering can account for the magnetic moment of LaCoO_3 in the temperature range between 90 and 500 K.

One of the consequences of the presence of the intermediate-spin state is that the thermally excited species is Jahn-Teller distorted, because of the degeneracy of the e_g state [15]. One would therefore expect Jahn-Teller distortion with the evolution of the LS–IS transition. This would be detected more by the phonon spectrum than by the diffraction measurements. Therefore, the infrared spectrum of LaCoO_3 crystal indeed shows anomalous splitting of the phonon bands and intensity variations across the spin-state transition. The role of the e_g orbital ordering as proposed by Yamaguchi et al. [15]

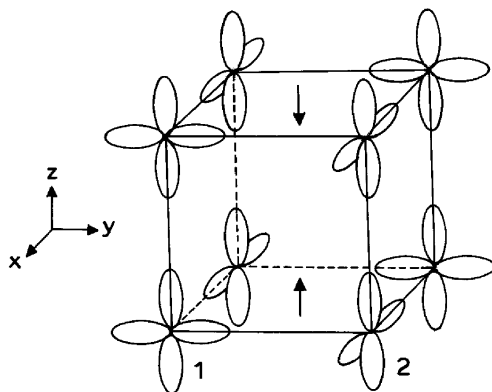


Fig. 6 Spin and orbital ordering in an orbital-ordered intermediate spin state for occupied e_g orbitals. For simplicity the perfect cubic structure of Co ions is shown (from [8])

is shown in Fig. 7. The electronic transition as well as optical conductivity data show that the semiconductor to metal transition occurs at 500 K where the spin-state (LS-IS) transition is complete. A large change in the electronic structure as well as an increase in carrier concentration is expected at the transition [16].

Ultrasonic measurements on LaCoO_3 between 400 K and 600 K show lattice softening around the transitions at 100 K and 500 K. The temperature dependence of the elastic modulus is explained by a model involving three spin (low-spin, intermediate-spin and high-spin) states coupled with the lattice [17]. The pressure dependence of the magnetic susceptibility of LaCoO_3 shows that the energy gap between the low-spin and the intermediate-spin states increases with increase in pressure [18]. The linear part of the pressure dependence at low pressures is consistent with the explanation of the spin-state transition. The quadratic dependence at high pressure reflects the volume dependence of the excited magnetic state. Neutron diffraction measurements have shown lattice expansion at 500 K, indicating a second transition in addition to the one at 100 K. The data are explained on the basis of the three spin-state model [19], the transition at 100 K representing the low-spin to intermediate-spin state transition and the one at 500 K due to a transition from the intermediate-spin state to a state resulting from the mixing of intermediate-spin and high-spin states.

Sudheendra et al. [20] have observed splitting of the stretching bands of rare earth cobaltates in the infrared absorption spectra around the transition temperature (Fig. 8). The transitions were at 120 K, 220 K and 275 K, respectively, in LaCoO_3 , PrCoO_3 and NdCoO_3 , where the intensities of the stretching and bending modes associated with the low-spin state decrease accompanied by an increase in the intensities of the bands due to the intermedi-

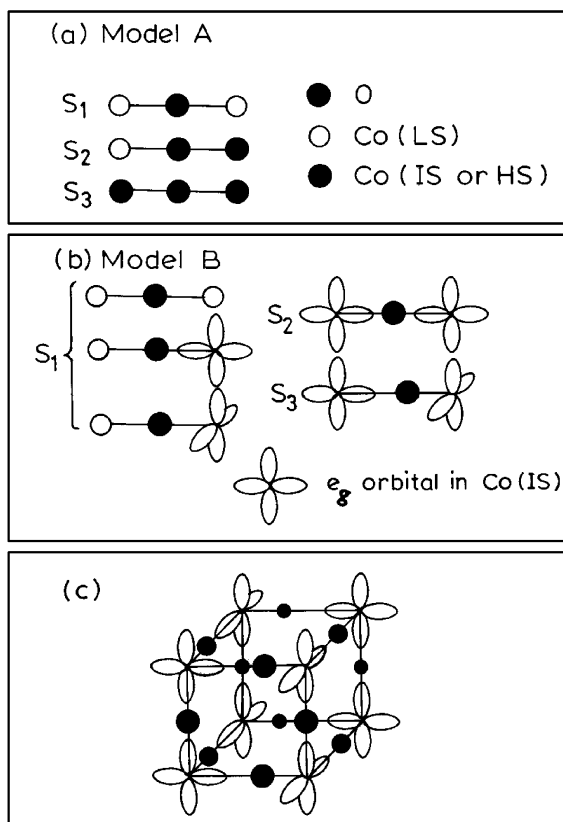


Fig. 7 (a) Model A: The local bonds, namely Co (LS)–O–Co(LS), Co (LS)–O–Co (IS or HS), and Co (IS or HS)–O–Co (IS or HS), are assigned to the stretching phonon modes S_1 , S_2 , and S_3 , respectively, in which the IS or HS species is thermally excited randomly at the respective sites. (b) Model B: Three kinds of Co (LS)-containing bonds are assigned to the S_1 mode, and two kinds of Co (IS)-O-Co (IS) bonds in the orbital-ordered IS state to the S_2 and S_3 modes. (c) The orbital-ordered IS state according to the LDA+U calculation [8], indicating that the intensity ratio of S_2 to S_3 equals 1:2 (from [15])

ate-spin state (Fig. 9). The vibration frequencies due to both of the spin-states decrease with increase in temperature, showing anomalies around the transition.

To the best of our knowledge, there are no reports of the optical phonons in the Raman spectrum over the temperature range of 30–300 K, which includes the spin-state transition of LaCoO_3 . Such a study has just been carried out by us on LaCoO_3 crystals in the temperature range 30–300 K. Group theoretical analysis gives the following optical phonon modes at the zone center of the $R\bar{3}c$ structure of LaCoO_3 [21]

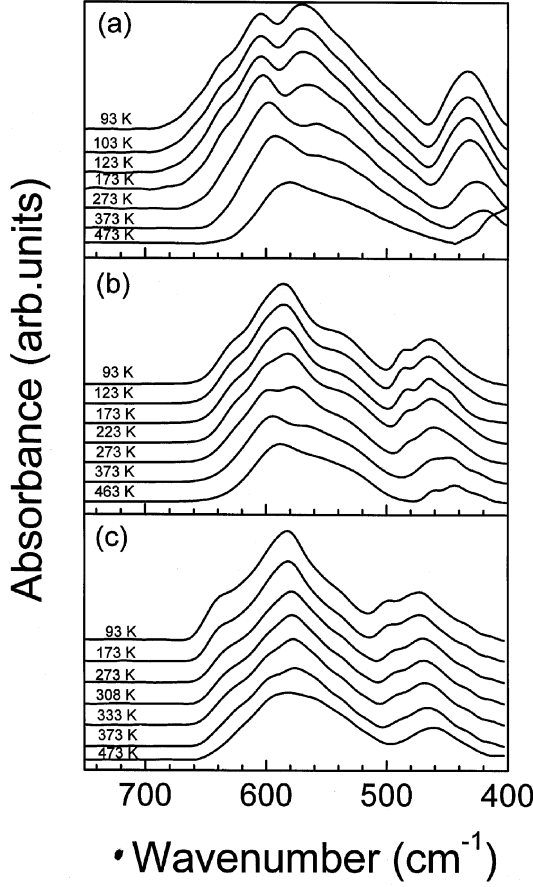


Fig. 8 IR spectra of (a) LaCoO₃, (b) PrCoO₃, and (c) NdCoO₃ crystals at different temperatures (from [20])

$$\Gamma(D_{3d}^6) = 2A_{1u} + 3A_{2g} + A_{1g}(R) + 3A_{2u}(IR) + 4E_g(R) + 5E_u(IR) \quad (a)$$

Therefore, LaCoO₃ should have five modes ($A_{1g} + 4E_g$) which are Raman active. In Fig. 10, we show the observed Raman spectrum of LaCoO₃. The bands can't be completely assigned due to the rhombohedral distortion of the perovskite structure. Anomalies (for example due to local lattice distortions) are readily seen in the phonon spectrum [16, 20], but cannot often be detected by the diffraction measurements. In the Raman spectrum, we observe 11 modes at 170, 180, 210, 228, 273, 313, 319, 380, 570, 650 and 750 cm⁻¹, as shown in Fig. 10 [22].

In the Raman study of rhombohedrally distorted LaAlO₃ and LaMnO₃ reported in the literature, LaMnO₃ consisting of the Jahn-Teller (J-T) distorted Mn³⁺ ion shows additional peaks due to local distortions which are absent

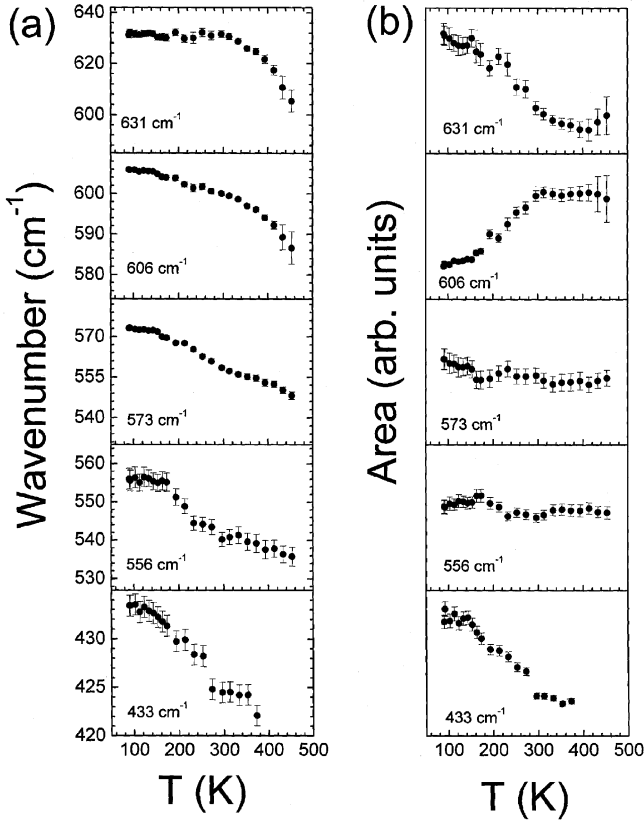


Fig. 9 Temperature-dependence of (a) frequencies and (b) the areas under the deconvoluted bands of LaCoO_3 (from [20])

in the spectrum of LaAlO_3 [23]. In LaCoO_3 , the Jahn-Teller distortion of the $\text{Co}^{\text{IS}}\text{-O}$ octahedra lowers the local atomic site symmetry and the new bands can be considered as the J-T distortion activated modes, otherwise forbidden in the $R\bar{3}c$ structure.

Polarization studies show that the peaks at 170 and 180 cm^{-1} are of E_g symmetry and this E_g mode can be assigned to vibration of the La-O bond, just as in LaMnO_3 and LaAlO_3 [23], where only one mode exists. The appearance of two modes associated with the La ion could be due to the variation in the La-O bond distance [24], which could experience different types of short-range ordering of the e_g orbital in the IS state [15]. As seen from Figures 10 and 11a, these modes tend to merge around 120 K to give a single vibration mode of La. As the temperature approaches that of the spin state transition at 120 K there is also a marked hardening of the 170 cm^{-1} mode and softening of the 180 cm^{-1} mode (120–200 K). Below 120 K, the 170 cm^{-1}

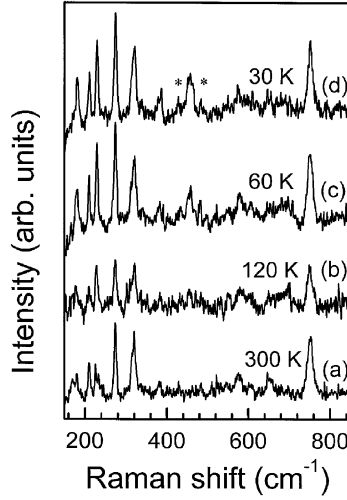


Fig. 10 Raman spectra of LaCoO₃ at (a) room temperature, (b) 120 K, (c) 60 K and (d) 30 K (from [22])

band disappears and the 180 cm⁻¹ mode hardens with decreasing temperature. It therefore appears that these two modes of E_g symmetry are coupled through the J-T distortion of the Co³⁺ (IS) ion. Calculations using the coupled mode equation show the coupling strength increasing with increase in temperature. Below 120 K, the coupling strength is negligible, possibly because of very low population of the IS state Co³⁺ ions at lower temperatures [22].

From Figures 10 and 11(b-d), we also notice the following: (i) There is a broad band centered around 580 cm⁻¹ and 650 cm⁻¹. (ii) The line shape of the broad band changes with temperature. (iii) A sharp peak appears around 450 cm⁻¹ below 120 K [22]. These modes do not exhibit polarization properties expected for an E_g mode. On comparison with the Raman spectra of isostructural LaMnO₃ and LaAlO₃, we find that the spectrum of LaCoO₃ is similar to that of LaMnO₃ and different from that of LaAlO₃. This could be due to the fact that J-T distortions occur in both LaCoO₃ and LaMnO₃, but not in LaAlO₃. The J-T distortion in CoO₆ octahedra lowers the local symmetry causing the new bands to appear, otherwise forbidden in the R $\bar{3}$ c structure as reported in [23].

The widths and shapes of the 580 and 650 cm⁻¹ bands can't be explained with such a simple approach and it is pertinent to examine similar broad bands observed above T_c in the doped lanthanum manganates. Non-coherent J-T distortion can be small or large. Small lattice perturbation affects the phonon lifetime, causing line broadening. In the case of the large distortion, the translational symmetry of the oxygen sublattice can be totally lost in cer-

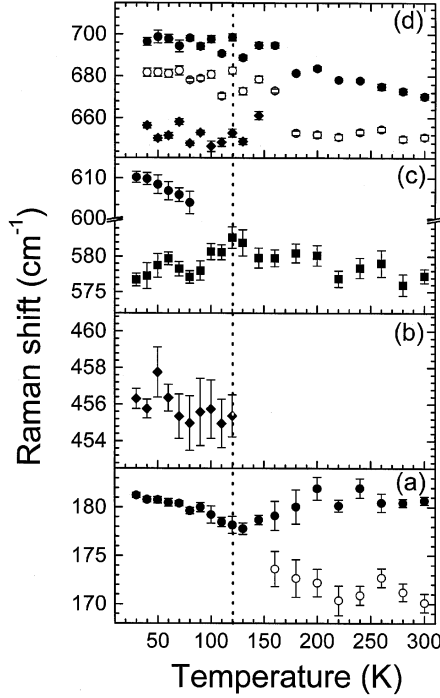


Fig. 11 Temperature dependence of the Raman shift for different bands: (a) 170 and 180 cm^{-1} ; (b) 455 cm^{-1} ; (c) 580 cm^{-1} ; and (d) 650 cm^{-1} (from [22])

tain crystallographic planes. This relaxes the selection rules and causes all of the phonon states of the corresponding phonon branches to become Raman-active. The resulting phonon spectrum will represent a one-phonon density of states. Keeping this in mind, one could assume that the density-of-states is the origin of the broad band around 550–700 cm^{-1} (Fig. 10). Such a feature has been seen in the LaMnO_3 as well. [23]. At room temperature, the J-T effect is weak, but as one lowers the temperature this effect increases, leading to the fine structure in the density-of-states as seen in the Raman spectrum. This would give rise to new features in the broad band in the 550–700 cm^{-1} range. The appearance of new features, as well as the behavior of the bands at room temperature and at 120 K arise from the increase in the population of the IS state in the mixed state (see Fig. 11c,d). If the fine structure in the Raman spectrum is ignored, the average frequencies of the modes do not show any anomaly across the transition. This is consistent with the infrared data which show the normal thermal effect for the high frequency modes [20]. The temperature variation of the integrated intensity of the broad bands centered around 580 and 650 cm^{-1} is shown in Fig. 12. The intensity increases in the 300–100 K range and decreases below about 100 K,

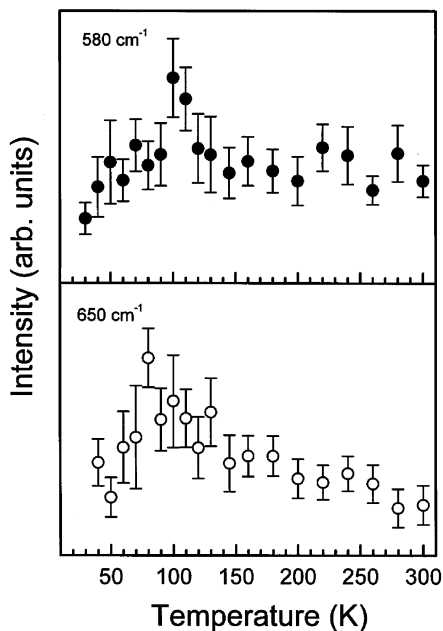


Fig. 12 Temperature dependence of the cumulative intensity of the broad bands centered around 580 cm^{-1} and 650 cm^{-1} (from [22])

consistent with the decrease in the percentage of total distorted CoO_6 octahedra at low temperatures [26]. We also observe a sharp band near 450 cm^{-1} surrounded by the weak satellites at low temperatures (see Fig. 10c and Fig. 11b). The origin of this band is not clear at this point. Its position is similar to that of the predicted bending E_g mode in rhombohedral LaMnO_3 . We do not see any appreciable change in the other modes with the change in temperature (Fig. 10).

The structural properties of LaCoO_3 have been studied recently by Radaelli and Cheong [24], by neutron diffraction in the temperature range 5 K to 1000 K. The study shows that the change in the spin state in this temperature interval affects the unit cell volume and the structural parameters such as the metal to oxygen bond distance. The temperature variation of the La-O distance shown in Fig. 13 reveals an increase in the distance at both the 100 K and 500 K transitions. The structure shows thermal expansion in these temperature regions, which is understood in terms of the change in the ionic radius of Co (or the Co-O bond distance) across the spin-state transitions. Both the structural data and the temperature dependence of magnetic susceptibility can be modeled satisfactorily on the basis of the three spin-state activated behavior. In Fig. 14, the linear thermal expansion of LaCoO_3 is shown along with the fit of the data to a three spin-state model.

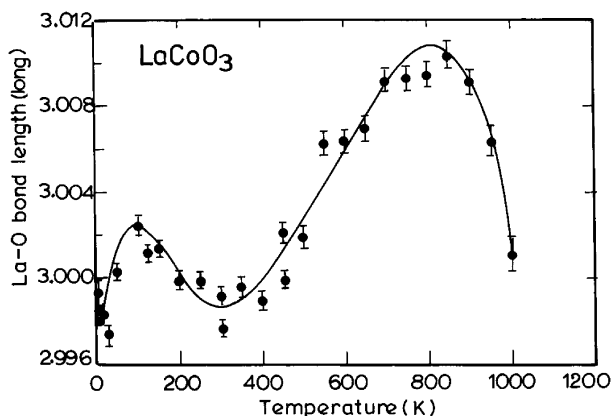


Fig. 13 Temperature dependence of the “long” La–O bond distance in LaCoO_3 , as determined from neutron diffraction data. The solid line is a guide to the eye (from [24])

Most studies suggest that the LS–IS model, or preferably the LS–IS–HS model, explain the properties of LaCoO_3 , especially the magnetic susceptibility behavior (Fig. 15). Based on an early soft x-ray absorption spectroscopic study in the 80 to 630 K range, Abbate et al. [25] suggested that LaCoO_3 was in a highly covalent low-spin state in the 80–300 K range. The mixed spin-state is attained gradually around 600 K, with the main contribu-

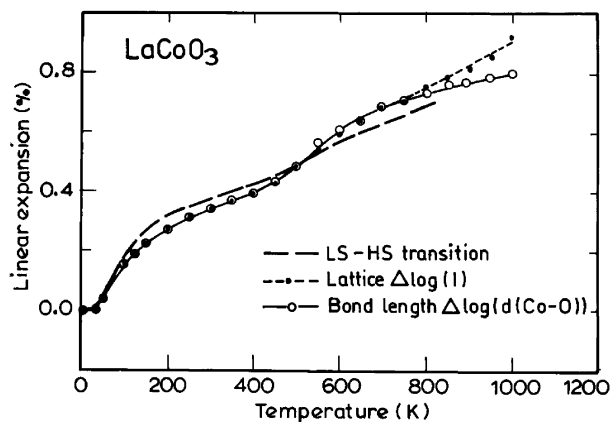


Fig. 14 Spin-state anomalies of the LaCoO_3 unit cell and internal parameters. Circles: the non-phonon component of the Co–O bond length expansion, obtained from the Rietveld bond length values by subtracting a single Einstein oscillator with $T_E=700$ K. Diamonds: the non-phonon component of the linear (unit-cell) thermal expansion. The high-temperature deviation, due to the formation of oxygen vacancies, is clearly visible. The solid and dashed lines are the pure magnetic thermal expansion and the magnetic + vacancies thermal expansion, respectively (from [24])

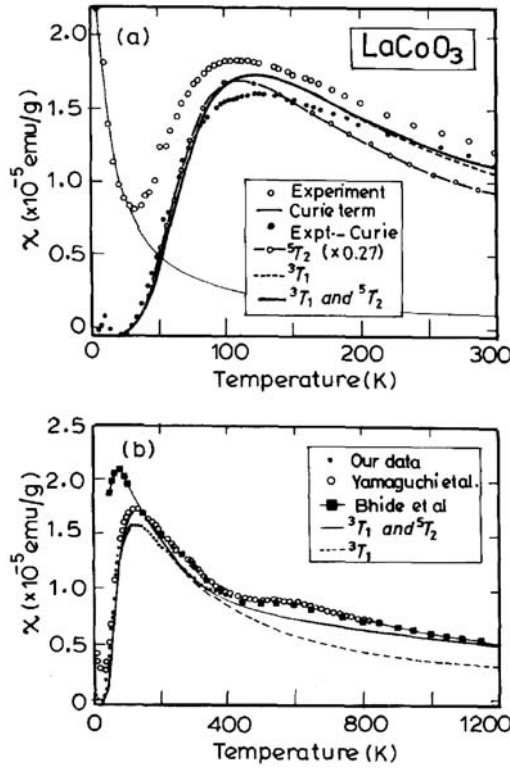


Fig. 15 (a) Magnetic susceptibility of LaCoO_3 . Applied magnetic field was 10 kOe. Circle-dashed line (${}^5T_2$); the ${}^1A_1$ - ${}^5T_2$ two state (LH) model, with an activation energy (E_p) of 266 K. Note that magnitude is reduced by a factor of 0.27. Dashed line (${}^3T_1$); the ${}^1A_1$ - ${}^3T_1$ two-state (LI) model with an activation energy (E_p) of 257 K. Solid line (${}^3T_1$ and ${}^5T_2$); the ${}^1A_1$ - ${}^3T_1$ - ${}^5T_2$ three state (LIH) model with an activation energy 275 K (E_{p1}) and 1731 K (E_{p2}). (b) LI model (dashed line) and LIH model (solid line) compared with the previous experimental data (filled circles), Yamaguchi et al. [12] (open circles) and Bhide et al. [5] (open squares) (from [26]). Here, L, I, and H denote LS, IS and HS

tion to the spin-state mixture coming from the ${}^5T_2$ state. No evidence for charge disproportionation from Co^{3+} to Co^{2+} and Co^{4+} was found in the 80–630 K range. These early observations are, however, not correct, since the occurrence of IS state [8] was not recognized at that time. In a recent study of the electronic structure of LaCoO_3 by photoemission spectroscopy and x-ray absorption spectroscopy [26], spectra have been analyzed based on a configuration-interaction cluster model for the LS, IS and HS states and their mixtures (Fig. 16). The ground state in the LS state is found to have mixed d^6 and d^7L character, representing charge transfer from the ligand to the metal (which is maximum in the LS state due to its empty e_g orbitals). Based on the analysis of the magnetic susceptibility for the various level or-

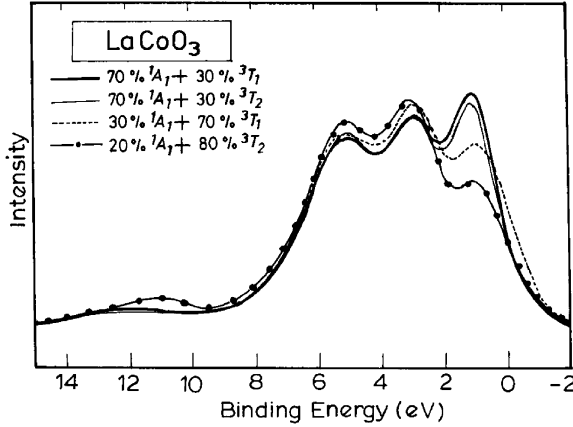


Fig. 16 Simulation of the temperature-dependent x-ray photoelectron spectra of LaCoO_3 for the two types (${}^1\text{A}_1\text{--}{}^3\text{T}_1$ and ${}^1\text{A}_1\text{--}{}^5\text{T}_2$) of the mixed initial states. 70% ${}^1\text{A}_1 + 30\%$ ${}^3\text{T}_1$ and 70% ${}^1\text{A}_1 + 30\%$ ${}^3\text{T}_2$ corresponding to ~ 80 K and 30% ${}^1\text{A}_1 + 70\%$ ${}^3\text{T}_1$ and 20% ${}^1\text{A}_1 + 80\%$ ${}^3\text{T}_2$ corresponding to ~ 300 K (from [26])

derings of the three spin-states, the low temperature transition around 100 K is assigned to a gradual LS–IS transition (Fig. 15).

Making the self-energy correction to the local three-body scattering to the Hartree-Fock approximation, the spectral density for the LS phase, and the excitation spectrum of LaCoO_3 , have been studied using a multi-orbital tight binding model [27]. The spectral density of the paramagnetic state (after the low temperature spin-state transition) can be simulated by mixing the spectral weight of the LS, IS and HS states. Zhuang et al. [28] have studied the magnetically ordered states of the double cell of LaCoO_3 , including the low-spin, intermediate-spin and high-spin states as well as their combinations. Unrestricted Hartree-Fock calculations show that the ground state of the system depends on the crystal-field splitting and Hund's coupling. For a fixed value of Hund's coupling, the ground state changes from the LS state to the LS–HS ordered state and finally to a HS–HS antiferromagnetic state. According to this model, the IS state is much higher in energy than the magnetically ordered LS–HS state and the IS will never be the ground state within the used parameter range [28]. This study suggests that the transition around 100 K is from the low-spin to the LS–HS ordered state.

4

$\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$

Substitution of Sr^{2+} for La^{3+} in LaCoO_3 gives rise to major changes in the properties. The available information on the properties of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ up

to 1995 has been reviewed [29]. With an increase in x , large ferromagnetic clusters containing holes are formed. In these clusters, the cobalt ion appears to be in the intermediate-spin state configuration. There is segregation of hole-rich ferromagnetic regions and hole-poor regions. In the hole-poor region, the material behaves more like LaCoO_3 exhibiting the LS-IS spin-state transition of Co^{3+} . It has been suggested that for the small x , the LS configuration of Co^{3+} is stable at low temperatures. At $x \leq 0.1$, the properties are close to those of LaCoO_3 [29, 30]. However, with increase in x , the IS and HS states appear to become more stable than the LS state, as verified by photoemission spectra [27]. With increase in temperature there is a transition from the LS state of Co^{3+} to the IS state. The tetravalent cobalt ions formed by Sr^{2+} substitution appear to be in the intermediate-spin state ($t_{2g}^4 e_g^1$) state [31].

Photoemission and x-ray absorption spectroscopy studies establish the intermediate-spin state of Co to be dominant in the ferromagnetic phase of

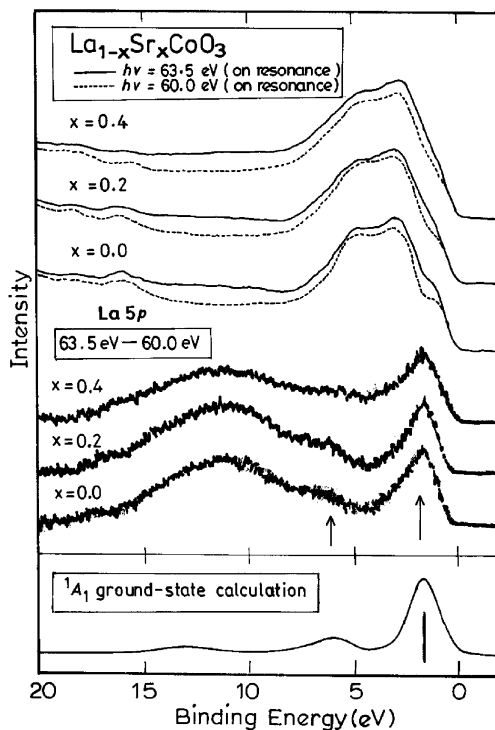


Fig. 17 Upper panel: Co $3p$ - $3d$ resonant-photoemission spectra of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$. Lower panel: On-off difference spectra compared with a configuration-interaction cluster-model calculation for the low-spin ($^1A_1$) ground state [26]. From the experimental spectra, the background due to secondary electrons has been subtracted and the intensity has been normalized to the total integrated intensity (from [32])

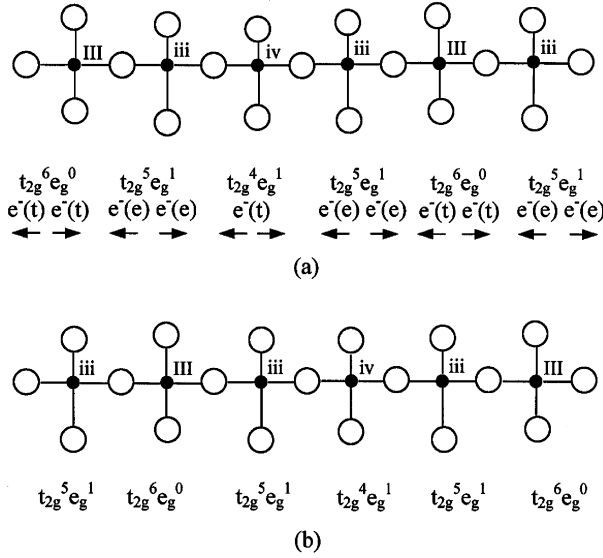


Fig. 18 Schematic representation of hole transfer on the low-spin subarray, for the dynamic ordering of intermediate-spin and low-spin cobalt ions. In the diagrams, large open circles represent oxygen ions, while the small solid circles correspond to cobalt ions: (a) initial configurations; (b) new situation after transfer of the hole

$\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ [32]. Resonant photoemission spectra near the core absorption threshold have yielded useful results. When $x=0.2$, there is hardly any change in the spectrum which is similar to that of LaCoO_3 . Small changes in the spectrum occur when $x=0.4$, showing evidence for the change from the LS to the IS state of Co^{3+} . Detailed calculations on the electronic structure of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ as a function of x show that hole doping stabilizes the intermediate-spin state [33]. Therefore, the spin-state transition by hole doping is from the LS to the IS state just as in the temperature-induced transition in LaCoO_3 . The small changes in the resonance-photoemission spectra as shown in Fig. 17, combined with the configuration-interaction (CI) cluster model calculations on LaCoO_3 [26], suggest the existence of the intermediate-spin state in the ferromagnetic phase [32]. It is interesting that in SrCoO_3 , the Co^{4+} ion is also in the intermediate-spin state [34]. The spin-state transition in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ seems to affect its magneto-resistance properties [35].

Figure 18 shows the hole dynamics in the low-spin, Co(III) , and intermediate-spin, Co(iii) , subarray in the presence of the tetravalent cobalt ion, which is also in the intermediate-spin state, Co(iv) . Here, the localized electrons only fluctuate from one cobalt to another. In such configuration fluctuation, the Co(III) ions transfer two t_{2g} electrons equally to each of the six neighboring Co(iii) ions, and the Co(iii) ions transfer back two e_g electrons equally to each of the six neighboring Co(III) ions, without giving any net

charge transfer, only an interchange of spin states. In this situation, the intermediate-spin state Co(IV) transfers a single t_{2g} electron to its neighbors. The missing t_{2g} electron becomes condensed as a t_{2g} hole on one of the neighboring cobalt centers that has undergone an interchange from an intermediate-spin state to a low-spin state, followed by an intermediate-spin Co(IV) state.

5 Models

There are several models to explain the features of the HS–LS transition in Fe^{2+} complexes [6, 36]. Any good model for the spin-state transition in LaCoO_3 should explain the following important experimental observations: (a) occurrence of the low-spin state up to about 420 K, (b) an increase in the higher spin-state (IS/HS) in the 420–650 K range and (c) possible ordering of the spin states at 650 K. A simple model based on two-level thermal population analysis would only predict a smooth variation with temperature. Such a model will also not predict a predominant IS–HS population at high temperatures. Chesnut [37] included spin-lattice interaction to improve the two-level model. The crystallographic changes at 650 K were later rationalized within the framework of Bari and Sivardiere [38]. Kurzynski [39] extended the model of Bari and Sivardiere to include both static and dynamic strains. Zimmermann and König [40] included the effect of low symmetry ligand fields and spin-orbit coupling. Ramasesha et al. [41] have proposed a two-phonon model where the spin states are mixed by the ion cage mode. Kambara [42] proposes a microscopic model wherein the coupling between the d electrons and the lattice has a definite meaning. Kambara [43] also treats the intramolecular distortion as a dynamic variable and takes intermolecular coupling into account. In spite of these models, some of the features of the spin-state transition of LaCoO_3 are not entirely explained. The gradual nature of the transition with temperature is, however, inherent in the model of Ramasesha et al. [41].

6 Conclusions

The spin-state transition in LaCoO_3 , first considered as a simple thermal excitation from a low-spin state to a high-spin state, has emerged to be considerably more interesting and complex. While IR and Raman spectroscopy throw light on the local distortions accompanying the transition, photoemission and related techniques provide useful information about the changes in the electronic structure. The transition seems to be best understood with a

three spin-state model (LS–IS–HS). The effect of hole doping on the spin-state transition parallels that of the thermal transition, and the interaction between the different spin-states of the Co^{4+} and Co^{3+} is understood reasonably well.

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References

1. Rao CNR, Raveau B (1998) *Transition Metal Oxides: Structure, Properties, and Synthesis of Ceramic Oxides*. Wiley-VCH, Weinheim, Germany
2. Heikes RR, Miller RC, Mazelsky A (1964) *Physica* 30:1600
3. Jonker GH (1966) *J Appl Phys* 37:1424
4. Raccach PM, Goodenough JB (1967) *Phys Rev* 155:932
5. Bhide VG, Rajoria DS, Rao GR, Rao CNR (1972) *Phys Rev B* 6:1021
6. Rao CNR (1985) *Int Rev Phys Chem* 4:19
7. Señaris-Rodríguez MA, Goodenough LB (1995) *J Solid State Chem* 116:224
8. Korotin MA, Ezhov SY, Solovyev IV, Anisimov VI, Khomskii D, Sawatzky GA (1996) *Phys Rev B* 54:5309
9. Arunarkavalli T, Kulkarni GU, Rao CNR (1993) *J Solid State Chem* 107:299
10. Thornton G, Owen IW, Diakun GP (1991) *J Phys-Condens Mat* 3:417
11. Madhusudan WH, Jagannathan K, Ganguly P, Rao CNR (1980) *J Chem Soc Dalt Trans* 1397
12. Yamaguchi S, Okimoto Y, Taniguchi H, Tokura Y (1996) *Phys Rev B* 53:R2926
13. Barman SR, Sarma DD (1994) *Phys Rev B* 49:13979
14. Itoh M, Sugahara M, Natori I, Motoya K (1995) *J Phys Soc Jpn* 64:3967
15. Yamaguchi S, Okimoto Y, Tokura Y (1997) *Phys Rev B* 55:R8666
16. Tokura Y, Okimoto Y, Yamaguchi S, Taniguchi H, Kimura T, Takagi H (1998) *Phys Rev B* 58:R1699
17. Murata S, Isida S, Suzuki M, Kobayashi Y, Asai K, Kohn K (1999) *Physica B* 263–264:647
18. Asai K, Yokokura O, Suzuki M, Naka T, Matsumoto T, Takahashi H, Môri N, Kohn K (1997) *J Phys Soc Jpn* 66:967
19. Asai K, Yoneda A, Yokokura O, Tranquada JM, Shirane G, Kohn K (1998) *J Phys Soc Jpn* 67:290
20. Sudheendra L, Seikh MM, Raju AR, Narayana C (2001) *Chem Phys Lett* 340:275
21. Tajima S, Masaki A, Uchida S, Matsuura T, Fueki K, Sugai S (1987) *J Phys C Solid State Phys* 20:3469
22. Seikh MM, Sudheendra L, Narayana C, Rao CNR (unpublished results)
23. Iliev MN, Abrashev MV (2001) *J Raman Spectrosc* 32:805
24. Radaelli PG, Cheong S-W (2002), *Phys Rev B* 66:094408
25. Abbate M, Fuggle JC, Fujimori A, Tjeng LH, Chen CT, Potze R, Sawatzky GA, Eisaki H, Uchida S (1993) *Phys Rev B* 47:16124
26. Saito T, Mizokawa T, Fujimori A, Abbate M, Takeda Y, Takano M (1997) *Phys Rev B* 55:4257
27. Takahashi M, Igarashi J (1997) *Phys Rev B* 55:13557
28. Zhuang M, Zhang W, Ming N (1998) *Phys Rev B* 57:10705

29. Se  ar  s-Rodr  guez MA, Goodenough JB (1995) J Solid State Chem 118:323
30. Bhide VG, Rajoria DS, Rao CNR, Rao GR, Jadhao VG (1975) Phys Rev B 12:2832
31. Bahadur D, Kollali S, Rao CNR, Patni MJ, Srivastava CM (1979) J Phys Chem Solids 40:981
32. Saitoh T, Mizokawa T, Fujimori A, Abbate M, Tokura Y, Takano M (1997) Phys Rev B 56:1290
33. Ravindran P, Fjellvag H, Kjekshus A, Blaha P, Schwarz K, Luitz J (2001) Cond-Mat 0104308
34. Zhuang M, Zhang W, Hu A, Ming N (1998) Phys Rev B 57:13655
35. Mahendiran R, Raychaudhuri AK (1996) Phys Rev B 54:16044
36. G  tlich P, Hauser A, Spiering H (1994) Angew Chem Int Ed 33:2024
37. Chesnut DB (1964) J Chem Phys 40:405
38. Bari RA, Sivardiere J (1972) Phys Rev B 5:4466
39. Kurzynski M (1976) J Phys C 9:3731
40. Zimmermann R, K  nig E (1977) J Phys Chem Solids 38:779
41. Ramasesha S, Ramakrishnan TV, Rao CNR (1979) J Phys C 12:1307
42. Kambara T (1979) J Chem Phys 70:4199
43. Kambara T (1981) J Chem Phys 74:4557

Spin Crossover in Cobalt(II) Systems

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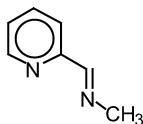
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Abstract Cobalt(II), a d^7 ion, can exist in a low spin doublet state or a high spin quartet state. Both spin-state configurations are known in four-, five- and six-coordinate complexes. For each of these coordination numbers, systems are known where the two spin states may be thermally interconverted. For four-coordinate and some five-coordinate systems these interconversions are best regarded as configurational equilibria; in other instances a spin transition is involved. The features of these transitions show similarities to, but also marked differences from, those in iron(II) systems. The smaller change in spin associated with the transition ($\Delta S=1$) and the operation of a Jahn-Teller effect in the doublet state species confer special characteristics on the cobalt(II) systems.

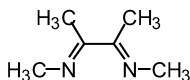
Keywords Cobalt(II) · Terpyridine · Configurational equilibria · Spin transition · Spin crossover

1 Introduction

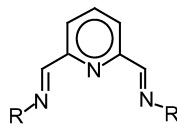
Both high spin and low spin configurations are possible for six-coordinate cobalt(II), a d^7 ion, and, as with iron(II), these show markedly different properties; complexes with the latter configuration frequently showing a strong propensity for oxidation. The most significant difference in physical properties is the magnetism of the complexes, the magnetic moments generally being in the range 4.7–5.2 μ_B for high spin (quartet state $^4T_1$) and 1.8–2.2 μ_B for low spin (doublet state ^2E) complexes. In 1960 Figgins and Busch reported intermediate magnetic moments at room temperature for the iodide salts of the $[\text{CoN}_6]^{2+}$ derivatives of the bidentates 1 and 2 and the tridentate 3 ($R=\text{CH}_3$) [1]. This led them to suggest that for these there is an equilibrium mixture of low spin and high spin species in each instance.



1



2



3

This is the first report of the spin transition phenomenon for cobalt(II) and it is significant that these ligand diimine and terimine systems are typical of those which have come to form one of the major classes of crossover systems for six-coordinate cobalt(II). Such systems figure prominently in iron(II) spin crossover chemistry too, but the important distinction is that the intrinsic field strength required to effect spin-pairing in cobalt(II) is greater than that for iron(II) [2]. Therefore, ligands such as 1, 2, 3 and their parent imines, 2,2'-bipyridine (bpy) and 2,2':6',2''-terpyridine (trpy) effect complete spin-pairing in iron(II), but those related systems which generate the spin crossover situation in iron(II) yield purely high spin six-coordinate cobalt(II). A further, very perceptive observation was made by Figgins and Busch concerning, in particular, the tendency for spin-pairing in cobalt(II) in derivatives of tridentates such as 3 [3]. They pointed out that all four of the distal donor atoms in a bis(tridentate)metal system, where the tridentate is a planar, conjugated system, must coordinate in an equatorial plane of the octahedron. It is primarily the metal d_{xy} orbital which contributes to the π -interaction with these donor atoms. On the other hand, both the d_{yz} and d_{zx} metal orbitals are oriented for π -interaction with the two central donor atoms, leading to a prediction of much stronger bonding along the $\text{N}_{\text{central}}\text{-M-N}_{\text{central}}$ axis. Simple geometrical considerations also predict that the $\text{M-N}_{\text{central}}$ bonds should be shorter than the $\text{M-N}_{\text{distal}}$. This is equivalent to the imposition of a tetragonal distortion (compression) on the metal ion environment, and this is more compatible with the low spin than the high spin configuration for cobalt(II), a strong Jahn-Teller effect being associated

with the former. The first actual characterisation of a spin transition in six-coordinate cobalt(II), that reported by Stoufer, Busch and Hadley, was for a coordinated, planar tridentate system ($3 \text{ (R=NH}_2\text{)}$) [4]. Shortly afterwards Hogg and Wilkins [5] reported a strong anion-dependence of the magnetism of salts of $[\text{Co}(\text{trpy})_2]^{2+}$ ($\text{trpy}=2,2':6',2''\text{-terpyridine}$) and the temperature-dependence of the magnetism of $[\text{Co}(\text{trpy})_2]\text{Br}_2\cdot\text{H}_2\text{O}$, for which μ_{eff} changed from $3.1 \mu_{\text{B}}$ at 351 K to $1.9 \mu_{\text{B}}$ at 77 K, with a moment of $2.2 \mu_{\text{B}}$ in aqueous solution at 293 K. They left the interpretation of these observations open but commented that “it was tempting to explain the results in terms of a low spin–high spin equilibrium”.

2

Comparison of Cobalt(II) and Iron(II) Systems

The transition in six-coordinate Co(II) systems from low spin to high spin involves a change from a $^2\text{E} \text{ (t}_{2\text{g}}^6\text{e}_\text{g}^1\text{)}$ to a $^4\text{T}_1 \text{ (t}_{2\text{g}}^5\text{e}_\text{g}^2\text{)}$ ground state. Such a transition involves the transfer of just a single electron from the $\text{t}_{2\text{g}}$ to the e_g level, in contrast to the similar process in Fe(II) or Fe(III) where a two-electron transfer occurs. This is the source of several important differences in the features of spin transitions in Co(II) and, in particular, Fe(II). Perhaps the most significant is the change in metal–donor atom distances accompanying the change. Although the information is far less extensive for Co(II) than for Fe(II), it seems that the doublet→quartet change in six-coordinate Co(II) results in an expansion of the metal–donor atom distance of $\sim 0.10 \text{ \AA}$, compared with $\sim 0.20 \text{ \AA}$ for the singlet→quintet change in Fe(II). Consistent with this, the magnitude of both thermodynamic parameters ΔH and ΔS associated with the spin change is less for Co(II) than for Fe(II). This has implications too for the relative dynamics of the spin changes and for the nature of the spin transition curves, which in the vast majority of instances for Co(II) are of the gradual kind.

As a consequence of the reduced volume changes associated with change in spin state for Co(II), together with the possibility of spin-state mixing through spin-orbit coupling effectively reducing the forbidden nature of the transition, spin interconversion is expected to be more rapid for Co(II) than for Fe(II) and even for Fe(III). Very rapid relaxation of the spin equilibrium in the $[\text{Co}(\text{trpy})_2]^{2+}$ system has been detected from both Raman laser temperature-jump [6] and ultrasonic relaxation experiments, with an upper limit of 0.2 ns for the relaxation time in water at 298 K [7]. In contrast to this, the spin state lifetime for the $[\text{CoN}_6]^{2+}$ complex of the hydrazone **3** (R=NHCH_3) is reported as $83\pm 23 \text{ ns}$, longer than that for several iron(III), and even some iron(II) systems. It is suggested that in this instance the inner-sphere reorganisation accompanying the spin change may be rate-deter-

mining and be hindered by intramolecular interactions involving the NHCH_3 groups of one ligand and the pyridine ring of the second ligand [8].

Although the spin transition phenomenon in cobalt(II) is well-established, the number of systems characterised is considerably fewer than for Fe(II). This may simply reflect a relative lack of interest in the Co(II) case, possibly because of the paucity of abrupt transitions in this instance. A further contributing factor is likely to be the unavailability of a technique as informative and diagnostic as Mössbauer spectroscopy is for Fe(II) systems. Although Mössbauer emission spectral studies of ^{57}Co -labelled samples have been performed, these are much more relevant to the nature of the ^{57}Fe decay products than to the cobalt species [9]. In contrast, electron spin resonance (e.s.r.) spectroscopy is more widely applicable for Co(II) systems. While it is not appropriate for the derivation of a spin transition curve, as Mössbauer spectroscopy is for Fe(II), it has been applied to demonstrate unequivocally the presence of doublet state Co(II) with a characteristic signal at $g \sim 2$ in crossover systems, and therefore to establish that a genuine spin transition, rather than a temperature-dependent mixing of spin states is involved [10]. In principle, the technique should be able to detect quartet state Co(II) in these systems too, but at higher temperatures where the two spin states are expected to be approximately the same energy, the spin-lattice relaxation time for the quartet state is normally sufficiently short to broaden its ESR signal to the extent that it is not observable. For $[\text{Co}(\text{trpy})_2](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$, for which the high spin fraction is relatively high at low temperatures, signals are observed for both spin states at 4.2 K [11]. The observation of individual ESR signals establishes a limit for the rate of interconversion of the low spin and high spin states – it must be slower than the inverse time-scale of the ESR experiment, 10^{10} s^{-1} .

Measurement of the temperature-dependence of magnetism remains the principal technique for the identification and characterization of the nature of a spin transition in Co(II). But this is less diagnostic than for Fe(II) systems. In the low spin state the magnetic moment for Co(II) is generally close to the spin-only value [12] but the precise value is difficult to ascertain for an incomplete transition. In addition, the value for high spin, six coordinate Co(II) falls into a fairly broad range of $\sim 4.7\text{--}5.2 \mu_{\text{B}}$ and moreover is itself appreciably temperature-dependent, this being determined principally by the ligand field strength, spin-orbit coupling and, particularly in the region of the doublet $\leftrightarrow$ quartet spin crossover, mixing of doublet and quartet levels [13]. Therefore, determination of the high spin and low spin fractions from the temperature-dependence of magnetism is far from straightforward, and generally the nature of a spin transition is assumed to follow broadly the nature of the temperature-dependence of the magnetic moment.

A further important point of difference between Fe(II) and Co(II) arises from the contributions of Jahn-Teller effects. For Fe(II) these are operative in the high spin state, but to a relatively minor degree, whereas for Co(II)

the low spin state is subject to a strong Jahn-Teller effect arising from the single e_g electron. As mentioned above, this can be accommodated by the coordination of planar, tridentate ligands which will impart a compressed structure on the coordination environment. Coordination of a planar quadridentate will provide a strong equatorial field and may lead to doublet state square-planar complexes, but further coordination at axial sites can weaken this and lead to population of the quartet state in five- and six-coordinate derivatives. Such tetragonally elongated systems provide many important instances of the spin transition phenomenon in Co(II).

As with Fe(II), spin transitions in Co(II) are observed for systems with coordination numbers less than six and this is a rather broader area for Co(II). While in certain instances these can be considered to be examples of configurational equilibria (planar-tetrahedral, square pyramidal-trigonal bipyramidal), they are not fundamentally different from those changes which occur in six-coordinate species where structural changes also occur. Many of the important features of these were established in the 1960s and 1970s and were outlined in reviews of Sacconi and his co-workers [14]. Only modest developments in this area have been reported since then.

3

Bis(Tridentate) Systems

3.1

Bis(Terpyridine) Systems

Since the initial report of the anomalous magnetic properties of bis(terpyridine)cobalt(II) salts, this system has been widely studied. The early observation of Hogg and Wilkins of the pronounced anion and solvation influences on the course of the spin transition has since been extended by several groups, and the properties of the various salts investigated are summarized in Table 1. It is noted that for some of the salts different hydrates are reported by different groups, and in some instances slightly different magnetic properties have been observed for the same hydrate. The existence of different phases for the one species has been proposed [11]. It may be that in some instances the actual hydration assigned is not reliable, since this is usually obtained by difference after elemental analysis and the compounded errors of this procedure are incorporated into the estimation of the extent of hydration [18]. The clearest indication of the extent of hydration comes from actual structure determination and this has been achieved for a number of salts.

The first structural studies were reported for the bromide trihydrate at 295 K where the magnetism ($\mu_{\text{eff}}=2.9 \mu_B$) indicates the presence of both spin states. In this structure, one of the bromide ions is disordered over two sites

Table 1 Magnetic properties of solid salts of $[\text{Co}(\text{trpy})_2]^{2+}$ and their hydrates

Anion	Solvate	$\mu_{\text{eff}} (\mu_{\text{B}})$ (K)	Reference
Br^-	H_2O	2.7 (293); 1.9 (77)	5
Br^-	H_2O	2.76 (313); 1.83 (113)	11
Br^-	$2\text{H}_2\text{O}$	2.05 (97); 2.91 (309)	15
Br^-	$3\text{H}_2\text{O}$	2.26 (150); 2.94 (300)	16
Br^-	$3\text{H}_2\text{O}$	2.94 (300)	17
Br^-	$3\text{H}_2\text{O}$	3 (293); 1.9 (4.2)	11
Cl^-	H_2O	2.1 (193)	5
Cl^-	$3.5\text{H}_2\text{O}$	1.95 (104); 2.40 (311)	15
Cl^-	$3.5\text{H}_2\text{O}$	3.84 (100); 4.17 (300)	16
Cl^-	$5\text{H}_2\text{O}$	2.50 (293); 2.10 (113)	10
Cl^-	$5\text{H}_2\text{O}$	3 (293); 1.9 (4.2)	11
Cl^-		4.46 (150); 4.65 (300)	16
I^-	H_2O	2.03 (100); 3.40 (300)	16
I^-	$2\text{H}_2\text{O}$	2.29 (103); 3.60 (300)	15
I^-	$2\text{H}_2\text{O}$	2.2 (120); 3.66 (295)	18
I^-	$1.5\text{H}_2\text{O}$	3 (293); 1.9 (4.2)	11
I^-		2.31 (100); 3.97 (300)	16
F^-	$3.5 \text{H}_2\text{O}$	1.94 (30); 2.15 (300)	16
F^-	$4.5\text{H}_2\text{O}$	3.56 (150); 4.00 (300)	16
ClO_4^-		4.3 (293)	5
ClO_4^-		2.25 (100); 4.49 (300)	16
ClO_4^-	H_2O	3.74 (300); 3.23 (100)	19
ClO_4^-	H_2O	3.75 (303); 113 (3.27)	10
ClO_4^-	$1.5\text{H}_2\text{O}$	2.24 (110); 3.96 (303)	15
ClO_4^-	$0.5\text{H}_2\text{O}$	3.5 (4.2); 4.2 (293)	11
ClO_4^-	$0.5\text{H}_2\text{O}$	4.29 (322); ~ 2.0 (80)	20
ClO_4^-	$1.3\text{H}_2\text{O}$	4.23 (295); 3.16 (4.2)	21
NCS^-	H_2O	2.82 (100); 4.01 (300)	16
NCS^-	$1.5\text{H}_2\text{O}$	2.47 (100); 3.79 (308)	15
NCS^-	$2\text{H}_2\text{O}$	4.0 (300)	22
NO_3^-		1.88 (100); 2.96(300)	16
NO_3^-	$0.5\text{H}_2\text{O}$	3 (293); 1.9 (4.2)	11
$[\text{Co}(\text{CN})_4]^{2-}$		2.58 (100); 3.21(300)	16
SO_4^{2-}	$6\text{H}_2\text{O}$	2.11 (97); 2.66 (326)	15
BPh_4^-		3.41 (97); 4.01 (322)	15

and it is suggested that thermal population of these sites may be linked to the thermal distribution of the spin states [17]. In a subsequent structure determination of the thiocyanate dihydrate at 295 K ($\mu_{\text{eff}}=4.0 \mu_{\text{B}}$ at 295 K) it was found that the exposure to x-rays for some time initiated a phase change involving ordering of the orientation of one of the anions. The Co-N distances are longer than in the bromide salt, consistent with the greater concentration of high spin species indicated by the magnetism [22].

The structure of the perchlorate hemihydrate was reported initially by Henke and Kremer at 293 K ($\mu_{\text{eff}}\sim 4.1 \mu_{\text{B}}$) and an average Co-N distance

0.07 Å longer than that for the bromide trihydrate was found [23]. The structure of the hemihydrate has been determined separately at 243 K [20]. It is noted that the two structures are in different space groups. This may indicate the existence of different polymorphs, or a change in structural phase with change in temperature. In the more recent report the magnetism of the perchlorate hemihydrate indicates an almost complete transition from low spin at 70 K to high spin at 320 K. In the same work the chloride pentahydrate is reported as almost entirely low spin over the same temperature range, a small and very gradual increase in the magnetic moment being evident above about 150 K. A further hydrate (1.3H₂O) of the perchlorate salt has been structurally characterized at 295 K ($\mu_{\text{eff}}=4.23 \mu_{\text{B}}$ at 295 K). Disorder in both the anion and water positions is evident [21]. The only instance where the structure of the one sample has been obtained at two temperatures is for the iodide dihydrate (at 295 K where $\mu_{\text{eff}}=3.2 \mu_{\text{B}}$, and at 120 K where $\mu_{\text{eff}}=2.2 \mu_{\text{B}}$). The structure at 120 K corresponds to that of the fully low spin species and so establishes the essential dimensions for this (Co–N_{central} and Co–N_{distal} distances are 1.912 Å and 2.083 Å, respectively) [22].

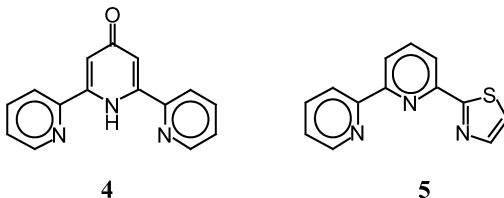
From a consideration of the available structural data for the various salts of [Co(trpy)₂]²⁺, together with an analysis of the relevant magnetic data, an estimate of the changes in the Co–N distances with change in ground state has been made [21]. It is found that the predominant change occurs in the Co–N_{central} distance (~0.21 Å), while the change in the Co–N_{distal} distance is only ~0.07 Å. As has been pointed out by Kremer, Henke and Reinen [11], the compression imposed along the N_{central}–Fe–N_{central} axis by the ligand geometry is superimposed on an elongation perpendicular to the direction of compression. This is a corollary of the Jahn-Teller effect arising from the remaining e_g electron in the low spin state, and this observation is supported by a significantly greater M–N_{distal}:M–N_{central} ratio in the low spin form of [Co(trpy)₂]²⁺ (1.09) than that for other low spin [M(trpy)₂]ⁿ⁺ systems where Jahn-Teller effects are not operative, Co(III) 1.04 [24], Fe(II) 1.05 [25], Ru(II) 1.05 [26].

The spin state of [Co(trpy)₂]²⁺ in solution appears to be dependent on either (or both) the solvent or the accompanying anion. Early reports (solvent unspecified) of a moment of 3.3 [16] and 3.1 μ_{B} [11] for the perchlorate indicate a substantial high spin fraction while the bromide has $\mu_{\text{eff}}=2.2 \mu_{\text{B}}$ in CD₃CN [5]. The hexafluorophosphate is low spin in CD₃CN [27] and has $\mu_{\text{eff}}=3.2 \mu_{\text{B}}$ at room temperature in deuterioacetone solution [28]. In all instances the moments reported are less for the species in solution than in the solid state at the same temperature. A theoretical treatment for relatively simple Co(II) six-coordinate systems has predicted a stabilization of the doublet state in solution and indicated that this also may apply to more complex systems [29].

3.2

Substituted Terpyridine Systems

2,6-bis(pyridin-2-yl)-4(1*H*)-pyridone **4** coordinates in the enol form and is therefore considered a substituted terpyridine [30]. The complexes $[\text{Co}_2]\text{X}_2$ are structurally and electronically similar to $[\text{Co}(\text{trpy})_2]\text{X}_2$. The sulfate salt is entirely high spin, the chloride monohydrate is essentially low spin, but the beginnings of a gradual transition are evident from about 150 K. An almost complete transition occurs for the perchlorate monohydrate in the range 100–300 K.



At 293 K the average $\text{Co}-\text{N}_{\text{central}}$ and $\text{Co}-\text{N}_{\text{distal}}$ distances are 1.994 Å and 2.131 Å, respectively, the average overall $\text{Co}-\text{N}$ distance being 2.09 Å [31]. There is in fact a remarkable family of 4-substituted-terpyridines available including multi-functional systems [32]. The detailed electronic properties of the solid $[\text{CoN}_6]^{2+}$ complex salts are likely to be of considerable interest. In some instances spin transitions have been identified in solution [33], while the systems reported by Constable and co-workers are low spin in solution [34]. The crystal structure of a system containing a chiral substituent in the 4-position has $\text{Co}-\text{N}$ bond lengths at room temperature which are indicative of a considerable high spin fraction [35]. With methoxy groups in the 4-position of each of the three pyridine rings there appears to be a favouring of the high spin state, at least in solution [28].

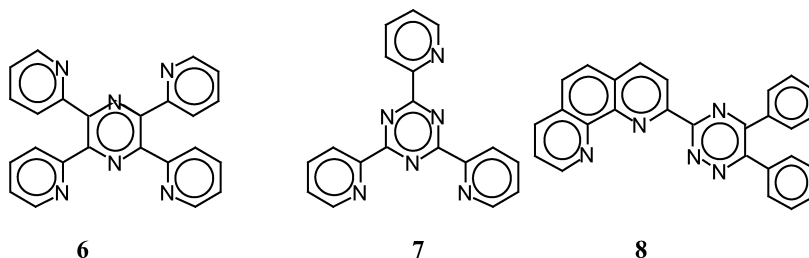
Substitution at the 6-position of one of the terminal rings in terpyridine is expected, from steric considerations, to favour the quartet state for $\text{Co}(\text{II})$ and this has been confirmed for the derivative of 6-bromo-terpyridine [27].

3.3

Terpyridine-Related Systems

The tridentate 6-(thiazol-2-yl)-2,2'-bipyridine **5** forms $[\text{M N}_6]^{2+}$ derivatives which are remarkably similar to those of terpyridine. The field strength of **5** is marginally less than that for terpyridine ($Dq(\text{Ni}^{2+})=1230 \text{ cm}^{-1}$, compared with 1260 cm^{-1} for trpy under the same conditions). The magnetic moment of $[\text{Co}_2](\text{BF}_4)_2$ displays significant temperature-dependence in the solid state ($\mu_{\text{eff}}=4.50 \mu_{\text{B}}$ at 303 K and $3.80 \mu_{\text{B}}$ at 89 K) and, to a lesser extent, in acetone solution, indicative of an incomplete transition [36].

The bromide heptahydrate, iodide tetrahydrate, selenocyanate monohydrate, nitrate hexahydrate and perchlorate monohydrate salts of $[\text{Co } 6_2]^{2+}$ are all virtually low spin at 293 K and show only a small increase in magnetic moment above this, though it is evident that there is the onset of a transition in all instances.



The chloride monohydrate is totally high spin at 297 K ($\mu_{\text{eff}}=5.02 \mu_{\text{B}}$) and its moment has decreased only slightly at 96 K ($4.63 \mu_{\text{B}}$) which may reflect the temperature dependence of the magnetism of the quartet state rather than any population of doublet state. The magnetic moment of the thiocyanate monohydrate shows strong temperature dependence ($\mu_{\text{eff}}=3.50$ and $1.79 \mu_{\text{B}}$ at 358 and 80 K, respectively) [37].

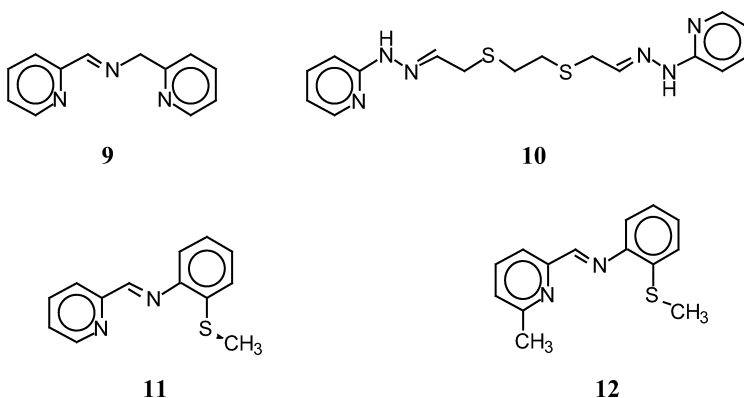
Eight salts containing $[\text{Co } 7_2]^{2+}$ were examined. All except the perchlorate monohydrate and chloride octahydrate are essentially high spin at 96 K. The magnetic moments of the perchlorate and chloride salts are strongly temperature dependent and indicative of gradual spin transitions ($\mu_{\text{eff}}=4.17 \mu_{\text{B}}$ (369 K) and $3.04 \mu_{\text{B}}$ (93 K) for the chloride; $\mu_{\text{eff}}=4.61 \mu_{\text{B}}$ (300 K) and $3.66 \mu_{\text{B}}$ (96 K) for the perchlorate) [37]. The triazine system 3-(1,10-phenanthroline-2-yl)-5,6-diphenyl-1,2,4-triazine **8** exerts a somewhat weaker field than terpyridine ($\text{Dq}(\text{Ni}^{2+})=1210 \text{ cm}^{-1}$). Despite this, the spin state properties of salts of its $[\text{Co } 8_2]^{2+}$ complex are very similar to those of $[\text{Co}(\text{trpy})_2]^{2+}$. Therefore a strong anion-dependence is found with the tetrafluoroborate being essentially high spin at 83 K ($\mu_{\text{eff}}=4.25 \mu_{\text{B}}$), while the nitrate and bromide salts are essentially low spin at the same temperature ($\mu_{\text{eff}}=2.44$ and $1.99 \mu_{\text{B}}$ for the nitrate and bromide, respectively) but a gradual increase in the magnetic moment is observed at higher temperatures ($\mu_{\text{eff}}=3.27$ and $2.89 \mu_{\text{B}}$ at 333 K) [38].

3.4

Tridentate Schiff Base Systems

The condensation of pyridine-2-carboxaldehyde or pyridine-2,6-dicarboxaldehyde with suitable molecules containing a primary amino group leads to tridentates with a terimine chromophore [39] similar to that in terpyridine. The $[\text{CoN}_6]^{2+}$ derivatives of several of these have been shown to have temperature-dependent magnetic moments characteristic of doublet $\leftrightarrow$ quartet

transitions. These include the hydrazone **3** ($R=NH_2$), the benzylimine system **3** ($R=C_6H_5-CH_2$) and the Schiff base **9** obtained from pyridine-2-carboxaldehyde and 2-picolyamine studied by Stoufer and co-workers [19]. They also reported the anomalous magnetism of the complex of the hydrazone system **10**. Although this coordinates as a sexadentate chelate, the geometry about the metal atom would be very similar to that in a bis(terpyridine) metal system with two NNS sequential donor atom moieties expected to coordinate in equatorial planes. In all instances the transitions observed are gradual and incomplete within the range 100–300 K. Actual tridentate systems with NNS donor atom sets have been reported (**11**, **12**) [40]. The quartet state for Co(II) is more accessible in the $[CoN_6]^{2+}$ derivative of the 6-methyl-pyridine system **12** than in that of **11**, suggesting a steric effect from the pyridyl methyl group.

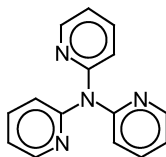


Simmons and Wilson have extended the studies of complexes of the system **3** to include the ligands where $R=C(CH_3)_3$, $CH(CH_3)_2$, $NHCH_3$, p -PhCH₃, CH_2Ph . In all instances the bis(ligand) Co(II) ion was isolated as the hexafluorophosphate [41]. The behaviour of these complexes has been studied both in the solid state and in solution. The percent high spin character follows the order for the R groups: $C(CH_3)_3 > CH(CH_3)_2 > p$ -PhCH₃ > CH_2Ph > $NHCH_3$, this being determined by a combination of both electronic and steric characteristics of the R group. Thermodynamic parameters for the spin equilibria in solution were determined. While these vary from system to system and are also somewhat solvent dependent, they fall into the range ~ 6 – 14 kJ mol⁻¹ for ΔH and ~ 15 – 42 J K⁻¹ mol⁻¹ for ΔS for the LS $\rightarrow$ HS change. In a separate study of these systems it was found that the rates for electron-transfer processes Co^{3+}/Co^{2+} , Co^{2+}/Co^+ were not dependent on the relative populations of singlet- and quartet-state species [42].

3.5

Bis(Tripyridylamine) Systems

Tripyridylamine **13** coordinates as a tridentate through the three pyridine nitrogen atoms, but differs fundamentally from terpyridine in that the three rings are not coplanar and *facial* coordination results. It provides a stronger field about Ni^{2+} than terpyridine ($Dq(\text{Ni}^{2+})$ values 1280 and 1265 cm^{-1} , respectively [43]), but Mössbauer spectral data reveal a more positive isomer shift for low spin $[\text{Fe } \mathbf{13}_2]^{2+}$, than for $[\text{Fe}(\text{trpy})_2]^{2+}$, indicative of poorer π -acceptor character [44].



13

Despite these differences, the Co(II) complex perchlorate of the unsubstituted ligand shows a virtually complete doublet $\leftrightarrow$ quartet transition ($\mu_{\text{eff}} = 2.15 \mu_{\text{B}}$ at 93 K and $4.82 \mu_{\text{B}}$ at 373 K). While the transition is gradual, it is distinctly less gradual than that in the other bis(tridentate)cobalt(II) systems discussed above, occurring mainly between 100 and 200 K. Clear differences in the vibrational spectra for the high spin and low spin species are seen. In the high spin state the infrared spectrum of the complex perchlorate resembles that of the zinc(II), copper(II) and nickel(II) complexes, whereas in the low spin state it is similar to that of the low spin iron(II) complex [45]. The average Co–N distance in $[\text{Co } \mathbf{13}_2](\text{ClO}_4)_2$, determined at 295 K where $\mu_{\text{eff}} = 4.7 \mu_{\text{B}}$, is 2.12 Å, only ~ 0.09 Å greater than the distance in the low spin form of $[\text{Co}(\text{trpy})_2]^{2+}$, suggesting the presence of a significant fraction of low spin species at 295 K, which, if present, may account for one of the Co–N distances for each ligand being considerably greater than the others [46]. In contrast to the perchlorate, the hexafluorophosphate salt is purely high spin. Introduction of a methyl-substituent into the 6-position of one of the pyridine rings also results in purely high spin behaviour, expected in the light of a probable steric effect. Methyl-substitution at the 4- or 5-position surprisingly has the same effect, despite an apparently stronger field [47].

4 Tris(Diimine) Systems

4.1 Tris(Bipyridine) Systems

Tris(bipyridine)cobalt(II) salts are normally considered to be purely high spin species, both in solution and in the solid state [48]. However, the incorporation of the complex cation into the cavities of zeolite Y causes the high spin species to undergo a transition to low spin [49]. This change was monitored by ESR measurements which showed conclusively the presence of doublet state Co(II) at 77 K. This system has been studied recently in more detail, the temperature dependence of the magnetism and electronic spectra being established and interpreted in terms of a gradual transition from completely low spin at $T < 75$ K ($\mu_{\text{eff}} = 1.9 \mu_{\text{B}}$) to a mixture of high spin and low spin species at elevated temperature ($\mu_{\text{eff}} \sim 3 \mu_{\text{B}}$ at 400 K) [50]. It is significant that the magnetism is independent of the extent of occupancy of the zeolite cage, suggesting that cooperative effects are likely to be minimal. The destabilisation of the high spin $^4T_1$ state relative to the low spin ^2E has been ascribed to a geometric change imposed on the complex by the charge distribution within the zeolite cavity. Calculations indicate that this results in a more closely octahedral environment (trigonal twist angle 55°) than the more trigonally distorted structure of the free complex (trigonal twist angle 40°). A related effect is observed when the $[\text{Co}(\text{bpy})_3]^{2+}$ cation is incorporated into the network structure adopted by systems of the kind $[\text{M}^{\text{II}}(\text{bpy})_3][\text{M}^{\text{I}}\text{M}^{\text{III}}(\text{ox})_3]$ [51]. The $[\text{Co}(\text{bpy})_3]^{2+}$ ions are located within the cavities of the network, the size of which are dependent on the nature of M^{I} and M^{III} . In $[\text{Co}(\text{bpy})_3][\text{NaCr}(\text{ox})_3]$ the cobalt is high spin $^4T_1(t_{2g}^5e_g^2)$ but in $[\text{Co}(\text{bpy})_3][\text{LiCr}(\text{ox})_3]$ the cavity is smaller and results in a chemical pressure being imposed on the system which destabilises the high spin state. This system therefore undergoes a gradual transition, μ_{eff} decreasing from $4.52 \mu_{\text{B}}$ at 300 K to $2.0 \mu_{\text{B}}$ at 10 K. The transition was also monitored by measurement of the temperature dependence of the single crystal electronic spectrum and the transition curves obtained from the two techniques are in good agreement. The thermodynamic parameters $\Delta H = 2.7 \text{ kJ mol}^{-1}$ and $\Delta S = 17 \text{ J mol}^{-1} \text{ K}^{-1}$ for the LS $\rightarrow$ HS conversion were evaluated from an analysis of the magnetic data. These compare with $\Delta H = 2.9 \text{ kJ mol}^{-1}$ and $\Delta S = 5.4 \text{ J mol}^{-1} \text{ K}^{-1}$ for the transition occurring in the zeolite cage [50].

The bond length change accompanying the transition has been estimated from structural data obtained at 10 K when the complex is in the low spin state (Co-N = 2.014 Å) and at 293 K where $\gamma_{\text{HS}} = 0.73$ (Co-N = 2.095 Å). The extrapolated value for $\gamma_{\text{HS}} = 1$ is 2.124 Å, exactly equal to the value in the corresponding Na system where there is no spin transition, and giving rise to a value of 0.11 Å for Δr , virtually the same as that estimated for the bis(trpy)

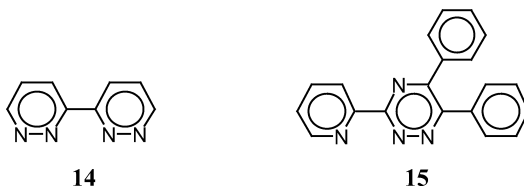
systems [21]. The trigonal twist angle in the complex cation changes from 51.2° at 10 K to 48.9° at 293 K.

From the electronic spectra an estimate of the change in ligand field strength accompanying the spin change was determined as $10Dq_{HS}=12700\text{ cm}^{-1}$ and $10Dq_{LS}=15300\text{ cm}^{-1}$ consistent with the ratio estimated from the measured changes in Co–N bond length accompanying the spin change.

4.2

Bipyridine-Related Systems

3,3'-Bipyridazine **14** provides a remarkably strong ligand field compared to that of 2,2'-bipyridine, the values for the ligand field splitting parameter Dq in the $[\text{Ni N}_6]^{2+}$ systems being 1320 and 1265 cm^{-1} , respectively [52].



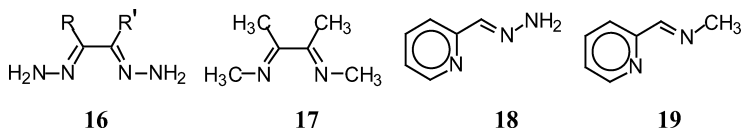
Therefore the $[\text{Co } \mathbf{14}_3]^{2+}$ ion is almost totally low spin at 89 K in the perchlorate and tetrafluoroborate salts, and the magnetic moment increases very gradually at higher temperatures reaching values of $3.06\ \mu_B$ for the tetrafluoroborate at 383 K and $2.60\ \mu_B$ for the perchlorate at 323 K, indicative of a partial, thermally-induced doublet $\leftrightarrow$ quartet transition in both salts. The transition is also observed in an aqueous solution of the perchlorate. The high field strength of **14** is believed to be due, at least in part, to its greater π -acceptor capacity and the reduced inter-ligand repulsions in its tris(ligand) complexes compared to those in the tris(bpy) systems, arising from the absence of the 6,6'-hydrogen atoms of bipyridine. It is these atoms which contribute substantially to the inter-ligand repulsions in tris(bpy) species. Consistent with this, there is a small increase in the trigonal distortion in the iron(II) and nickel(II) complexes compared to that in the corresponding complexes of bipyridine [53].

3-(Pyridin-2-yl)-5,6-diphenyl-1,2,4-triazine **15** may be regarded as a substituted bipyridine. It has a slightly stronger field than bipyridine with a $Dq(\text{Ni}^{2+})$ value of 1275 cm^{-1} and this is apparently sufficient to increase the accessibility of the doublet state in $[\text{Co } \mathbf{15}_3]^{2+}$. In $[\text{Co } \mathbf{15}_3](\text{BF}_4)_2$ μ_{eff} increases smoothly from $2.42\ \mu_B$ at 83 K to $3.77\ \mu_B$ at 383 K, and is indicative of a thermally-induced, incomplete doublet $\leftrightarrow$ quartet transition [38].

4.3

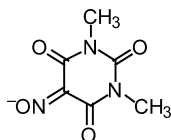
Bidentate Schiff Base Systems

Several Schiff base type diimine systems have been shown to give tris(ligand) cobalt(II) complexes which have magnetic moments with anomalous temperature dependence [19].



The field strengths of these ligands are comparable to, or slightly greater than that of bipyridine, as measured by the $\text{Dq}(\text{Ni}^{2+})$ values extracted from the electronic spectra of the $[\text{Ni N}_6]^{2+}$ species (values for 16 ($\text{R}=\text{R}'=\text{CH}_3$), 17, 18, 19 and bpy are 1280, 1266, 1272, 1267 and 1265 cm^{-1} , respectively). The effects of variations in the substituents in the hydrazone 16 were examined [54]. For $\text{R}=\text{R}'=\text{H}$ the intraligand repulsions are less than for the dimethyl system and its $\text{Dq}(\text{Ni}^{2+})$ value (1320 cm^{-1}) was the highest obtained; that for 16 $\text{R}=\text{H}$, $\text{R}'=\text{CH}_3$ (1290 cm^{-1}) also being greater than that for the dimethyl derivative. The involvement of the ^2E state in these systems was confirmed by observation of signals (g values in the range 2.07–2.14) characteristic for this state in the ESR spectra of the complex salts in the solid state and in solution [10]. From the relative intensity of the signal at different temperatures an estimate of the fraction of molecules in the ^2E state was made. This was reasonably consistent with values extracted from the magnetic data. Quantitative models based on a Boltzmann-type distribution of the spin states in these and related $[\text{CoN}_6]^{2+}$ systems have been applied [15, 16, 55]. These take into account the effects of spin-orbit coupling along with first- and second-order Zeeman effects and allow for different vibrational partition functions for the low spin and high spin states, together with a temperature dependence of the energy separation of the doublet and quartet states. The number of parameters involved in the fitting procedures applied is alarmingly high. The limitations of this approach were later highlighted by Kennedy and co-workers [56] who noted that cooperative interactions, as in iron(II) systems, are a likely important contribution to the detailed magnetic behavior. This was further demonstrated by Müller, Spiering and Gülich [57] who observed a dependence of the nature of the spin transition curve for $[\text{Co } 19_3](\text{ClO}_4)_2$ on the method of preparation and on mechanical treatment (grinding), effects rather more commonly seen in iron(II) spin cross-over systems and indicative of cooperative interactions influencing the course of a spin transition in cobalt(II) systems, even for gradual transitions, as they do in iron(II) and iron(III).

An interesting example of a tris(bidentate) mixed-ligand system shows spin crossover behaviour in cobalt(II). Dimethyl-violuric acid loses a proton and coordinates as the anion **20** to give the low spin $[\text{Co } \mathbf{20}_3]^-$ anion [58].



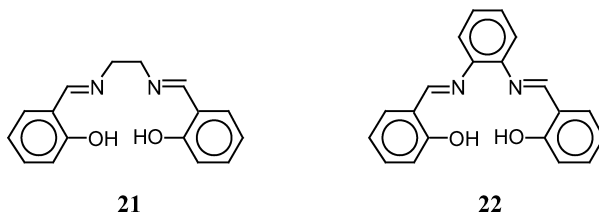
20

Progressive replacement of **20** by 1,10-phenanthroline (phen) leads to low spin $[\text{Co } \mathbf{20}_2 \text{ phen}]$, spin crossover $[\text{Co } \mathbf{20}(\text{phen})_2]^+$ and high spin $[\text{Co}(\text{phen})_3]^{2+}$. The doublet $\leftrightarrow$ quartet transition in $[\text{Co } \mathbf{20}(\text{phen})_2]\text{ClO}_4 \cdot 3\text{H}_2\text{O}$ is gradual and incomplete over the range 4–295 K [59]. ESR spectra confirm the presence of doublet state species at 295 K and below, the characteristic signal at $g=2.15$ increasing in intensity with decrease in temperature. An additional weak signal at $g=5.3$ is observed at 5 K and is assigned to a residual high spin fraction. The ΔH and ΔS values estimated for the LS $\rightarrow$ HS change are 1.7 kJ mol^{-1} and $16 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively, rather similar to those quoted above for $[\text{Co}(\text{bpy})_3]^{2+}$. In the structure of $[\text{Co } \mathbf{20}(\text{phen})_2]\text{ClO}_4 \cdot 3\text{H}_2\text{O}$ the cobalt coordination environment is axially distorted (elongated), both at 294 and 92 K, with the coordinated oxygen atom of **20** and a phenanthroline N atom in the axial positions. The average Co–N_{equatorial} and Co–X_{axial} distances are 1.977 and 2.137 Å at 294 K and 1.94 and 2.12 Å, respectively, at 92 K. These distances suggest greater fractions of low spin species at both temperatures than those indicated by the magnetic data.

5 Quadridentate Schiff Base Systems

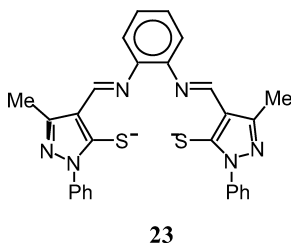
Earnshaw and co-workers [60] first reported the anomalous temperature dependence of the magnetism of certain derivatives of the cobalt(II) complexes of the anion of the Schiff Base **21** (salenH₂) and certain of its substituted derivatives. These are generally low spin and square planar but in some instances a significant temperature dependence of the magnetic moment was noted and this was interpreted in terms of a doublet $\leftrightarrow$ quartet transition. In those systems it was considered likely that the solid state structure involved interaction of neighbouring molecules through the bridging oxygen atoms, as confirmed for $[\text{Co}(\text{salen})]_2$ [61], leading to a lessening of the extreme tetragonal distortion of the square planar environment as favoured by low spin Co(II), and increasing the accessibility of the quartet state. Actual adducts believed to be five-coordinate were studied in which an axial water or pyridine molecule completed a square-pyramidal structure. These studies

were later extended by Marzilli and Marzilli [62] who found a temperature dependence of the magnetic moments of the five-coordinate Lewis base (such as imidazole, 1-methylimidazole, benzimidazole, 5,6-dimethyl-benzimidazole) adducts of the Co(II) derivatives of the anions of both Schiff bases **21** and **22** (salphH₂). This was observed for the systems in both the solution and solid states.



Kennedy and co-workers undertook a detailed study of the behaviour of heterocyclic base adducts of Co(salen) and Co(salph) [56]. They found a correlation between the base strengths of related axial ligands and the accessibility of the quartet state, and in addition noted a geometrical relationship which effectively linked the deviation of the cobalt atom out of the plane of the quadridentate towards the axial donor to the accessibility of the quartet state. They concluded that there is a delicate balance between these electronic and geometrical effects. A particularly interesting system is the benzimidazole adduct of Co(salph). This shows a rather abrupt change in magnetic moment at 110 K suggesting a structural phase transition, a discontinuous spin-state change or a combination of both. This remains one of the very few such transitions observed for cobalt(II). No thermal hysteresis was noted.

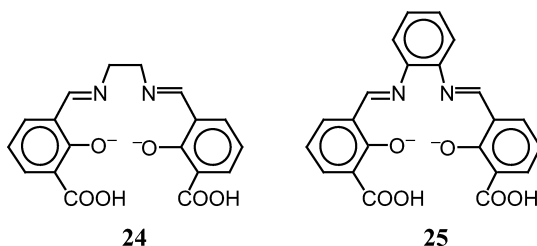
Five-coordinate *N*-methyl-imidazole adducts of the complexes with the N₂S₂ quadridentate **23**, and three related quadridentates in which the diamine involved in the Schiff base formation was 1,2-diamino-ethane, 1,3-diamino-propane and 1,2-diamino-cyclohexane have been reported [63].



All four complexes show transitions from essentially purely low spin at 77 K to high spin which are gradual and incomplete at the upper experimental temperature limit (320 K). The structure of the adduct of the complex of **23** was determined at 293 K, where it is estimated that the composition is ~60% high spin, and at 103 K where it is low spin. The structure approximates trigonal bipyramidal with the imidazole group in the equatorial plane

along with S-1 and N-2 of the sequence S-1 N-1 N-2 S-2 of donor atoms in the Schiff base, N-1 and S-2 being in the axial sites. Significant differences in the angles and distances are observed at the two temperatures. The Co–N_{imidazole} distance is actually longer at 103 K while the other Co–donor atom bond lengths are shorter than at 293 K.

An extension of the salen **21** and salph **22** systems to the carboxy-substituted anionic ligands **24** and **25** has produced the first instances of abrupt transitions in cobalt(II) with associated thermal hysteresis. In contrast to the complexes of the unsubstituted ligands, the cobalt(II) complexes of these ligands form six-coordinate in addition to five-coordinate adducts with a variety of Lewis bases. This has been attributed to the electron-withdrawing effect of the carboxylic acid substituents. These adducts have been extensively characterized by a variety of techniques, and the important features of these systems have been highlighted by Zarembowitch [64].



The bis(pyridine) adduct [Co **24**(py)₂] shows an abrupt, almost complete spin transition associated with thermal hysteresis ($T_{1/2\downarrow}=115$ K; $T_{1/2\uparrow}=127$ K). The occurrence of a phase change in this system is indicated by the appearance of distinct peak profiles for the high spin and low spin species in the x-ray powder diffraction patterns measured in the vicinity of the electronic spin transition [65]. The low spin species could be detected by ESR measurements. Replacement of the axial pyridine donors by β -picoline results in a purely high spin species, as does extension of the alkyl bridge to 1,3-propyl [66]. When water occupies the axial sites the transition is displaced to lower temperatures and becomes somewhat more abrupt with $T_{1/2\downarrow}=81.5$ K and $T_{1/2\uparrow}=84.6$ K. When the axial ligands are 4-methyl-pyridine a gradual transition is observed, and an analysis in terms of a thermal equilibrium gave $\Delta H=2.3$ kJ mol⁻¹ and $\Delta S=5.8$ J mol⁻¹ K⁻¹. With axial 4-*t*-butyl-pyridine the transition retains the abrupt nature and is centred at higher temperatures ($T_{1/2\downarrow}=138$ K; $T_{1/2\uparrow}=154$ K), correlating with the greater σ -donor power of the axial base [67]. Values of $\Delta H=1.9$, 1.4, 2.4 kJ mol⁻¹ and $\Delta S=23$, 11, 17 J mol⁻¹ K⁻¹ associated with the abrupt LS→HS transitions in the diaqua, dipyridine and di(4-*t*-bupy) adducts, respectively, have been obtained from differential scanning calorimetry measurements. It is noted that these are significantly lower than values obtained for abrupt transitions in iron(II).

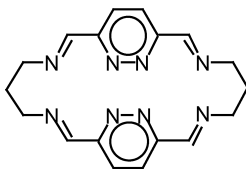
For the *trans* diaqua adduct of the complex of **25** a strong influence of hydration is evident, the complex being predominantly high spin when anhydrous but showing a complete and somewhat abrupt transition with hysteresis ($T_{1/2\downarrow}=107$ K; $T_{1/2\uparrow}=110$ K) as a monohydrate. Intermolecular hydrogen-bonding involving the lattice water is proposed to account for the difference [68].

Spin transitions in the [Co **24** L₂] (L=py, H₂O, 4-*t*-bu-py, 3-me-py) systems have been induced by application of pressure. Of these four systems only the 3-methyl-pyridine adduct does not undergo a thermal transition and, consistent with this, the pressure required to bring about the transition is considerably greater (75 kbar) than that required for the other three systems (2–8 kbar). In these experiments the transitions were monitored by near-edge x-ray absorption measurements [69].

The only system for which x-ray crystal structure data are available is [Co **25**(py)₂] in its high spin form. The structure reveals the expected pronounced axial elongation, with Co–N_{py} distances=2.262 Å and the mean Co–equatorial donor atom distance=2.079 Å [70]. Interestingly, the crystal packing reveals obvious π -stacking which may reasonably be expected to play a role in the cooperativity of the transitions in some of these systems. EXAFS studies established average changes in the Co–donor atom distances accompanying the spin change to be 0.12 Å for the pyridine adduct of the complex of **24** and 0.09 Å for the corresponding diaqua adduct [71].

Among the five-coordinate adducts of [Co **25**] is that in which the axial ligand is the photoactive *trans*-1-(4-methylphenyl)-2-(pyridyl)ethene. This shows gradual SCO [72].

The planar quadridentate system has been ingeniously adapted to incorporate bridging pyridazine units to give the binucleating molecule **26** [73].



26

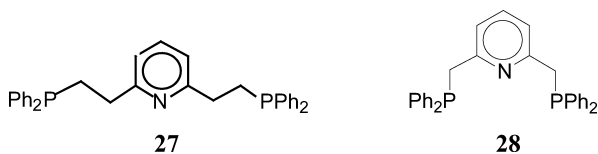
The binuclear complex with two axial thiocyanate ions on each cobalt, one N-bonded, the other S-bonded, and that with methyl cyanide molecules in axial sites undergo gradual, incomplete spin transitions together with exchange coupling. With two waters coordinated to each cobalt the complex is high spin and with chloro groups in the axial sites it is low spin. The average Co–N_{equatorial} bond length is 2.104 Å in the diaqua system in both the perchlorate (as a water/methylcyanide solvate) (high spin at 158 K) and the dithionate octahydrate (high spin at 163 K), the average Co–O_{axial} distances being 2.074 and 2.069 Å, respectively for the two salts. In the low spin aceto-

nitrile system (at 170 K) and the thiocyanato system (at 163 K) the average Co–N_{equatorial} distance is 1.983 and 1.951 Å, respectively, the average Co–N_{axial} distance in the acetonitrile system being 2.131 Å.

6

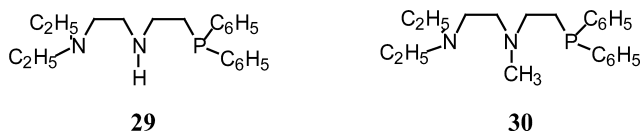
Five-Coordinate [Co(Tridentate)X₂] Systems

Five-coordinate complexes of cobalt(II) can be either high spin or low spin and, in addition, as seen above for adducts of planar, quadridentate Schiff base complexes, may exhibit transitions between the two states. Much of the early work in this area involved coordination of tridentate systems with the two remaining sites being occupied by halide or pseudohalide ions, and has been reviewed by Sacconi and co-workers [14, 74].



2,6-(Diphenylphosphinoethyl)pyridine **27** and 2,6-(diphenylphosphino-methyl) pyridine **28** give [Co LX₂] complexes which span the range of spin-state properties. For X=Cl the complexes are purely high spin, for X=Br spin transitions are observed and for X=I the complexes are low spin, but with the onset of a transition at T>250 K for L=**27**. For **28** the complex with X=NCS was also found to show a spin transition [75, 76]. Sacconi has drawn attention to the strong influence of the nephelauxetic effect of the donor atoms, greatest for the iodide ion, in determining the spin state of systems such as these [77]. The complexes of **27** are believed to be distorted trigonal bipyramidal. In contrast, those of **28**, in which steric effects require coordination as an essentially planar moiety, are believed to be distorted square pyramidal, the three donor atoms of **28** occupying sites in the basal plane.

Sacconi and co-workers have studied the properties of complexes of **29** and **30**, which are related to the systems above. Interest centres on the thiocyanato complexes. [Co **29**(NCS)₂] shows a gradual transition from essentially low spin at 79 K ($\mu_{\text{eff}}=2.16 \mu_{\text{B}}$) to almost completely high spin at 418 °K ($\mu_{\text{eff}}=4.32 \mu_{\text{B}}$).



The complex of **30** remains high spin at low temperature [78]. The HS→LS change in the complex of **29** can also be induced by an increase in

pressure [79]. The structure of both complexes has been determined at 298 K [80] and that of **29** at 120 K as well [81]. The structures of the complex of **29** are described as intermediate between square pyramidal and trigonal bipyramidal, with an increase in distortion to an elongated square pyramid at low temperature. The principal geometrical changes accompanying the increasing population of the doublet state are an increase in the $N_{\text{terminal}}\text{--Co--P}$ angle of 10° and contractions in the Co–P and Co– N_{central} distances of 0.08 and 0.11 Å, respectively. The involvement of a doublet state in the transition was confirmed by ESR data. $[\text{Co } \mathbf{30}(\text{NCS})_2]$ is essentially trigonal bipyramidal.

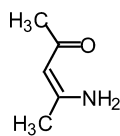
7

Configurational Equilibria

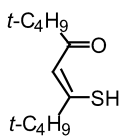
7.1

Planar ↔ Tetrahedral Equilibria

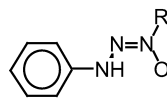
Planar-tetrahedral equilibria in Co(II) systems were first reported for uncharged complexes of β -ketoamine systems such as **31** and various further substituted derivatives. These involve a change from a doublet (planar) to a quartet (tetrahedral) ground state.



31



32



33

For the planar → tetrahedral conversion in the complex of **31** $\Delta H = 3 \text{ kJ mol}^{-1}$ and $\Delta S = 19 \text{ J K}^{-1} \text{ mol}^{-1}$, values not too dissimilar from those associated with the doublet → quartet change in six-coordinate complexes [82]. A similar equilibrium has been observed in the Co(II) derivative of the anion of monothio-dipivaloylmethane **32**; for this CoO_2S_2 system $\Delta H = 20 \text{ kJ mol}^{-1}$ and $\Delta S = 63 \text{ J K}^{-1} \text{ mol}^{-1}$ [83].

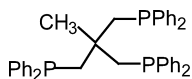
Such planar ↔ tetrahedral equilibria have been characterized more recently for a series of uncharged Co(II) complexes of the anion of the triazene-1-oxide **33** containing various substituents in the phenyl ring. Remarkably, in two instances both the planar and the tetrahedral forms have been isolated in the solid state, the actual form isolated being dependent on the reaction solvent and temperature. ΔH and ΔS values are in the range $1\text{--}15 \text{ kJ mol}^{-1}$ and $5\text{--}30 \text{ J K}^{-1} \text{ mol}^{-1}$ [84].

7.2

Four-Coordinate $\leftrightarrow$ Five-Coordinate Equilibria

For the first cobalt(II) system shown to exhibit a doublet $\leftrightarrow$ quartet spin change in solution, dithiocyanato-bis(triethylphosphine)cobalt(II), a configurational equilibrium is involved. This complex is tetrahedral with a magnetic moment of $4.45 \mu_B$ in the solid state but has strongly temperature-dependent magnetic moment, infrared and electronic spectra in solution. This has been interpreted as a (low spin) five-coordinate $\leftrightarrow$ (high spin) tetrahedral equilibrium. The five-coordinate species is believed to involve a dimeric structure involving two bridging and two terminal thiocyanato groups on each cobalt atom [85].

The tridentate 1,1,1-tris(diphenylphosphino-methyl)ethane **34** forms the monomeric and low spin complex $[\text{Co } \mathbf{34} \text{ Cl}_2]$ which is distorted trigonal bipyramidal with a phosphorus and a chloride ion occupying axial sites [86]. In solution this is in equilibrium with a tetrahedral high spin species.



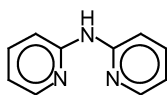
34

In the formation of the tetrahedral species, one of the Co–P bonds has broken. The configurational/spin change has been monitored by measurement of the temperature dependence of both the electronic spectrum and the magnetism. For the doublet (five-coordinate) $\rightarrow$ quartet (four-coordinate) change $\Delta H = 21 \pm 3 \text{ kJ mol}^{-1}$ and $\Delta S = 85 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$ (as determined from the magnetic measurements – similar values were obtained from the spectroscopic data). These results were obtained for a solution in tetrahydrofuran; the equilibrium is found to be solvent-dependent. The entropy change is significantly greater than values reported for other doublet $\rightarrow$ quartet changes and this is ascribed to the additional gain of rotational and vibrational degrees of freedom of the “dangling” arm of the ligand in the tetrahedral complex.

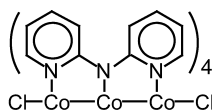
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Trinuclear Systems

In its deprotonated form (dpa) dipyridylamine **35** reacts with cobalt(II) chloride to give a linear metal-metal bridged tricobalt unit $\text{Co}_3(\text{dpa})_4\text{Cl}_2$. Each of the terminal Co atoms has a chloro and four pyridyl groups coordinated while the four amido nitrogens coordinate equatorially to the central cobalt (represented by **36**).



35



36

These remarkable systems have been studied in considerable detail and their behaviour has again brought into question the validity of the proposed distinction between spin isomers and bond-stretch isomers [87]. The solvates $\text{Co}_3(\text{dpa})_4\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ and $\text{Co}_3(\text{dpa})_4\text{Cl}_2 \cdot 2\text{CH}_2\text{Cl}_2$ both have an $S=1/2$ ground state at low temperature. In the former, the two Co–Co distances are the same (2.3369(4) Å at 296 K) while in the latter they are different, the short and long separations being 2.299(1) and 2.4719(1) Å, respectively, at 298 K [88]. These relationships hold down to 20 K, though the actual values become smaller. The magnetic moment of $\text{Co}_3(\text{dpa})_4\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ remains $2.07 \mu_B$ over the range 8–160 K and then steadily increases to $3.8 \mu_B$ at 350 K, without having reached a maximum value. This has been interpreted in terms of an incomplete spin transition. For $\text{Co}_3(\text{dpa})_4\text{Cl}_2 \cdot 2\text{CH}_2\text{Cl}_2$, the magnetic moment levels off at ~ 250 K to $4.86 \mu_B$ and an analysis of the magnetism for a single crystal establishes in this instance that a virtually complete transition to a quartet state has occurred. It is concluded that this molecule containing the unsymmetrical Co_3 sequence is composed of a diamagnetic pair of Co(II) atoms joined by a single metal–metal bond and an “isolated” paramagnetic five-coordinate Co(II) centre. The observed spin crossover behaviour in this instance is localized on the five-coordinate cobalt atom.

A further extensive series of solvates for this system has been described [89] and for all of these a doublet ground state at low temperature with a gradually increasing population of a quartet state above ~ 100 K has been found.

The neutral complex can be oxidized with NOBF_4 to give a +1 cation isolated as $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]\text{BF}_4 \cdot 2\text{CH}_2\text{Cl}_2$. This is again trinuclear but has an $S=0$ ground state up to ~ 50 K. Beyond this temperature a significant, gradual increase in the magnetic moment occurs, reaching $3.45 \mu_B$ at the upper experimental limit, 350 K [90]. Uniquely for a cobalt system, the plot of the temperature dependence of the magnetism reveals a two-step transition. This has been ascribed to involvement of a state of intermediate spin ($S=1$) in the ultimate conversion to an $S=2$ state. There is no plateau observed in the spin transition curve and the two transitions therefore overlap to a considerable extent. Significantly, the two-step nature is revealed by the temperature dependence of the magnetism for the sample both in the solid state and in solution, and so cannot be ascribed to lattice effects. A straightforward analysis of the system in terms of two equilibria revealed $T_{1/2}=201$ K for the singlet $\rightarrow$ triplet transition and 281 K for the triplet $\rightarrow$ quintet transition for the species in solution (315 and 330 K, respectively, in the solid). Although two-step transitions are well characterized for iron(II) systems in the solid state, they have not been observed for solutions, and the application of Mössbauer

spectroscopy in particular generally confirms for solid systems the involvement of singlet and quintet states only in both steps.

While they are strictly beyond the scope of this survey, it is appropriate in the context of multinuclear systems to draw attention to a family of trinuclear, triangular cobalt cyclopentadienide derivatives which display singlet $\leftrightarrow$ triplet transitions in both the solid state and in solution [91].

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Conclusions

While the spin crossover phenomenon in cobalt(II) is less prevalent than in iron(II), it nevertheless is manifested in a diverse range of systems. Most of the features apparent in iron(II) systems are found in cobalt(II) as well, but perhaps the most striking feature of iron(II) systems, the relatively frequent appearance of hysteresis associated with thermal transitions, is found to only a minor degree in cobalt(II). In addition, the LIESST effect, observable for a wide variety of iron(II) systems, has not been reported for cobalt(II). Both of these observations can probably be traced principally to the smaller change in the metal–donor atom distance associated with the spin change in cobalt(II), this arising from the smaller change in total spin; $\Delta S=1$ for Co(II), $\Delta S=2$ for six-coordinate Fe(II). The other important distinction lies in the Jahn-Teller effect operative in low spin Co(II). This has a strong influence on the nature of the ligand systems able to support spin crossover.

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References

1. Figgins PE, Busch DH (1960) *J Am Chem Soc* 82:820
2. Griffith JS (1956) *J Inorg Nucl Chem* 2:229
3. Figgins PE, Busch DH (1961) *J Phys Chem* 65:2236
4. Stoufer RC, Busch DH, Hadley WB (1961) *J Am Chem Soc* 83:3732
5. Hogg R, Wilkins RG (1962) *J Chem Soc* 341
6. Beattie JK, Sutin N, Turner DH, Flynn GW (1973) *J Am Chem Soc* 95:2052
7. Beattie JK (1988) *Adv Inorg Chem* 32:1
8. Dose EV, Hoselton MA, Sutin N, Tweedle MF, Wilson LJ (1978) *J Am Chem Soc* 100:1141
9. a. Gülich P, Garcia Y, Woike T (2001) *Coord Chem Revs* 219–221:839; b. Maeda Y, Ohshio H, Takashima Y (1982) *Bull Chem Soc Jpn* 55:3500
10. Schmidt JG, Brey WS, Stoufer RC (1967) *Inorg Chem* 6:268
11. Kremer S, Henke W, Reinen D (1982) *Inorg Chem* 21:3013

12. Figgis BN, Nyholm RS (1959) *J Chem Soc* 338
13. König E, Kremer S (1974) *Ber Bunsen Phys Chem* 78:786
14. a. Morassi R, Bertini I, Sacconi L (1973) *Coord Chem Revs* 11:343; b. Sacconi L (1971) *Pure App Chem* 27:161
15. Harris CM, Lockyer TN, Martin RL, Patil HRH, Sinn E, Stewart IM (1969) *Aust J Chem* 22:2105
16. Judge JS, Baker WA, *Inorg Chim Acta* (1967) 1:68
17. Maslen EN, Raston CL, White AH (1974) *J Chem Soc* 1803
18. Figgis BN, Kucharski ES, White AH (1983) *Aust J Chem* 36:1527
19. Stoufer RC, Smith DW, Clevenger EA, Norris TE (1966) *Inorg Chem* 5:1167
20. Oshio H, Spiering H, Ksenofontov V, Renz F, Gülich P (2001) *Inorg Chem* 40:1143
21. Figgis BN, Kucharski ES, White AH (1983) *Aust J Chem* 36:1537
22. Raston CL, White AH (1976) *J Chem Soc Dalton Trans* 7
23. Henke W, Kremer S (1982) *Inorg Chim Acta* 65:L115
24. Figgis BN, Kucharski ES, White AH (1983) *Aust J Chem* 36:1563
25. Baker AT, Goodwin HA (1985) *Aust J Chem* 38:207
26. Craig DC, Scudder ML, McHale W-A, Goodwin HA (1998) *Aust J Chem* 51:1131
27. Constable EC, Housecroft CE, Kulke T, Lazzarini C, Schofieldm ER, Zimmermann Y (2001) *J Chem Soc Dalton Trans* 2864
28. Hathcock DJ, Stone K, Madden J, Slaterry SJ (1998) *Inorg Chim Acta* 282:131
29. Schmiedekamp AM, Ryan MD, Deeth RJ (2002) *Inorg Chem* 41:
30. Constable EC, Cargill Thompson AMW, Tocher DA, Daniels MAM (1992) *New J Chem* 16:855
31. Gaspar AB, Munoz MC, Niel V, Real JA (2001) *Inorg Chem* 40:9
32. Schubert US, Eschbaumer C (2002) *Angew Chem Int Ed* 41:2892; Constable EC, Housecroft CE, Cattalini, M, Phillips D (1998) *New J Chem* 193
33. a. Storrier GD, Colbran SB, Craig DC (1997) *J Chem Soc Dalton Trans* 3011; b. Storrier GD, Colbran SB, Craig DC (1998) *J Chem Soc Dalton Trans* 1351
34. Maestri M, Armaroli N, Balzani V, Constable EC, Cargill Thompson AMW (1995) *Inorg Chem* 34:2759
35. Constable EC, Kulke T, Neuburger M, Zehnder M (1997) *New J Chem* 21:1091
36. Childs BJ, Craig DC, Scudder ML, Goodwin HA (1998) *Inorg Chim Acta* 274:32
37. Goodwin HA, Sylva RN, Vagg RS, Watton EC (1969) *Aust J Chem* 22:1605
38. Goodwin HA, Smith FE (1973) *Inorg Chim Acta* 7:541
39. Krumholz P (1965) *Inorg Chem* 4:612
40. Chia PSK, Livingstone SE (1969) *Aust J Chem* 22:1825
41. Simmons MG, Wilson LJ (1977) *Inorg Chem* 16:126
42. Zhu T, Su CH, Lemke BK, Wilson LJ, Kadish KM (1983) *Inorg Chem* 22:2527
43. McWhinnie WR, Kulasingam GC (1966) *J Chem Soc A* 1199
44. Berrett RR, Fitzsimmons BW, Owusu AA (1968) *J Chem Soc A* 1575
45. Barnard PFB, Chamberlain AT, Kulasingam GC, McWhinnie WR, Dosser RJ (1970) *Chem Commun* 520
46. Kucharski ES, McWhinnie WR, White AH (1978) *Aust J Chem* 31:2647
47. Barnard PFB, Lancaster JC, Fernandopulle ME, McWhinnie WR (1973) *J Chem Soc Dalton Trans* 2172
48. Figgis BN, Gerloch M, Lewis J, Mabbs FE, Webb GA (1968) *J Chem Soc A* 2086
49. Mizuno K, Lunsford JH (1983) *Inorg Chem* 22:3484
50. Tiwary SK Vasudevan S (1998) *Inorg Chem* 37:5239
51. Sieber R, Decurtins S, Stoeckli-Evans H, Wilson C, Yufit D, Howard JAK, Capelli SC, Hauser A (2000) *Chem Eur J* 6:361

52. Onggo D, Rae AD, Goodwin HA (1990) *Inorg Chim Acta* 178:151
53. Goodwin HA, Kepert DL, Patrick JM, Skelton BW, White AH (1984) *Aust J Chem* 37:1817
54. Fisher HM, Stoufer RC (1966) *Inorg Chem* 5:1172
55. Williams DL, Smith DW, Stoufer RC (1967) *Inorg Chem* 6:590
56. Kennedy BJ, Fallon GD, Gatehouse BMKC, Murray KS (1984) *Inorg Chem* 23:580
57. Müller EW, Spiering H, Gülich P (1984) *Inorg Chem* 23:119
58. Garcia-Espana E, Ballester M-J, Lloret F, Moratal JM, Faus J, Bianchi A (1988) *J Chem Soc Dalton Trans* 101
59. Faus J, Julve M, lloret F, Real JA, Sletten J (1994) *Inorg Chem* 33:5535
60. Earnshaw A, Hewlett PC, King EA, Larkworthy LF (1968) *J Chem Soc A* 241
61. DeIasi R, Holt SL, Post B (1971) *Inorg Chem* 10:1498
62. Marzilli LG, Marzilli PA (1972) *Inorg Chem* 11:457
63. Nivorozhkin AL, Toftlund H, Nielsen M (1994) *J Chem Soc Dalton Trans* 361
64. Zarembowitch J (1992) *New J Chem* 16:255
65. König E, Ritter G, Dengler J, Thuéry P, Zarembowitch J (1989) *Inorg Chem* 28:1757
66. Zarembowitch J, Kahn O (1984) *Inorg Chem* 23:589
67. Thuéry P, Zarembowitch J (1986) *Inorg Chem* 25:2001
68. Claude R, Zarembowitch J, Philoche-Levisalles M, d'Yvoire F (1991) *New J Chem* 15:635
69. Roux C, Zarembowitch J, Itie JP, Verdaguer M, Dartyge E, Fontaine A, Tolentino H (1991) *Inorg Chem* 30:3174
70. Charpin P, Nierlich M, Vigner D, Lance M, Thuéry P, Zarembowitch J, d'Yvoire F (1988) *J Cryst Spectros* 18:5
71. Thuéry P, Zarembowitch J, Michalowicz A, Kahn O (1987) *Inorg Chem* 26:851
72. Tuna F, Patron L, Rivière E, Boillot M-L (2000) *Polyhedron* 19:1643
73. Brooker S, Duncan J de G, Kelly RJ, Plieger PG, Moubaraki B, Murray KS, Jameson GB (2002) *J Chem Soc Dalton Trans* 2080
74. Sacconi L (1972) *Coord Chem Revs* 8:351
75. Kelly WSJ, Ford GH, Nelson SM (1971) *J Chem Soc A* 388
76. Dahlhoff WV, Nelson SM (1971) *J Chem Soc A* 2184
77. Sacconi L (1970) *J Chem Soc A* 248
78. Morassi R, Mani F, Sacconi L (1973) *Inorg Chem* 12:1246
79. Sacconi L, Ferraro JR (1974) *Inorg Chim Acta* 9:49
80. Orlandini AB, Calabresi C, Ghilardi CA, Orioli PL, Sacconi L (1973) *J Chem Soc Dalton Trans* 1383
81. Gatteschi D, Ghilardi CA, Orlandini A, Sacconi L (1978) *Inorg Chem* 17:3023
82. Everett GW, Holm RH (1968) *Inorg Chem* 7:776
83. Gerlach DH, Holm RH (1969) *Inorg Chem* 8:2292
84. Wolny JA, Rudolf MF, Ciunik Z, Gatner K, and Wolowicz S (1993) *J Chem Soc Dalton Trans* 1611
85. Nicolini M, Pecile C, Turco A (1965) *J Am Chem Soc* 87:2379
86. Heinze K, Huttner G, Zsolnai L, Schober P (1997) *Inorg Chem* 36:5457
87. Rohmer MM, Strich A, Bénard M, Malrieu J-P (2001) *J Am Chem Soc* 123:9126
88. Clérac R, Cotton FA, Daniels LM, Dunbar KR, Kirschbaum K, Murillo CA, Pinkerton AA, Schultz AJ, Wang X (2000) *J Am Chem Soc* 122:6226
89. Clérac R, Cotton FA, Daniels LM, Dunbar KR, Murillo CA, Wang X (2001) *Inorg Chem* 40:1256
90. Clérac R, Cotton FA, Dunbar KA, Lu T, Murillo CA, Wang X (2000) *J Am Chem Soc* 122:2272
91. Wakatsuki Y, Okada T, Yamazaki H, Cheng G (1988) *Inorg Chem* 27:2958

Thermal Spin Crossover in Mn(II), Mn(III), Cr(II) and Co(III) Coordination Compounds

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Abstract This chapter considers thermal spin crossover occurring in transition metal compounds other than those of Fe(II), Fe(III) and Co(II). Unusual magnetic properties of several coordination and organometallic complexes of Mn(II), Mn(III), Cr(II) and Co(III) are discussed in the light of their structural features.

Keywords Spin crossover · Manganese · Chromium(II) · Cobalt(III) · Metallocenes

List of Abbreviations

SCO	Spin crossover
ST	Spin transition
HS	High spin
LS	Low spin
dmpe	1,2-Bis(dimethylphosphino)ethane
depe	1,2-Bis(diethylphosphino)ethane
tmtaa	Dibenzotetramethyltetraaza[14]annulene

1 Introduction

The fact that most of the reported spin crossover (SCO) complexes are coordination compounds of Fe(II) and Fe(III), to a lesser extent of Co(II) and only in a few cases of Cr(II) and Mn(III), may be explained on the grounds

Table 1 HS and LS state configurations for 3dⁿ coordination compounds in O_h symmetry

	Ion	HS	LS
d ⁴	Cr(II) Mn(III)	⁵ E _g , S=2	³ T _{1g} , S=1
d ⁵	Mn(II) Fe(III)	⁶ A _{1g} , S=5/2	² T _{2g} , S=1/2
d ⁶	Fe(II) Co(III)	⁵ T _{2g} , S=2	¹ A _{1g} , S=0
d ⁷	Co(II)	⁴ T _{1g} , S=3/2	² E _g , S=1/2

of basic concepts of ligand field theory [1, 2]. It is well known that for octahedral symmetry (O_h), there are two ways of accommodating the valence d electrons over the t_{2g} and e_g orbitals in compounds with 4, 5, 6 and 7d-electrons (Table 1).

If the symmetry is lower than O_h, e.g. in tetragonally distorted octahedral compounds with D_{4h} symmetry, there is further splitting of the t_{2g} and e_g orbitals [1, 2], and high-spin (HS) and low-spin (LS) configurations also become possible in d⁸ systems [3].

The question why some transition metal ions have a stronger tendency to form LS complexes than others may be discussed qualitatively after Griffith and Orgel [4]. Three kinds of energy terms have to be considered: the ligand field splitting energy $\Delta=10\text{ Dq}$ (for O_h symmetry), the Coulomb repulsion energy π_c required for pairwise occupation of d orbitals, and the quantum mechanical exchange energy π_e which stabilises the system due to pair formation with parallel electron spins. If π_c is the increase in Coulomb repulsion energy for d⁴ and d⁷ complexes, and $2\pi_c$ for d⁵ and d⁶ complexes, the *mean spin pairing* energy per unit of 10 Dq is then $\pi=\pi_c+\pi_e$. The complex adopts HS behaviour if $10\text{ Dq}<\pi$, and LS behaviour if $10\text{ Dq}>\pi$. The contribution of π_e plays a dominant role in the energy balance (more important than π_c) and can be evaluated by determining the change of the number of pairs of parallel spins per unit of 10 Dq between HS and LS state. This number is 3 for d⁴ and d⁵ complexes, and 2 for d⁶ and d⁷ complexes [1]. This means the loss of stabilizing exchange energy on going from HS to LS electron configuration is higher for d⁴ and d⁵ than for d⁶ and d⁷ complexes. Complexes of d⁶ ions in particular show the tendency to adopt the LS state at relatively weaker ligand fields than d⁴ and d⁵ complexes. This finds confirmation by the following selection of complexes: with the exception of [CoF₆]³⁻, which is HS, all other Co(III) complexes like [Co(H₂O)₆]³⁺, [Co(NH₃)₆]³⁺ (d⁶), are LS, while [Mn(H₂O)₆]²⁺, [Mn(NH₃)₆]²⁺, [Fe(H₂O)₆]³⁺, [Fe(NH₃)₆]³⁺ (d⁵) and [Cr(H₂O)₆]²⁺, [Cr(NH₃)₆]²⁺ (d⁴) are of the HS type.

The question why it is much easier to penetrate the region where thermally-induced spin transition (ST) may occur (see Chap. 2 by Hauser in this

Table 2 Crystal field splitting, Δ , and mean spin pairing energy, π , for $[M(H_2O)_6]^{n+}$ complexes

	Ion	π^a/cm^{-1}	Δ/cm^{-1}
d^4	Cr(II)	23,500	13,900
	Mn(III)	28,000	21,000
d^5	Mn(II)	25,500	7,800
	Fe(III)	30,000	13,700
d^6	Fe(II)	17,600	10,400
d^7	Co(II)	22,500	9,300

^a These data refer to the free ions

series) may also be discussed on the basis of the hexaqua complexes $[M(H_2O)_6]^{n+}$ with special emphasis of the relevant π and 10 Dq values [5] (Table 2).

Due to the so-called nephelauxetic effect [1], the values for π are reduced by 20% or more in coordination compounds depending on the nature of the ligands. It can be seen that with Fe(II) compounds it is the easiest to reach the critical field strength, by choosing the proper ligands, where SCO occurs. With Cr(II) compounds, on the other hand, it is very difficult to prepare a SCO compound, due principally to the high instability towards oxidation. For the second and third transition series (4d, 5d) SCO is extremely rare, and this arises primarily from the much stronger ligand fields induced by the ions of these series.

In this chapter we shall review examples of SCO compounds with Mn(III) (d^4), Cr(II) (d^4), Mn(II) (d^5) and Co(III) (d^6).

2 Manganese Compounds

$[Mn(CN)_6]^{3-}$ and $MnH_3(dmpe)_2$ with $dmpe=1,2\text{-bis(dimethylphosphino)ethane}$ are LS ($^3T_{1g}$, $S=1$) Mn(III) complexes [6, 7]. All other Mn(III) complexes are known to be HS (^5E_g , $S=2$) [5, 8]. The first SCO d^4 system was identified in 1981 [9]. $[Mn(\text{pyrol})_3\text{tren}]$ represents a mononuclear chelate type Mn(III) complex where $(\text{pyrol})_3\text{tren}$ is the trianionic Schiff base resulting from the condensation of pyrrole-2-carboxaldehyde with tris(2-aminoethyl)amine triaminotriethylamine (tren). In this compound, which crystallises in the cubic space group $I_{\bar{4}3d}$, the manganese ion lies on a threefold axis and is octahedrally surrounded by six nitrogen atoms. The structure determined at room temperature shows that these coordinating atoms come from three pyrrole groups at 2.05 Å and three amino groups at 2.14 Å (Fig. 1). The coordination is distorted about the C_3 axis from octahedral toward trigonal-prismatic symmetry [9].

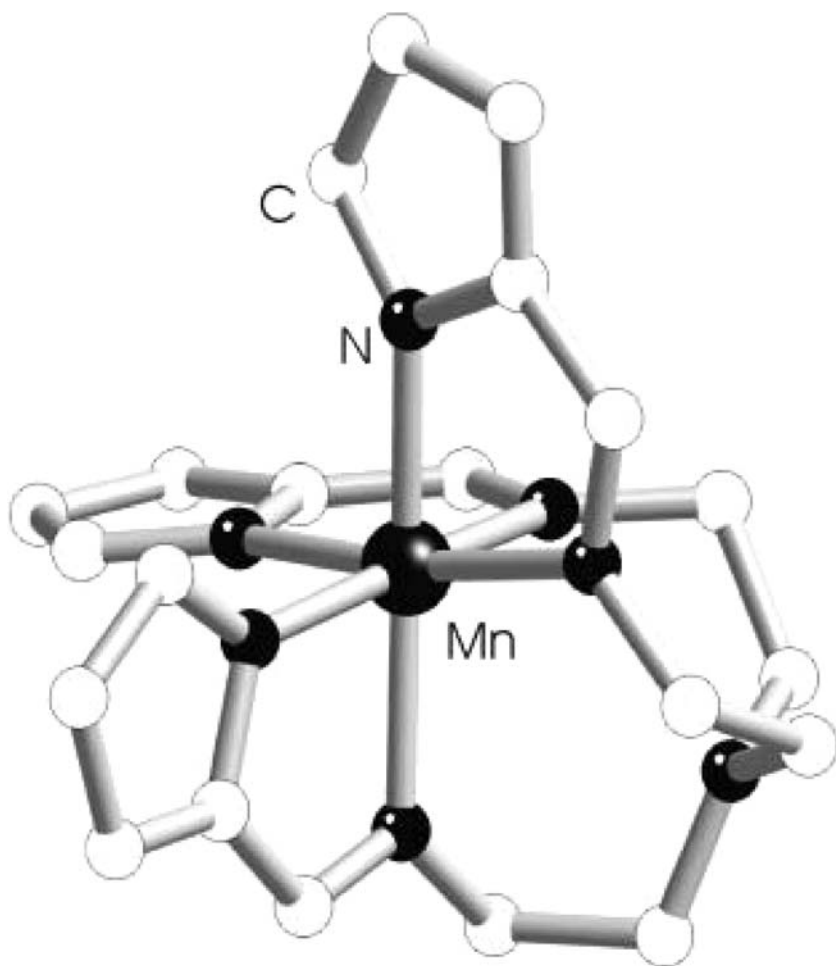


Fig. 1 View of the mononuclear unit of $[\text{Mn}(\text{pyrol})_3(\text{tren})]$ at 293 K. *Black and white small spheres correspond to nitrogen and carbon atoms, respectively. The larger black sphere corresponds to the Mn(III) ion*

The magnetic properties have been investigated down to 5 K [9] (Fig. 2). On lowering the temperature, $\chi_{\text{M}}T$ remains constant down to ~ 45 K at $2.7 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ which is characteristic of a d^4 HS state. At 43.7 K, a sudden drop of the $\chi_{\text{M}}T$ product is observed which is followed below 41 K by a smooth decrease which is due to the temperature dependent population of the $^3T_1$ ground state levels arising from spin orbit coupling after distortion from O_h symmetry [9]. Thus, this coordination compound reveals a very abrupt ST from $S=2$ to $S=1$ around 44 K. This transition temperature actually represents one of the lowest ever observed.

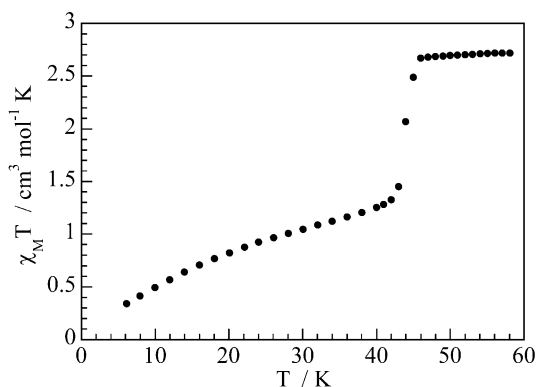


Fig. 2 $\chi_M T$ vs T plot for $[\text{Mn}(\text{pyrol})_3(\text{tren})]$ [9]

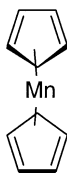
This transition has been analysed by DSC down to 3 K confirming a first order phase transition at ~ 44 K with $\Delta S = 13.8 \text{ J K}^{-1} \text{ mol}^{-1}$ [10]. Recent Raman experiments show that most of the active vibrational modes are nearly independent of the spin states suggesting that this complex does not undergo classical SCO behaviour in which the vibrational entropy is dominant [11]. The experimental entropy value is actually well accounted for by the contribution of spin multiplicity $\Delta S = R \ln(5/3)$, and of Jahn-Teller configurations of the ^5E_g HS species, $\Delta S_{JT} = R \ln 3$, giving a total value of $13.4 \text{ J K}^{-1} \text{ mol}^{-1}$ [12]. This compound has also been subject to magnetic measurements under an external field up to ~ 23 T. A slight decrease of the transition temperature (~ 1.5 K) was observed and could be modelled within the framework of a revised mean-field model [10]. This result is in agreement with an earlier investigation of the magnetic field effect on the SCO behaviour of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ [13] and a later study on the same SCO compound under pulsed high magnetic field [14]. Two other Mn(III) SCO coordination compounds are known, one including a porphyrin unit [15], another one a salen-type Schiff base [16]. They both exhibit gradual SCO behaviour below room temperature in the solid state.

The discovery of photo-induced electron transfer leading to a sizeable magnetisation in Prussian blue analogues [17] provided a remarkable impetus to the field of photomagnetism [18]. $\text{Rb}^{\text{I}}\text{Mn}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ belongs to this family and shows at low temperature a spontaneous magnetisation with an ordering temperature of 12 K, revealing ferromagnetic interactions ($J = +1.1 \text{ cm}^{-1}$). Interestingly, at much higher temperatures, a wide and symmetric hysteresis loop of ~ 73 K width, was observed with $T_{1/2\downarrow} = 231$ K and $T_{1/2\uparrow} = 304$ K [19a].

This phenomenon was originally interpreted as a result of Mn(II) (d^5) SCO behaviour between a HS state ($S = 5/2$) and an intermediate spin state ($S = 3/2$) driven by a cooperative Jahn-Teller distortion in the LS $\text{Fe}(\text{III})\text{C}_6$

moiety of this ferricyanide complex [19a]. Very recent experiments using XAS and XRD with synchrotron radiation, however, have revealed that this interpretation is not correct. Instead, it has been suggested [19b] that a temperature dependent electron transfer takes place converting the high temperature phase containing $\text{Mn}^{\text{II}}(\text{S}=5/2)\text{-NC-Fe}^{\text{III}}(\text{S}=1/2)$ to the low temperature phase containing $\text{Mn}^{\text{III}}(\text{S}=2)\text{-NC-Fe}^{\text{II}}(\text{S}=0)$.

Spin state equilibrium has been reported in solution for the mangano-cene derivatives $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Mn}$ with $\text{R}=\text{H, Me, Et}$ [20–24] and followed by NMR spectroscopy. Temperature dependent ^1H NMR experiments of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}$ carried out in toluene revealed an anomalous temperature dependence of the magnetic susceptibility between ~ 183 and 314 K.



This behaviour was interpreted in terms of a thermal equilibrium between the LS $^2\text{E}_{2g}$ ground state and the HS $^6\text{A}_{1g}$ state [24]. At higher temperatures, a second spin exchange process was suggested by the authors to be due to the rapid equilibrium between mainly $^6\text{A}_{1g}$ and $^2\text{A}_{1g}$ spin states of the compound [24]. Better resolved ^2H NMR spectra were obtained for $(\eta^5\text{-C}_5\text{D}_4\text{R})_2\text{Mn}$. The thermodynamic parameters of the spin state equilibrium were determined ($\Delta\text{H}=12.8$ kJ mol $^{-1}$ and $\Delta\text{S}=84$ J mol $^{-1}$ K $^{-1}$) and only the $^2\text{E}_{2g}$ (LS) and $^6\text{A}_{1g}$ (HS) states were identified [25]. The molecular structures of $(\text{MeCp})_2\text{Mn}$ in the HS and LS states have been determined in the gas phase by electron diffraction, the Mn-C(Cp) bond distances being $2.42(1)$ Å (HS) and $2.14(2)$ Å (LS) [26]. These bond distances were obtained by least-squares refinement on the intensity data [27] for a series of various dihedral angles between the MeCp rings.

An unusual $\text{S}=2 \leftrightarrow \text{S}=0$ spin state equilibrium was found for a nitrosyl Mn complex, $[(\text{tmtaa})\text{Mn}\{\text{NO}\}]\cdot\text{THF}$ with $\text{H}_2\text{tmtaa}=\text{dibenzotetramethyltetraaza}$ [14]annulene [28]. Its crystal structure is depicted in Fig. 3. In this compound, the Mn ion is in a slightly distorted square pyramidal environment, the metal being displaced by $0.448(2)$ Å from the N_4 basal plane formed by the macrocyclic tmtaa ligand having its usual saddle shape conformation [29]. The nitrosyl group, which is quasi linear with $\text{Mn-N-O}=174.9(6)^\circ$, coordinates from the apical position giving a MnN_5 core.

The magnetic properties of $[(\text{tmtaa})\text{Mn}\{\text{NO}\}]\cdot\text{THF}$ have been recorded in the solid state. A gradual decrease of the magnetic moment was observed from 300 to 100 K, before reaching a plateau ($\sim 100\text{--}4$ K). The electronic configuration of the Mn ion is still debated [28], but this behaviour identifies a $\text{S}=2 \leftrightarrow \text{S}=0$ SCO system. The ST is incomplete at both the high and low temperature limits [28], occurs without any hysteresis effect, and is character-

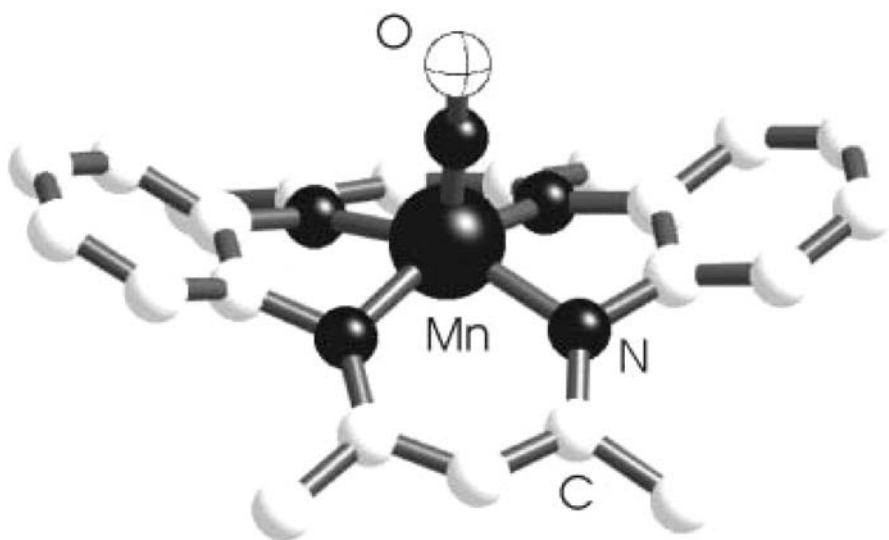


Fig. 3 View of the mononuclear unit of $[(\text{tmtaa})\text{Mn}\{\text{NO}\}]$ at 143 K. Black, white and equatorial small spheres correspond to nitrogen, carbon and oxygen atoms, respectively. The larger black sphere corresponds to the Mn(II) ion

ised by a $T_{1/2}$ of 213 K. The enthalpy and entropy changes associated with the ST in this compound are $\Delta H = 4.0 \text{ kJ mol}^{-1}$ and $\Delta S = 11.3 \text{ J mol}^{-1} \text{ K}^{-1}$ [28]. The latter agrees with the expected entropy change arising from the spin multiplicity change $S=2 \leftrightarrow S=0$ with $\Delta S = R \ln[(2S+1)_{\text{HS}}/(2S+1)_{\text{LS}}] = 13.4 \text{ J mol}^{-1} \text{ K}^{-1}$. These thermodynamic quantities are unusually small for a $S=2 \leftrightarrow S=0$ SCO system. It is noted that the transition is very gradual, and this is indicative of very weak cooperativity.

3 Chromium Complexes

$[\text{CrI}_2(\text{depe})_2]$ with $\text{depe} = 1,2\text{-bis}(\text{diethylphosphino})\text{ethane}$, represents the first Cr(II) SCO coordination compound reported in the literature [30]. In this mononuclear complex, the metal ion is octahedrally coordinated by two iodide ions in *trans* position and two bidentate phosphine ligands (Fig. 4).

The bond lengths have been found as $\text{Cr-I} = 3.068(0) \text{ \AA}$ and $\text{Cr-P} = 2.50\text{--}2.53 \text{ \AA}$ at room temperature. These Cr-P distances are $\sim 0.15 \text{ \AA}$ longer than those reported for the LS mononuclear complex, $[\text{CrCl}_2(\text{dmpe})_2]$ [31] with $\text{Cr-P} = 2.36\text{--}2.37 \text{ \AA}$. Interestingly, $[\text{CrBr}_2(\text{depe})_2]$ shows a small amount of HS Cr(II) ions at room temperature, whereas $[\text{CrCl}_2(\text{depe})_2]$ is LS over the whole experimental temperature range [30].

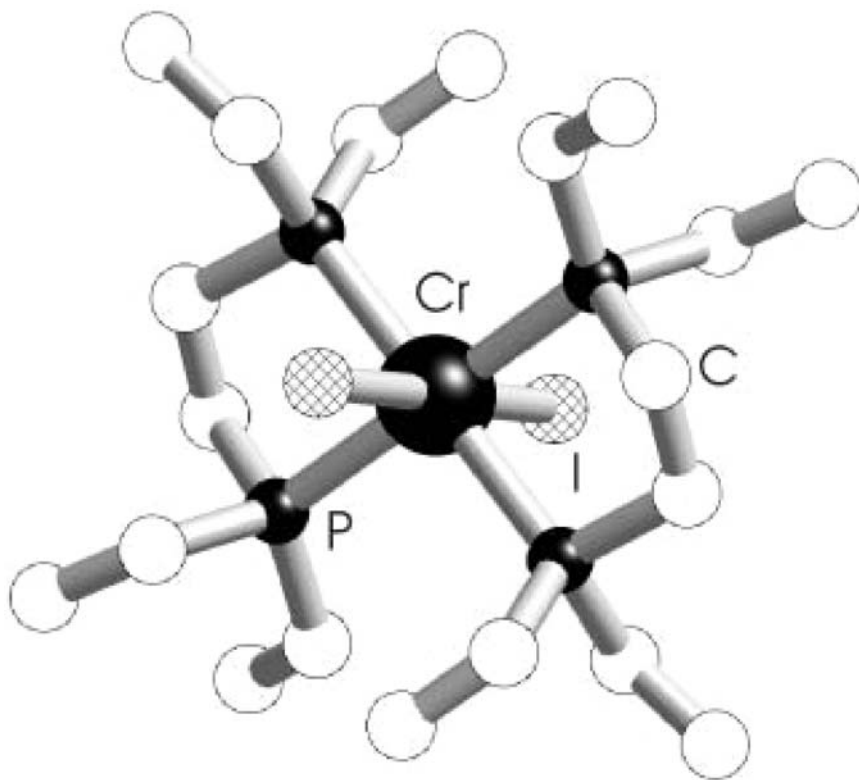


Fig. 4 View of the mononuclear unit of $[\text{CrI}_2(\text{depe})_2]$ at 293 K

$[\text{CrI}_2(\text{depe})_2]$ exhibits a sharp and complete ST around $T_{1/2} \sim 170$ K between HS ($S=2$) and LS ($S=1$) states without any detectable hysteresis at ambient pressure (Fig. 5).

This transition is accompanied by a colour change from purple-brown (HS) to brilliant violet (LS). The magnetic properties have also been recorded under external pressure using a custom-made pressure cell. With increasing pressure, the ST curves are shifted towards higher temperatures: the ST temperatures $T_{1/2}$ have been evaluated to be 220 K at 3.7 kbar; 258 K at 4.4 kbar; 283 K at 5.4 kbar; and a complete LS state is observed at 8 kbar (Fig. 5) [32]. This pressure induced spin state change observed at room temperature from HS to LS can be paralleled with the one obtained by chemical substitution from iodide to chloride in the coordination sphere of Cr(II) in $[\text{CrI}_2(\text{depe})_2]$ [30]. The transition has also been studied by infrared spectroscopy (in the $4000\text{--}30\text{ cm}^{-1}$ range at 300 and 91 K) and calorimetric measurements using an adiabatic calorimeter in the 14–300 K range [33]. A sharp heat capacity anomaly arising from the ST was found at ~ 171 K. The enthalpy and entropy changes were evaluated to be $\Delta H = 6.6\text{ kJ mol}^{-1}$ and

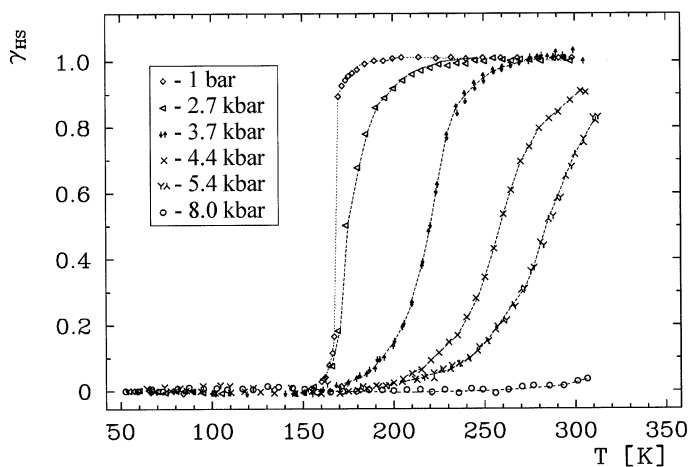
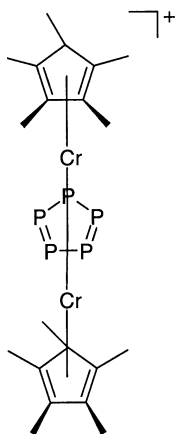


Fig. 5 γ_{HS} as a function of temperature for $[\text{CrI}_2(\text{depe})_2]$ over the temperature range 50–310 K, and at different pressures [32]

$\Delta S = 39.4 \text{ J mol}^{-1} \text{ K}^{-1}$. The entropy gain has been well accounted for in terms of the contribution from the change in the spin manifold (10%), the change in the metal-ligand skeletal vibrations ($\sim 75\%$) and the change in the barrier heights hindering the internal rotation of the total of eight methyl moieties of the two depe ligands ($\sim 15\%$) (See Fig. 4). This strongly cooperative ST has been explained in terms of the large compressibility due to the facile polarizability of the iodide ligands [33].

Two triple-decker chromium dinuclear complexes of formula $[(\eta^5\text{-C}_5\text{Me}_5)(\text{Cr}(\mu^2: \eta^5\text{-P}_5)\text{Cr}(\eta^5\text{-C}_5\text{Me}_5))](\text{A})$ ($\text{A} = \text{PF}_6^-$, SbF_6^-) were reported to show unusual magnetic properties below room temperature (Fig. 6) [34].



At 300 K, the $\chi_{\text{M}}T$ value is consistent with the one predicted for two non-interacting Cr centres. Upon cooling, $\chi_{\text{M}}T$ remains constant down to ~ 150 K,

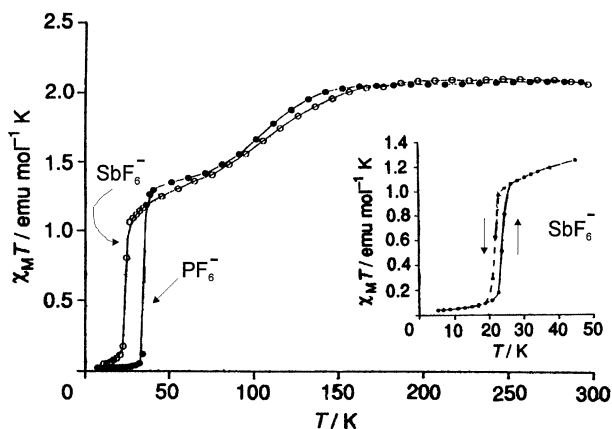


Fig. 6 $\chi_M T$ vs T plot for $[(\eta^5\text{-C}_5\text{Me}_5)(\text{Cr}(\mu^2\text{:}\eta^5\text{-P}_5)\text{Cr}(\eta^5\text{-C}_5\text{Me}_5))](\text{A})$ with $\text{A}=\text{PF}_6^-$ (filled circles), SbF_6^- (open circles). The inset shows the thermal hysteresis for the SbF_6^- salt (adapted from [30a])

then smoothly decreases from 150 K to ~ 50 K before suddenly dropping to zero at 33 K for the hexafluorophosphate salt, and at 23 K for the hexafluoroantimonate derivative. This sharp decrease is accompanied by a hysteresis loop of ~ 2 K for the two compounds. As an example, the hysteresis loop of the hexafluoroantimonate derivative is shown in the inset of Fig. 6.

The first decrease was interpreted by the authors as a result of intramolecular antiferromagnetic spin-spin interactions, and the second one as a result of a spin state transition [34]. This magnetic behaviour could also be due to the subsequent ST of the two chromium sites, leading to a two-step conversion. Preliminary temperature dependent X-ray investigations have been recently carried out by Goeta and Howard on the hexafluoroantimonate derivative revealing a crystallographic phase transition, the crystal system being orthorhombic at 290 K and monoclinic at 170 K and 12 K [35]. More detailed investigations are needed to clarify this unusual behaviour. A mononuclear sandwich chromium complex, $(\text{Cp}(\text{iPr})_4)_2\text{Cr}$, was also reported to exhibit a gradual thermal SCO behaviour in the solid state with $T_{1/2} \sim 150$ K [36].

4 Cobalt(III) Complexes

Thermal SCO has long been well established in oxo compounds like LaCoO_3 and related systems, with $\text{LS} (\text{S}=0) \leftrightarrow \text{HS} (\text{S}=2)$ transitions at or well above room temperature (see Chap. 11 by CNR Rao et al. in this series). Regarding octahedral Co(III) complexes, nearly all are known to be LS, including

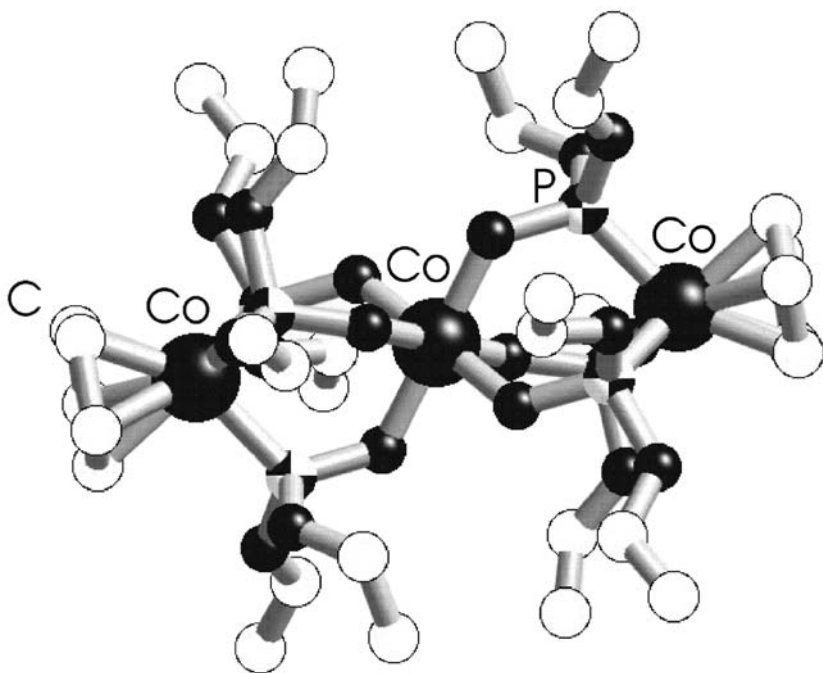


Fig. 7 View of the trinuclear unit of $[\{(C_5H_5)CoP(O)(OEt)_2\}_2Co]PF_6$. Black and white, black, and white spheres correspond to phosphorous, oxygen and carbon atoms, respectively. The larger black spheres correspond to Co(III) ions [43]

$[Co(H_2O)_6]^{3+}$. The exceptions are the HS complexes, $[CoF_6]^{3-}$ and $[CoF_3(H_2O)_3]$ [37, 38]. The first Co(III) SCO complex was discovered by Kläui et al. [39, 40] in $[CoL_2]PF_6$, where the central Co(III) ion is octahedrally coordinated by two tridentate oxygen tripod ligands, where $L=\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}^-$ including a diamagnetic anionic Co(III) half-sandwich complex [41–43] (Fig. 7).

A gradual SCO is observed in both the solid state and in solution accompanied by a thermochromism; the compound is dark green at room temperature and becomes bright yellow upon cooling.

The existence of temperature dependent SCO in various solvents was followed by ^{31}P NMR [41]. This method was preferred over ^1H NMR for several reasons: (i) the ^{31}P resonance multiplet can be used as an internal standard; (ii) the paramagnetic shifts are larger, and only one single resonance is observed from the cation as compared to ^1H NMR. The relative shifts $\Delta\nu/\nu_0$ have been followed as a function of temperature down to ca. 180 K. Very minor differences were observed for the SCO behaviour in the different solvents. Average values of ca. 24 kJ mol $^{-1}$ for the enthalpy change ΔH° , and ca. 70 J mol $^{-1}$ K $^{-1}$ for the entropy change ΔS° , which are practically constant

for all the solvents under study, have been found by fitting the experimental data to the following expression:

$$\frac{\Delta\nu}{\nu_0} = \frac{C}{T(1 + e^{\Delta G^0/RT})} + \left(\frac{\Delta\nu}{\nu_0}\right)_{LS} \quad (1)$$

The relatively large ΔS° values were attributed to the large size and flexibility of the ligand which enhance the vibrational degree of freedom accessible upon spin conversion [44, 45].

In another ^{31}P NMR study [45], the SCO behaviour in solution of a whole series of $[\text{CoL}_2]^+$ complexes was investigated, where the oxygen tripod ligands $\{(\text{C}_5\text{H}_5)\text{Co}[\text{P}(\text{O})\text{R}_2]_3\}$ were modified by introducing the substituents $\text{R}=\text{OCH}_3$, OC_2H_5 , $\text{OCH}(\text{CH}_3)_2$, $\text{OCH}_2\text{CH}_2\text{CH}_3$, $\text{OCH}_2\text{C}(\text{CH}_3)_3$, C_2H_5 , CH_2 , C_6H_5 , differing in bulkiness and electronic induction effects. In fact, the SCO behaviour, as reflected in the $(\Delta\nu/\nu_0)(T)$ curve, has been found to vary more or less within this series of substituents, which was interpreted as being due to a combination of steric and electronic influence affecting the ligand field strength. Very similar results were obtained from magnetic measurements on these complexes in solid state [45].

It is worth noting that these Co(III) complexes represent a very unusual class of compounds in that the oxygen tripod ligands L apparently are placed in the *spectrochemical series* right between F^- and H_2O , where a small window of the critical ligand field strength separates the large majority of Co(III) LS complexes from the only Co(III) HS complexes known so far, viz. $[\text{CoF}_6]^{3+}$ and $[\text{CoF}_3(\text{H}_2\text{O})_3]$. There is no other coordinating atom than F and O known up to now, and it certainly took special skill (and probably luck) to fine-tune the Co(III)-O bonding properties of the present ligand L in order to induce thermal SCO. In fact, the ligand field spectra of the related transition metal complexes $[\text{ML}_2]$ with $\text{M}=\text{Co(II)}$, Ni(II) and Cu(II) characterize L^- as very hard ligands whose position in the spectrochemical series is near that of fluoride [45].

An anomalous temperature dependence of the magnetic moment was recently observed below room temperature in the solid state for two Co(III) octahedral complexes, $\text{Co(4-methylpiperazine-1-carbodithioic acid)}_3\text{Br}_3$ and $\text{Co}_2(2\text{-methylpiperazine-1,4-dicarbodithioate})_3$. The smooth variation of the magnetic moment for these CoS_6 core compounds was attributed to SCO behaviour [46].

5 Concluding Remarks

Several examples of coordination and organometallic SCO compounds with d^4 - d^6 electronic configurations have been discussed. These compounds, which are either mononuclear or oligonuclear, exhibit a variety of ST curves

ranging from abrupt, gradual, stepwise, incomplete, and even hysteretic. It is worthwhile to notice that spin state equilibrium can also be encountered for Ni(II) (d^8) complexes as a consequence of a tetrahedral (HS) $\leftrightarrow$ square-planar (LS) interconversion [47–52]. For instance, this is found for the sandwich type complex, $[\text{Me}_5\text{C}_5\text{Ni}(\text{acac})]$, in the solid state between 150–300 K, as well as in solution (toluene and THF) as deduced from ^1H NMR spectroscopy [50]. This magnetic change, which does not occur within the same symmetry, differs from normal SCO and hence is not considered in detail in this chapter.

Further research could be directed to the quest of polymeric complexes so as to enhance the knowledge on cooperative phenomena associated with SCO behaviour. Another appealing perspective would be to consider possible spin state change in second row transition elements. In this instance, $[\text{Mo}(\text{OPr}^i)_2(\text{bipy})_2]$ represents such a complex exhibiting a spin state equilibrium [53].

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References

1. Schläfer HL, Gliemann G (1967) Einführung in die Ligandenfeldtheorie. Akademische Verlagsgesellschaft, Frankfurt/Main
2. Figgis BN (1966) Introduction to ligand fields. Interscience Publ., New York, London
3. Barefield EK, Busch DH, Nelson SM (1968) Q Rev Chem Soc London 22:457
4. Griffith JS, Orgel LE (1957) Q Rev Chem Soc London 11:381
5. Cotton FA, Wilkinson G (1988) Advanced inorganic chemistry, 5th edn. Wiley, New York
6. Charles ID, Frank MJ (1970) J Inorg Nucl Chem 32:555
7. Cooke AH, Duffies HJ (1955) Proc Phys Soc London Sect A A68:32
8. Holloway CE, Melnik M (1996) Rev Inorg Chem 16:101
9. Sim PG, Sinn E (1981) J Am Chem Soc 103:241
10. Garcia Y, Kahn O, Ader JP, Buzdin A, Meurdesoif Y, Guillot M (2000) Phys Lett A 271:145
11. Nakano M, Matsubayashi G, Matsuo T (2003) Adv Quantum Chem 44:617
12. Nakano M, Matsubayashi G, Matsuo T (2002) Phys Rev B 66:212412
13. Qi Y, Müller EW, Spiering H, Gülich P (1983) Chem Phys Lett 101:503
14. Nègre N, Consejo C, Goiran M, Bousseksou A, Varret F, Tuchagues JP, Barbaste R, Askenazy S, Haasnoot JG (2001) Physica B 294:91
15. Kaustov L, Tal ME, Shames AI, Gross Z (1997) Inorg Chem 36:3503
16. Zelentsov VV, Somova IK (1974) Zh Obshch Khim 44:1309
17. (a) Sato O, Iyoda T, Fujishima A, Hashimoto K (1996) Science 272:704; (b) Verdaguer M (1996) Science 272:698
18. Gülich P, Garcia Y, Woike T (2001) Coord Chem Rev 219/221:839
19. (a) Ohkoshi S, Tokoro H, Utsunomiya M, Mizuno M, Abe M, Hashimoto K (2002) J Phys Chem B 106:2423; (b) Ohkoshi S et al. (2003) Private communication

20. Ammeter JH, Bucher R, Oswald N (1974) *J Am Chem Soc* 96:7883
21. Swizer ME, Wang R, Rettig ME, Maki AH (1974) *J Am Chem Soc* 96:7669
22. Ammeter JH (1978) *J Magn Reson* 30:299
23. Cozak D, Gauvin F (1987) *Organometallics* 6:1912
24. Cozak D, Gauvin F, Demers J (1986) *Can J Chem* 64:71
25. Köhler FH, Schlesinger B (1992) *Inorg Chem* 31:2853
26. Almennige A, Samdal S, Haaland A (1977) *J Chem Soc Chem Comm* 14
27. Seip MH, Strand TG, Stölevik R (1969) *Chem Phys Lett* 3:1937
28. Franceschi F, Hesschenbrouck J, Solari E, Floriani C, Re N, Rizzoli C, Chiesi-Villa A (2000) *J Chem Soc Dalton Trans* 4:593
29. (a) Cotton FA (1990) 9:2553; (b) Mountford P (1998) *Chem Soc Rev* 27:105
30. (a) Halepoto DM, Holt DGL, Larkworthy LF, Leigh GL, Povey DC, Smith GW (1989) *J Chem Soc Chem Comm* 1322; (b) Halepoto DM, Holt DGL, Larkworthy LF, Povey DC, Smith GW (1989) *Polyhedron* 8:1821
31. Girolami GS, Wilkinson G, Galas AM, Thornton-Pett M, Hursthouse MB (1985) *J Chem Soc Dalton Trans* 1339
32. Gütllich P, Gaspar AB, Ksenofontov V, Garcia Y (2004) *J Phys Condens Matter* 16:1087
33. Sorai M, Yumoto Y, Halepoto DM, Larkworthy LF (1993) *J Phys Chem Solids* 54:421
34. Hughes AK, Murphy VJ, O'Hare D (1994) *J Chem Soc Chem Comm* 2:163
35. Goeta AE, Howard JAK (2001) Fourth TMR-TOSS-Meeting, Bordeaux, France
36. Sitzmann H, Schär M, Dormann E, Kelemen M (1997) *Z Anorg Allg Chem* 623:1850
37. Hoppe R (1956) *Recl Trav Chim Pays-Bas* 75:569
38. Clark HC, Cox B, Sharpe AG (1957) *J Chem Soc* 4132
39. Kläui W (1979) *J Chem Soc Chem Comm* 700
40. Kläui W (1979) *Z Naturforsch B* 34:1403
41. Gütllich P, McGarvey BR, Kläui W (1980) *Inorg Chem* 19:3704
42. Eberspach W, El Murr N, Kläui W (1982) *Angew Chem Int Ed Engl* 21:915
43. Kläui W. Private communication
44. Navon G, Kläui W (1984) *Inorg Chem* 23:2722
45. Kläui W, Eberspach W, Gütllich P (1987) *Inorg Chem* 26:3977
46. Manhas BS, Verma BC, Kalia SC (1995) *Polyhedron* 14:3549
47. Morassi R, Bertini I, Sacconi L (1973) *Coord Chem Rev* 11:343
48. Kläui W, Schmidt K, Bockmann A, Hofmann P, Schmidt HR, Stauffert P (1985) *J Organomet Chem* 286:407
49. Werner H, Ulrich B, Schubert U, Hofmann P, Zimmer-Gasser B (1985) *J Organomet Chem* 297:27
50. Smith ME, Andersen RA (1996) *J Am Chem Soc* 118:11,119
51. laCour A, Findeisen M, Hazell R, Hennig L, Olsen CE, Simonsen O (1996) *J Chem Soc Dalton Trans* 16:3437
52. Chmielewski PJ, Latos-Grazynski L (2000) *Inorg Chem* 39:5639
53. Chisholm MH, Kober EM, Ironmonger DJ, Thornton P (1985) *Polyhedron* 4:1869

Valence Tautomeric Transition Metal Complexes

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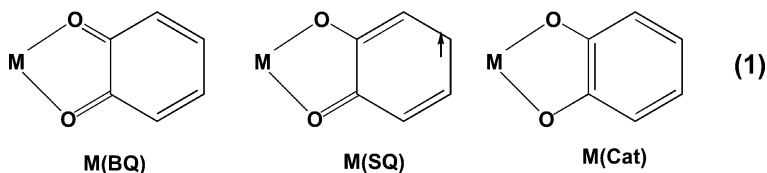
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Abstract Valence d-orbital energies of the first row transition metals are close to the frontier π -orbital energies of *o*-benzoquinones. Complexes prepared with quinone ligands most commonly have the quinone coordinated with the metal in the form of a semiquinonate (SQ) radical-anion or as a catecholate (Cat) dianion. In a few unique complexes it has been possible to observe intramolecular electron transfer between localized metal and quinone electronic levels. Electron transfer is accompanied by changes in magnetism and spectral properties that have made it possible to observe metal-ligand electron transfer under equilibrium conditions in solution and in the solid state. This effect has been considered as an example of valence tautomerism (VT). In this review we present the results of studies on the physical properties of complexes that undergo VT, with a view of the scope of VT for complexes containing a variety of quinone ligands and with different metal ions.

Keywords Transition metal · Semiquinone · Catechol · Electron transfer

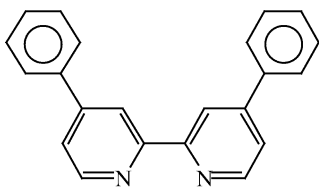
1 Introduction

Interest in the photochemistry of transition metal complexes, and, specifically, on complexes that may serve as photocatalysts, has included investigations on metal-ligand electron transfer reactions. Excitation generally requires a light source with energy in the UV or visible region, and the lifetime of the excited state is relatively short. The reactivity of the excited state, and its practical utility, depend on the symmetry, spin multiplicity, and energy difference between the donor metal and acceptor ligand orbitals. Studies on $[\text{Ru}(\text{bpy})_3]^{2+}$ have defined a diverse field of photochemical research. As the coordination chemistry of *o*-quinone ligands has developed over the past 30 years it has been found that the energy of the redox-active quinone π -orbital is quite close to the energies of transition metal d-orbitals [1, 2]. Consequently, electrochemical reactions may occur at either the ligand or metal within a narrow potential range, and within a single chelate ring the question of charge distribution requires detailed magnetic, spectral, and structural characterization to resolve [3, 4]. Specifically, the metal-quinone chelate may adopt one of the three charge-localized electronic forms shown below (1) as redox isomers differing in charge distribution.

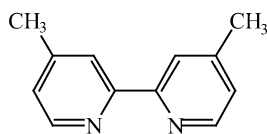


The energy difference between metal and quinone electronic levels is often in the low-energy visible or infrared, and, while the complexes have limited utility as photocatalysts, they may have practical utility as sensors [5].

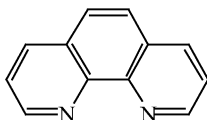
A variety of complexes containing unreduced *o*-benzoquinone ligands are known, but, as a diketone, the BQ ligand is a weak donor and it is readily subject to displacement. The catecholate (Cat) and radical semiquinonate (SQ) electronic forms are the most common modes of coordination. Catecholate ligands bond as strong σ and π donors, particularly to high oxidation state metal ions. The unpaired spin of semiquinonate ligands contributes to unique magnetic properties resulting from both M-SQ and SQ-SQ intramolecular spin coupling interactions [6]. In complexes where the ligand and metal valence electronic levels are particularly close in energy, equilibria between $\text{M}^{\text{I}}(\text{SQ})$ and $\text{M}^{\text{II}}(\text{Cat})$ redox isomers have been observed in solution and in the solid state. The equilibrium between redox isomers related by shifts in charge distribution was considered to be an example of valence tautomerism (VT) [7].



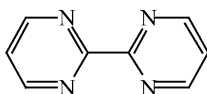
4,4'-diphenyl-2,2'-bipyridine
(dpbpy)



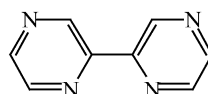
4,4'-dimethyl-2,2'-bipyridine
(dmbpy)



1,10-phenanthroline
(phen)



2,2'-bipyrimidine
(bpym)



2,2'-bipyrazine
(bpyz)

Observations on VT were described initially for complexes of cobalt where the metal ion shifts between HS-Co(II) and LS-Co(III) with electron transfer to an SQ ligand (2) [3, 8]. The spin change for the metal ion that accompanies the shift in charge distribution results in a large change in magnetism for the complex, providing a convenient probe that may be used to follow changes in the concentration of redox isomers. In this review we present a summary of the research carried out on Cat and SQ complexes of Co that exhibit coupled electron transfer (ET)/spin transition (ST) equilibria, with related observations on quinone complexes of Mn and Cu that exhibit valence tautomerism.

2

Initial Observations on Valence Tautomerism

Studies on magnetic exchange in radical semiquinonate complexes of paramagnetic metal ions included characterization on the $[\text{Co}^{\text{II}}(3,5\text{-DBSQ})_2]_4$ tetramer, where 3,5-DBSQ is the semiquinonate form of 3,5-di-*tert*-butyl-1,2-benzoquinone [9, 10]. In order to reduce the number of interacting paramagnetic centers, the tetramer was treated with 2,2'-bipyridine, giving the

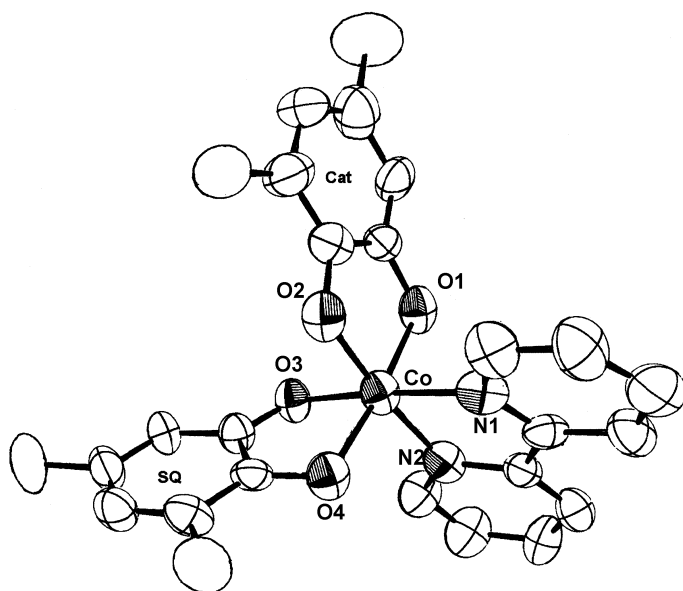


Fig. 1 View of the $[\text{Co}^{\text{III}}(\text{bpy})(3,5\text{-DBSQ})(3,5\text{-DBCat})]$ molecule

$[\text{Co}^{\text{II}}(\text{bpy})(3,5\text{-DBSQ})_2]$ monomer [7]. Magnetic characterization on a solid sample of the complex at room temperature indicated that it had a simple $S=1/2$ magnetic moment. EPR spectra recorded on a sample dissolved in toluene solution showed a simple radical spectrum at -50°C , but the spectrum collapsed as solution temperature was increased to room temperature. ^1H -NMR spectra recorded at temperatures slightly above room temperature contained sharp, but paramagnetically shifted, resonances for the protons of the 3,5-DBSQ ligands. Solution magnetic susceptibility measurements, recorded over the temperature range that the changes in EPR and NMR spectra were found to occur, showed a change in magnetic moment from a value that is slightly greater than the $S=1/2$ value at 200 K to a value of $4.3 \mu_{\text{B}}$ at 350 K. The high temperature value is close to the magnetic moment (per Co) obtained for $[\text{Co}^{\text{II}}(3,5\text{-DBSQ})_2]_4$ [10], and the low temperature value was close to the moment obtained in the solid state measurement. It was clear at this point that the form of the bpy complex present in toluene solution at temperatures above room temperature was $[\text{Co}^{\text{II}}(\text{bpy})(3,5\text{-DBSQ})_2]$, but it was unclear why the magnetic moment shifted to an $S=1/2$ value at lower temperature. A change in spin at the metal ion, from HS-Co(II) to LS-Co(II), was a possibility which, with strong antiferromagnetic Co-SQ exchange, would give a radical-centered $S=1/2$ spin state. Crystallographic characterization on the complex, Fig. 1, provided clear resolution to the question. One of the quinone ligands had C-O bond lengths of 1.358(10) Å and aromatic C-C bond lengths within the ring, as features that are com-

monly found for catecholate ligands. The second quinone ligand had shorter C-O lengths of 1.297(9) Å, and a pattern of ring C-C lengths that showed slight contraction (1.348(11) Å) at the bonds that would be double bonds for the *o*-benzoquinone electronic form. These structural features are characteristic of a semiquinonate ligand, and the complex was found to contain mixed charge Cat and SQ ligands coordinated to Co(III) in the neutral molecule. In accord with this localized assignment of charge, bond lengths to the metal were found to be short, as a signature of LS-Co(III).

The conclusion consistent with all of the experimental data has the complex in the form of Ls-Co(III) with mixed charge SQ and Cat ligands at the lower temperature range, LS-[Co^{III}(bpy)(3,5-DBSQ)(3,5-DBCat)], shifting to HS-Co(II) by intramolecular Cat→Co(III) electron transfer at higher temperature to give HS-[Co^{II}(bpy)(3,5-DBSQ)₂], with Co(III) and Co(II) redox isomers together at equilibrium in solution and in the solid state [7]. The product of electron transfer in the Co reduction step is a putative LS-Co(II) species, that undergoes rapid spin transition to the HS-Co(II) product. These observations have provided the opportunity for fundamental studies on electron transfer and spin transition under equilibrium conditions, and the potential for applications in switching and sensor development have stimulated investigations on this, and related complexes, as unusual examples of molecular bistability [5].

A few years after observations on the cobalt system were first reported, similar temperature-dependent shifts in electronic spectrum were observed for a related complex of manganese. Addition of pyridine to the [Mn^{II}(3,5-

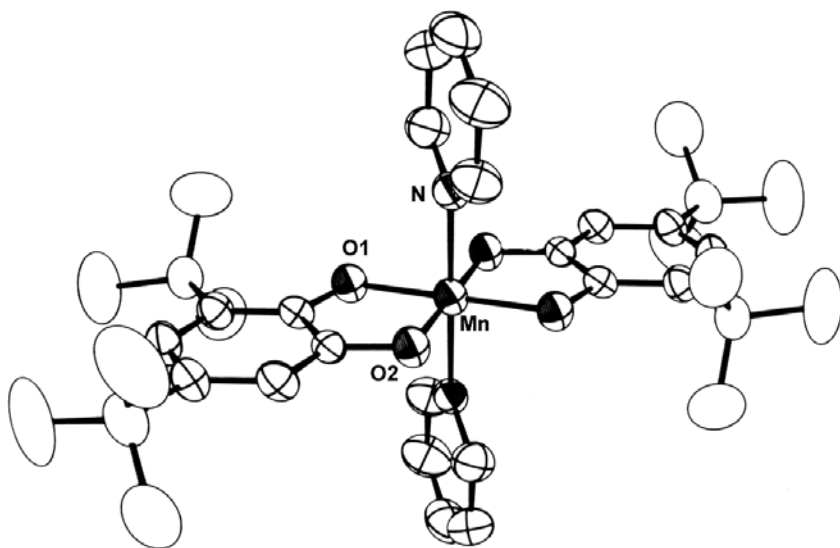


Fig. 2 View of the *trans*-[Mn^{IV}(py)₂(3,5-DBCat)₂] molecule

DBSQ)₂]₄ tetramer gave a product that was observed to be dark purple in color as a solid [11]. In toluene solution at room temperature the complex turned to the pale green color of the Mn(II) tetramer, but when cooled to temperatures below 200 K, the solution returned to the purple color of the solid. Crystallographic characterization on the purple crystals, Fig. 2, revealed features for the quinone ligands that identified them as catecholates, and short bond lengths to the Mn were characteristic of d³ Mn(IV). This system was identified as the second complex to exhibit valence tautomerism, with a two-electron transfer between the quinone ligands and the manganese center [11]. These observations were significant in indicating that the effects associated with the cobalt system might be general, extending to quinone complexes of other metals and, potentially, to other quinone ligands.

3 Photophysical Processes

Valence tautomers are characterized by different distributions of electron density, where interconversion between tautomers is accomplished by intramolecular electron transfer [12]. There are two important reasons for studying valence tautomeric complexes. First, they are unique model systems that provide insight into the factors affecting intramolecular electron transfer in coordination complexes. Second, from an applied perspective, the large changes in optical, structural and magnetic properties that accompany the valence tautomeric interconversion have potential applications in bistable molecular level switching materials [13].

Complexes that exhibit valence tautomerism are electronically labile, where two or more electronic states lie close in energy and this leads to significant vibronic interactions and an appreciable sensitivity to the environment. Other examples of electronic lability are found in mixed valence [14] and spin crossover [15] complexes. Electronically labile complexes are potential building blocks for molecular electronic devices [16]. An external perturbation (e.g., photons, electric field, magnetic field, etc.) on small collections of these molecules can lead to an interconversion between two electronic states. In fact, Gülich et al. [17] have shown that polycrystalline samples of Fe^{II} spin crossover complexes maintained at low temperatures (<20 K) can be reversibly interconverted between the *low-spin* and a long lived metastable *high-spin* state in the LIESST (light-induced excited spin state trapping) effect. Recently, Kahn et al. [18] have been able to prepare Fe^{II} spin crossover complexes in which the bulk samples display large hysteresis loops centered around room temperature. They were able to reversibly interconvert between stable *high-spin* and *low-spin* forms and have fabricated a display device where elements can be switched between the purple and white colored forms of the complex. Hauser [19] successfully

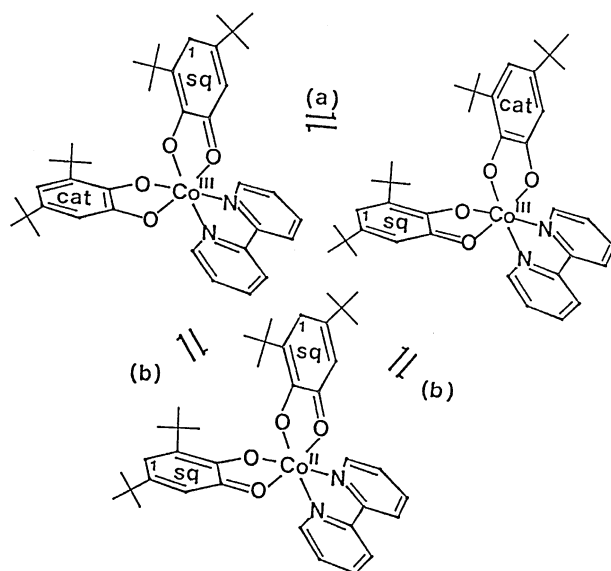


Fig. 3 Possible intramolecular electron transfer processes present for a valence tautomeric cobalt complex

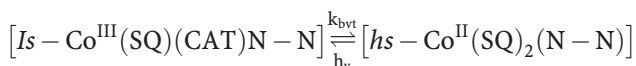
showed that Fe^{II} spin crossover complexes exhibit a large photorefractive effect between the *low-spin* and *high-spin* forms of Fe^{II} . He was able to induce dynamic as well as static holographic grating formation, the decay of which could be modulated by the temperature. This behavior is attractive for real-time holography applications.

Cobalt complexes with two *o*-quinone derived ligands have been shown to undergo a valence tautomeric interconversion between [*high-spin*- $\text{Co}^{\text{II}}(\text{SQ})_2(\text{N-N})$] to [*low-spin*- $\text{Co}^{\text{III}}(\text{SQ})(\text{CAT})(\text{N-N})$] where N-N is a chelating nitrogen donor ligand such as 2,2'-bipyridine (bpy) and where SQ^- and CAT^{2-} refer respectively to the singly and doubly reduced forms of the *o*-benzoquinone ligand. In these molecules an intramolecular electron transfer converts the *high-spin*- Co^{II} into a *low-spin*- Co^{III} ion, and one of the ligands is reduced by one electron from a semiquinone anion (SQ^-) to a catecholate (CAT^{2-}) ligand. There are two different mixed valence isomers of the LS- Co^{III} valence tautomer. The dynamical processes that are possible for such a valence tautomeric complex are summarized in Fig. 3.

The valence tautomeric interconversion (process b) can be thermally driven. Initially it was observed that the bipyridine complex in Structure (1) could exist in the LS- Co^{III} and HS- Co^{II} valence tautomeric forms in solution. In toluene at room temperature the HS- Co^{II} form predominates. A decrease in temperature leads to a stabilization of the LS- Co^{III} tautomer such that at temperatures below ~ 250 K the LS- Co^{III} form predominates. Chang-

ing the nitrogen donor ligand can be used to systematically shift the solution critical temperature ($T_{1/2}$) of the interconversion [19]. Valence tautomerism can also be thermally induced in the solid state. It was shown that the $[\text{LS-Co}^{\text{III}}(3,5\text{-DTBSQ})(3,5\text{-DTBCAT})(\text{phen})]\cdot\text{C}_6\text{H}_5\text{CH}_3$ to $[\text{HS-Co}^{\text{II}}(3,5\text{-DTBSQ})(\text{phen})]\cdot\text{C}_6\text{H}_5\text{CH}_3$ interconversion can be reversibly driven with temperature and that the interconversion occurs abruptly within a narrow temperature range of ~ 30 degrees.

The observation that pulsed laser excitation can be used to photoinduce effectively valence tautomerism is a significant achievement for it allows for the monitoring of the intramolecular electron transfer kinetics in these systems. Time resolved pulsed laser spectroscopy can be used to monitor the rate of back valence tautomerization (k_{bvt}):



The kinetics of the HS-Co^{II} to $\text{LS-Co}^{\text{III}}$ valence tautomeric interconversion are expected to be modulated by (i) the large amplitude changes in the nuclear positions (Δr) upon valence tautomerization and the vibrational mode ($\hbar\omega$) which make up the reaction coordinate (vibronic coupling), (ii) the nature of the electronic coupling (H_{if}) between donor and acceptor groups (electronic coupling), and (iii) the energy separations between tautomeric states (ΔE). The valence tautomeric process is similar to the HS-Fe^{II} to $\text{LS-Fe}^{\text{III}}$ spin-crossover interconversion. The kinetics of Fe^{II} spin crossover have been shown to be controlled by large Franck-Condon reorganization energies and zero point energy separation between *high-spin* and *low-spin* forms [2]. Average metal ligand bond length changes (Δr) for Fe^{II} spin crossover complexes are 0.16–0.22 Å. The cobalt valence tautomeric transformation is similarly characterized by large metal-ligand bond length changes of 0.18 Å, as well as internal ligand bond length changes. Furthermore, since spin-crossover and valence tautomerism can be thermally driven, the zero-point energy separations are of similar magnitude and are on the order of kT . The degree of electronic coupling in Fe^{II} spin crossover systems is low since the interconversion is a $\Delta S=2$ process and consequently is formally spin forbidden. It is expected that the degree of electronic coupling in the valence tautomeric systems is low due to poor overlap of donor and acceptor molecular orbitals. However, the spin multiplicity restriction to interconversion is lifted due to magnetic exchange coupling in the HS-Co^{II} tautomer. The spin allowed $\Delta S=0$ valence tautomeric interconversion likely occurs through the antiferromagnetically coupled $S=1/2$ state of the HS-Co^{II} tautomer and the $S=1/2$ state of the $\text{LS-Co}^{\text{III}}$ tautomer. The study of the kinetics of the valence tautomeric process can provide unique insights into the balance of Franck-Condon factors and electronic coupling which affect the intramolecular electron transfer event.

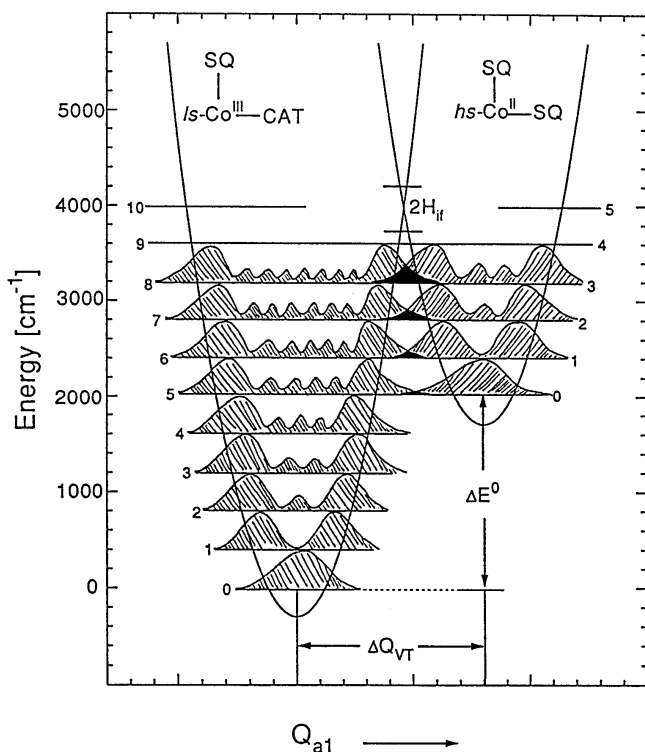


Fig. 4 Quantum mechanical potential energy diagram for the LS-Co^{III} and HS-Co^{II} valence tautomeric states, plotted along the totally symmetric normal coordinate Q with $\Delta Q = \sqrt{6}\Delta r$. In the simple SCC model, harmonic potentials with equal force constants are used. The vibrational energy levels are shown with the squares of the vibrational wave functions superimposed

The electronic lability associated with the valence tautomeric interconversion can be illustrated with the aid of the one-dimensional potential energy diagram shown in Fig. 4. The complex can exist in one of two states that are represented by the two harmonic potential energy curves shown in Fig. 4. Since the largest geometrical changes that accompany the valence tautomeric process are metal-ligand bond length changes where $\Delta r \approx 0.18 \text{ \AA}$, it can be assumed that the reaction coordinate is approximately equivalent to the totally symmetric stretching normal coordinate of the complex, where $\Delta Q = \sqrt{6}\Delta r$. The rate at which the HS-Co^{II} complex converts to the LS-Co^{III} complex depends on the magnitude of change in the reaction coordinate (ΔQ), the frequency of the active metal-ligand vibrational mode ($\hbar\omega$), the energy difference (ΔE) and the magnitude of the electronic coupling between the initial and final states (H_{if}).

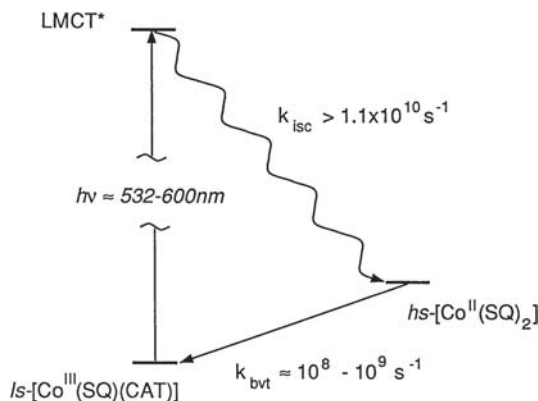


Fig. 5 Jablonski diagram for the photoinduced valence tautomeric process. The laser pulse into the 600 nm charge transfer absorption band of the LS-Co^{III} tautomer results in population of a LMCT excited state. Rapid intersystem crossing produces the HS-Co^{II} state followed by a slower back valence tautomerization

Pulsed laser photolysis, both on the picosecond (90 ps pulse) and the nanosecond (24 ns pulse) time scales, were carried out for solutions of four valence tautomeric Co complexes [12, 22]. The strategy for pulsed laser photolysis experiments is shown in Fig. 5, which shows a Jablonski diagram for the photoinduced valence tautomeric process. The change of the electronic absorption spectrum is monitored at some wavelength before, during, and after the laser pulse. Valence tautomeric complexes are particularly well suited for photophysical investigations, since the spectra of the ground and excited states can be obtained by varying the temperature. Pulsed laser experiments can be employed to look for transient bleaches and absorptions around isosbestic points. The largest change in absorption between the LS-Co^{III} and HS-Co^{II} tautomers occurs in the 700–800 nm range and in the near IR at 2500 nm.

Figure 6 shows the picosecond time-resolved transient curves obtained for a 298 K toluene solution of [Co(3,5-DTBSQ)₂(dpbpy)], where dpbpy is 4,4'-diphenyl-2,2'-bipyridine. A 532 nm pump pulse (90 ps pulse width FWHM) into the 600 nm LMCT band of the LS-Co^{III} tautomer results in a transient absorption monitored at 720 nm and a transient bleach monitored at 600 nm. Both of the transients can be well fit (solid lines) by single exponential functions with the same relaxation time constant of $\tau_{\text{obs}} = 1.2$ ns. Since there was no indication of a rise time, the HS-Co^{II} state is formed within the experimental resolution of 90 ps. At 298 K the K_{eq} value for this dpbpy complex in toluene was determined to be 0.24. Adams and Hendrickson [12] could consequently calculate $k = 6.71 \times 10^8 \text{ s}^{-1}$ for the back valence tautomerization (k_{bvt} in Fig. 5) of the dpbpy complex. Nanosecond laser spectroscopy was also used to determine the temperature dependence of k_{bvt} . For the

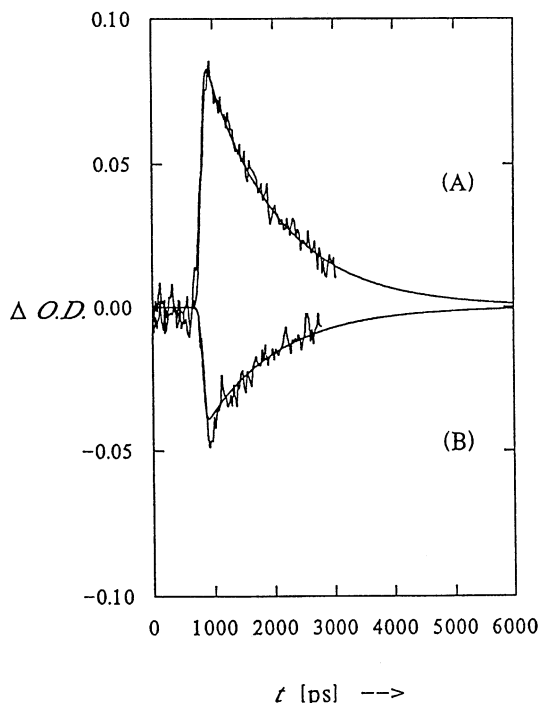


Fig. 6.A Changes in the transient absorption (ΔOD =change in absorption) of dpbpy complex **4** in toluene at 298 K monitored at 720 nm after excitation at 532 nm. **B** Transient bleach monitored at 600 nm after excitation at 532 nm. The *solid lines* represent a convolution of the instrument response function with a single exponential decay, where $\tau_{\text{obs}}=1.2$ ns for both data sets

dpbpy complex, nanosecond laser relaxation data were determined in the 110.5–198.1 K range for a 2-methyltetrahydrofuran solution and in the 153.3–298.0 K range for a toluene solution. In the 150–300 K range the relaxation rate data follows the Arrhenius law, $k_{\text{bvt}}=Ae^{-E_a/kT}$. The value of the activation energy E_a for the dpbpy complex was evaluated to be 856 cm^{-1} . At temperatures below 140 K the HS-Co^{II} to LS-Co^{III} interconversion relaxation rate deviates from the Arrhenius law. This relaxation rate tends to become temperature independent at these lower temperatures. It was concluded [12] that the valence tautomeric interconversions involve a quantum mechanical tunneling process as has been observed for Fe^{II} spin crossover complexes.

Adams and Hendrickson [12] showed that the valence tautomeric relaxation rate vs temperature data could be fit to the quantum tunneling rate law derived by Buhks and Jortner [23] as given in Eq. (1):

$$K=(2\pi/\hbar)g_f|H_{if}|^2G \quad (1)$$

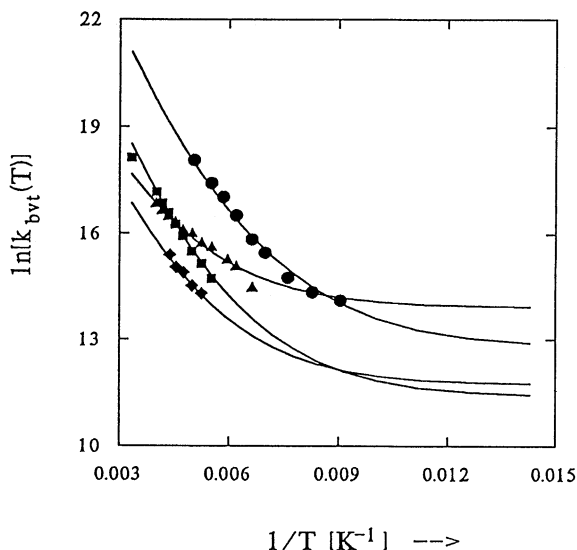


Fig. 7 Observed HS-[Co^{II}(SQ)₂(N-N)] to LS-[Co^{III}(SQ)(CAT)(N-N)] relaxation rates plotted as $\ln(k_{\text{bvt}})$ vs $1/T$ for complexes 1–4: (filled diamonds) [Co(3,5-DTBSQ)₂(phen)] in toluene; (filled squares) [Co(3,5-DTBSQ)₂(bpy)] in toluene; (open triangles) [Co(3,5-DTBSQ)₂(dmbpy)] in toluene; and (filled circles) [Co(3,5-DTBSQ)₂(dpbpy)]. In MTHF. The solid lines represent fits of the data to the Jortner equation Eq. (1)

The parameter g_f is the electronic degeneracy of the final state, i.e., $g_f(\text{HS-Co}^{\text{II}})=16$ and $g(\text{LS-Co}^{\text{III}})=4$. The thermally averaged Franck-Condon nuclear vibrational overlap factor G accounts for the contribution of solvent and metal-ligand vibrational modes. Figure 4 presents the important features of the theory in graphical form. Initially, the complex is, after photoexcitation and intersystem crossing, in the HS-Co^{II} state and has a Boltzmann population of oscillators all of which have the frequency ω . In Fig. 4, superimposed on each vibrational level is drawn the square of the vibrational wave function for that level. The complex tunnels from the HS-Co^{II} state to the LS-Co^{III} state, where the electronic energy of the HS-Co^{II} state is transformed into vibrational energy of the LS-Co^{III} state. In short, the HS-Co^{II} complex converts to a LS-Co^{III} complex by quantum mechanical tunneling not only at low temperatures, but also at room temperature. Figure 7 illustrates the fit of the relaxation rate data for four different valence tautomeric cobalt complexes. A temperature-independent tunneling is predicted for these complexes. Relaxation data need to be measured to low temperatures approaching liquid-helium temperature, in order to check this.

The HS-Co^{II} to LS-Co^{III} valence tautomeric interconversion is similar to the Fe^{II} spin cross-over interconversion. The single most prominent geometry changes for the Fe^{II} spin-crossover transformation and the valence tauto-

merism are the metal ligand bond length changes (Δr) of 0.16–0.22 Å. The cobalt complexes also present internal ligand geometry changes since an electron is transferred between the metal and ligand. The spin crossover relaxation process is thermally activated at elevated temperatures but at temperatures below ~140 K deviates from simple Arrhenius behavior and becomes temperature independent. This behavior is typical of a low temperature tunneling process. Likewise, the valence tautomeric process is thermally activated at high temperature, displaying similar activation energies (E_a) and preexponential factors (A) to Fe^{II} spin-crossover complexes. Furthermore the valence tautomeric relaxation begins to show deviations from Arrhenius behavior at ~140 K. Moreover, the observed relaxation rates of spin crossover and valence tautomerism are similar to within an order of magnitude.

Important work has elucidated some of the factors which modulate the rate of the Fe^{II} spin crossover interconversion. The large geometric changes, energy separations, and small values of the electronic coupling in spin crossover have been shown to be key factors which modulate the rate or spin crossover relaxation. Values for the rate of high-spin→low-spin crossover in solution at room temperature for Fe^{II} complexes that show thermally driven spin crossover are typically of the order of 10^6 – 10^8 s^{-1} . For the limited set of valence tautomeric complexes studied [12] the observed rates of back valence tautomerization are found to range from 10^7 to 10^8 s^{-1} . Since the geometric changes and energy separations in these valence tautomeric complexes are of similar magnitude and nature to Fe^{II} spin crossover complexes, it seems likely that the electronic coupling is of comparable magnitude. The small electronic coupling in these valence tautomeric complexes, however, likely results from fundamentally different origin. The electronic coupling between two states can conveniently be described by the electronic coupling matrix element (H_{if}) which is given as follows:

$$H_{if} = \langle \Psi_f | H | \Psi_i \rangle \quad (2)$$

where Ψ_i and Ψ_f correspond to the total electronic wave functions of the initial and final states and H is the total electronic Hamiltonian. Symmetry and spin restrictions are important factors in the evaluation of the extent of electronic coupling. The magnitude of H_{if} depends on the spin-multiplicity differences between initial and final states, the symmetry of the donor and acceptor orbitals of the initial and final electronic states, and the availability of electronic states that can mix with the donor and acceptor wavefunctions. The magnitude of H_{if} in spin crossover complexes is small since the Fe^{II} $^5\text{T}_2$ to $^1\text{A}_1$ spin crossover involves a $\Delta S=2$ transition and is formally spin forbidden and to first order $H_{if}=0$ (i.e., the $^5\text{T}_2$ and $^1\text{A}_1$ states are orthogonal). Consequently, for Fe^{II} spin crossover complexes the magnitude of H_{if} is dictated by a second order spin-orbit interaction through the intermediacy of a $^3\text{T}_1$ state:

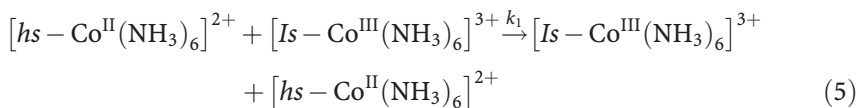
$$H_{if} = (\Psi_i | H_{SO} | \Psi_f) \quad (3)$$

Magnetic exchange coupling, however, in these cobalt valence tautomeric systems allows for a $\Delta S=0$ interconversion pathway and thus is formally spin-allowed. The HS-Co^{II} system is a magnetic exchanged coupled system having an $S=5/2$, two $S=3/2$, and an $S=1/2$ states in close energy proximity. The LS-Co^{III} tautomer is an $S=1/2$ system. The spin allowed valence tautomeric interconversion likely occurs through the $S=1/2$ state of the HS-Co^{II} tautomer. The cobalt valence tautomeric system is fundamentally a linked donor acceptor electron transfer system, where the molecular orbital symmetries of the donor and acceptor moieties are expected to influence the magnitude of H_{if} . The valence tautomeric interconversion from HS-Co^{II}(SQ)₂ to Co^{III}(SQ)(CAT) is an intramolecular electron transfer process and involves the initial transfer of an electron from the highest occupied HS-Co^{II} e_g^* donor orbital to the unoccupied π^* acceptor orbitals of the semiquinone ligands. Theoretical investigations of electronic coupling in electron transfer systems have shown that the magnitude of electronic coupling is approximated by the overlap in Eq. (4):

$$H_{if} \propto (\Psi_i | \Psi_f) \quad (4)$$

where Ψ_i and Ψ_f are the molecular orbitals of the initial and final states which donate and accept the electron, respectively. Density functional LACO electronic structure calculations [24] of cobalt valence tautomeric systems have shown the donor and acceptor orbitals to be orthogonal to each other and mixing has been shown to be negligible. Consequently H_{if} is not expected to be large. Such orbital symmetry restrictions have been shown to retard the rate of intramolecular electron transfer in linked Ru^{II}-Co^{III} systems. Since spin-restriction is likely lifted due to magnetic exchange coupling it is likely that an orbital symmetry restriction to back valence tautomerism is operative.

Another electron transfer system which has some similarities to the valence tautomeric system is the symmetric electron exchange reaction of hexaamminecobalt complexes in solution shown below. The study of the electron exchange in these systems has proved to be a long standing problem in coordination chemistry [25].



The rates of electron transfer in these complexes have been observed to be notoriously slow relative to analogous couples of other transition metal complexes such as Fe^{II}/Fe^{III} and Ru^{II}/Ru^{III}. In fact, relative to the hexamine-ruthenium complexes the bimolecular rate of electron transfer of the cobalt systems is $\sim 10^{13}$ times slower at room temperature.

4 Spectroscopic and Physical Measurements

Valence tautomeric complexes exhibit interesting spectroscopic and physical properties, and these can be briefly summarized for the series of complexes $[\text{Co}(\text{3,5-DTBSQ})(\text{"3,5-DTBQ"})]$, where "3,5-DTBQ" is either the semiquinone or catecholate form of the following ligands:

4.1 Magnetic Susceptibility

In addition to X-ray structural data, magnetic susceptibility measurements can be carried out to determine whether a given Co complex is of the HS-Co^{II} or $\text{LS-Co}^{\text{III}}$ form. Table 1 gives data [22] for six such complexes. From these data it can be concluded that at 300 K the dpbpy, dmbpy and bpy complexes are of the form of $[\text{Co}^{\text{III}}(\text{N-N})(\text{3,5-DTBSQ})(\text{3,5-DTBCAT})]$. They are low-spin Co^{III} complexes with one SQ^- ligand with a single unpaired electron. On the other hand, the phen, bpym and bpyz complexes have μ_{eff} values of 5.12, 5.08, and 4.01 μ_{B} at 300 K. These complexes are best described at 300 K as $[\text{Co}^{\text{II}}(\text{N-N})(\text{3,5-DTBSQ})_2]$ complexes with a high-spin Co^{II} exchange coupled to two $\text{S}=1/2$ SQ^- ligands. The variation in properties in this series reflects in part the changes in the reduction potentials for the series of diimine ligands.

Figure 8 shows the *solution* magnetic susceptibility data for four of the above complexes. The data were run for toluene solutions and are plotted as a fraction of the HS-Co^{II} tautomer vs temperature. These data can be fit (solid lines) assuming a simple equilibrium of $\text{HS-Co}^{\text{II}} \rightleftharpoons \text{LS-Co}^{\text{III}}$. The ΔH and ΔS values characteristic of these complexes were evaluated [12]. As with Fe spin crossover complexes, the valence tautomeric interconversion is entropy driven.

Table 1 Effective magnetic moments for polycrystalline samples of $[\text{Co}(\text{N-N})(\text{3,5-DTBSQ})(\text{"3,5-DTBQ"})]^{\text{a}}$

N-N Diiminium ligand	μ_{eff} (μ_{B})	
	100 K	300 K
dpbpy	1.84	2.00
dmbpy ^b	1.76	1.93
bpy ^b		1.92
phen ^c	1.73	5.12
bpym	4.04	5.08
bpyz	3.87	4.01

^a The ligand "3,5-DTBQ" is either the semiquinone or catecholate ligand depending on the diiminium ligand and the temperature

^b Crystallizes with $\cdot 1/2(\text{C}_6\text{H}_5\text{CH}_3)$ solvate

^c Crystallizes with $\cdot (\text{C}_6\text{H}_5\text{CH}_3)$ solvate

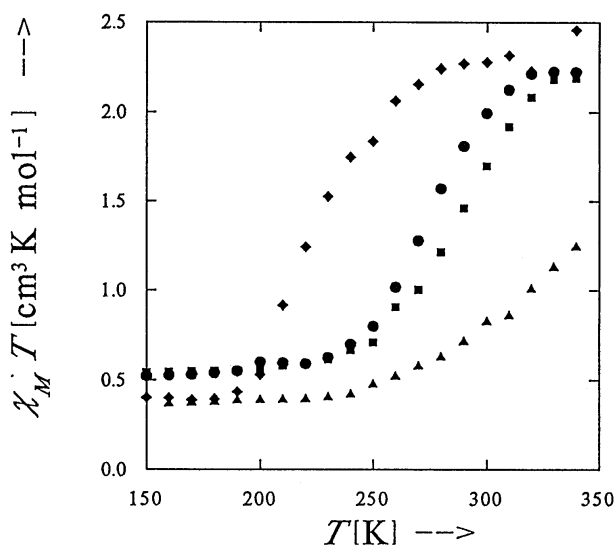


Fig. 8 Plots of the product $\chi_M T$ vs temperature evaluated from solution magnetic susceptibility data for: (filled diamonds) $[\text{Co}(\text{3,5-DTBSQ})_2(\text{phen})]$; (filled circles) $[\text{Co}(\text{3,5-DTBSQ})_2(\text{bpy})]$; (filled squares) $[\text{Co}(\text{3,5-DTBSQ})_2(\text{dmbpy})]$; and (open triangles) $[\text{Co}(\text{3,5-DTBSQ})_2(\text{dpbpy})]$. The solid lines represent fits of the data to a simple equilibrium

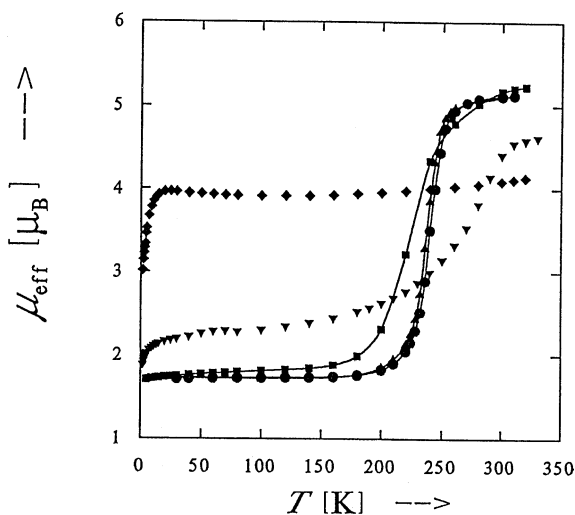


Fig. 9 Plots of the effective magnetic moment (μ_{eff}) vs temperature for the following complexes: (filled diamonds) $[\text{Co}(\text{phen})(\text{3,5-DTBSQ})_2]$ recrystallized from methylcyclohexane; (filled squares) $[\text{Co}(\text{phen})(\text{3,5-DTBSQ})_2] \cdot \text{C}_6\text{H}_5\text{Cl}$; (filled circles) increasing temperature; (filled triangles) decreasing temperature $[\text{Co}(\text{phen})(\text{3,5-DTBSQ})_2] \cdot \text{C}_6\text{H}_5\text{CH}_3$; (filled upside down triangles) a sample of $[\text{Co}(\text{phen})(\text{3,5-DTBSQ})_2] \cdot \text{C}_6\text{H}_5\text{CH}_3$ which was heated at 70°C under vacuum for 12 h

Variable-temperature magnetic susceptibility data have also been determined for polycrystalline samples of these Co complexes. Data for different forms of the phen complex are illustrated in Fig. 9. The sample recrystallized from methylcyclohexane remains as a HS-Co^{II} complex from 330 to 4 K. The toluene solvate crystals abruptly change from LS-Co^{III} to HS-Co^{II} in the 220–260 K region. The chlorobenzene solvate shows a more gradual transformation, taking over 100 degrees for completion. Finally, when toluene solvate molecules are pumped off the crystals an even more gradual transformation is observed. Solid-state ²H NMR data [26] show that there is an order-disorder phase transition involved in the abrupt conversion of the toluene solvate. The solvate molecules suddenly convert from static to dynamic in the crystals in the temperature range of the valence tautomerism interconversion.

4.2

Electronic Absorption Spectra

There are several spectroscopic techniques that can be used to monitor the valence tautomeric interconversions. Electron paramagnetic resonance and infrared spectroscopy have been employed, but electronic absorption spectroscopy gives more quantitative data. Typical data are shown in Fig. 10 for the dpbpy Co complex. It can be seen that the electronic absorption spec-

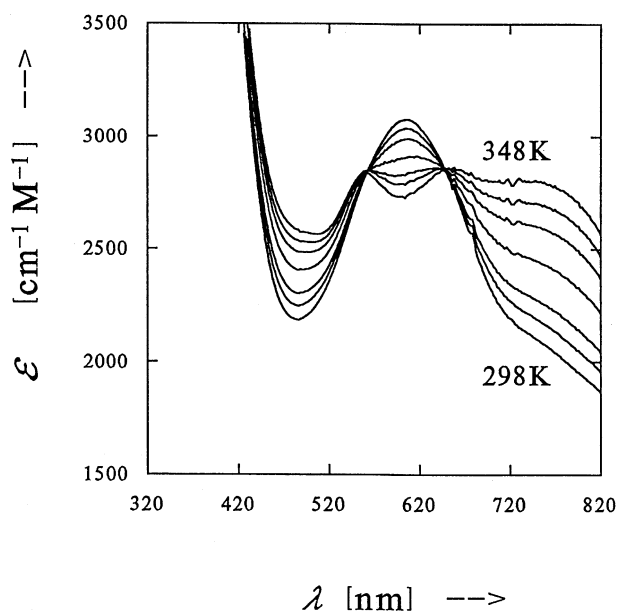


Fig. 10 Temperature dependence of the electronic absorption spectrum of a toluene solution of [Co(3,5-DTBSQ)(3,5-DTBCAT)(dpbpy)] obtained at 298, 303, 308, 318, 328, and 348 K. The molar extinction coefficient ϵ plotted vs the wavelength λ

trum changes in response to a change in temperature. At room temperature there is a band at 600 nm that is characteristic of the Co^{III} tautomer. As the temperature of the toluene solution is increased from 298 to 348 K the intensity of the 600 nm band decreases, while a band at 770 nm increases in intensity. This 770 nm band is characteristic of the Co^{II} tautomer, which also shows bands at ~ 655 and ~ 560 nm. The presence of isosbestic points indicates there are two different species present. The observed molar extinction coefficients (ϵ) are greater than $2500 \text{ M}^{-1} \text{ cm}^{-1}$ and indicates the transitions are of the charge-transfer type.

The Co^{III} tautomer also shows an absorption band in the near-IR region at about 2500 nm. This band is a mixed-valence intervalence charge transfer (IT) band involving excitation of an electron from the CAT^{2-} to the SQ^- ligand of the $[\text{Co}^{\text{III}}(\text{CAT})(\text{SQ})(\text{N}-\text{N})]$ complex.

5

Valence Tautomerism in Cobalt-Quinone Complexes Containing Various N-Donor Ancillary Ligands

It has been possible to prepare complexes of general form $\text{Co}(\text{N-donor})_2(\text{DBSQ})_2$ with a wide variety of ancillary nitrogen donor ligands and with both the 3,5-DBSQ and 3,6-DBSQ ligands. Complexes of both quinone

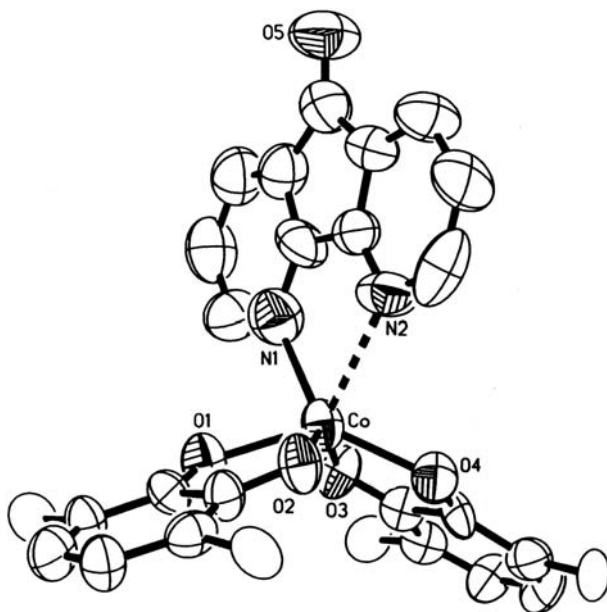


Fig. 11 View of trigonal prismatic $[\text{Co}^{\text{II}}(\text{diazfluorenone})(3,6\text{-DBSQ})_2]$

ligands exhibit valence tautomerism. The temperature range of the equilibrium between redox isomers has been found to be strongly dependent on N-donor effects. It has been possible to form complexes that have transition temperatures at either end of the temperature range for convenient experimental observation. For example, $[\text{Co}^{\text{III}}(\text{Ph}_2\text{bpy})(3,5\text{-DBSQ})(3,5\text{-DBCat})]$ and $[\text{Co}^{\text{III}}(\text{tmeda})(3,6\text{-DBSQ})(3,6\text{-DBCat})]$ show signs of transition to the $\text{Co}(\text{II})$ redox isomer at temperatures above 320 K, while $[\text{Co}^{\text{II}}(\text{NO}_2)_2\text{bpy})(3,6\text{-DBSQ})_2]$ and $[\text{Co}^{\text{II}}(\text{tmpda})(3,6\text{-DBSQ})_2]$ undergo transition to the $\text{Co}(\text{III})$ isomer at temperatures below 200 K [12, 27, 28]. Several of the HS- $\text{Co}(\text{II})$ redox isomers have been found to have trigonal prismatic structures in the solid state (Fig. 11) [27]. These complexes contain 3,6-DBSQ ligands, with the 5,5'-dinitro-2,2'-bipyridine, 5-nitrophenanthroline, and diazafluorenone ancillary ligands. The TP geometry is disfavored for LS- $\text{Co}(\text{III})$, and, in the solid state, these complexes fail to show a change in charge distribution at low temperature. *Trans* isomers have been prepared with pyridine, *trans*- $[\text{Co}^{\text{III}}(\text{py})_2(3,6\text{-DBSQ})(3,6\text{-DBCat})]$ [29], and with pyrazine, *trans*- $[\text{Co}^{\text{III}}(\mu\text{-pyz})(3,6\text{-DBSQ})(3,6\text{-DBCat})]_n$ [30], with the result that the change in geometry, from *cis* to *trans*, has little effect on VT. The 200 degree separation in transition temperature for $[\text{Co}^{\text{III}}(\text{tmeda})(3,6\text{-DBSQ})(3,6\text{-DBCat})]$ and $[\text{Co}^{\text{II}}(\text{tmpda})(3,6\text{-DBSQ})_2]$ is striking, Fig. 12, given the difference of one

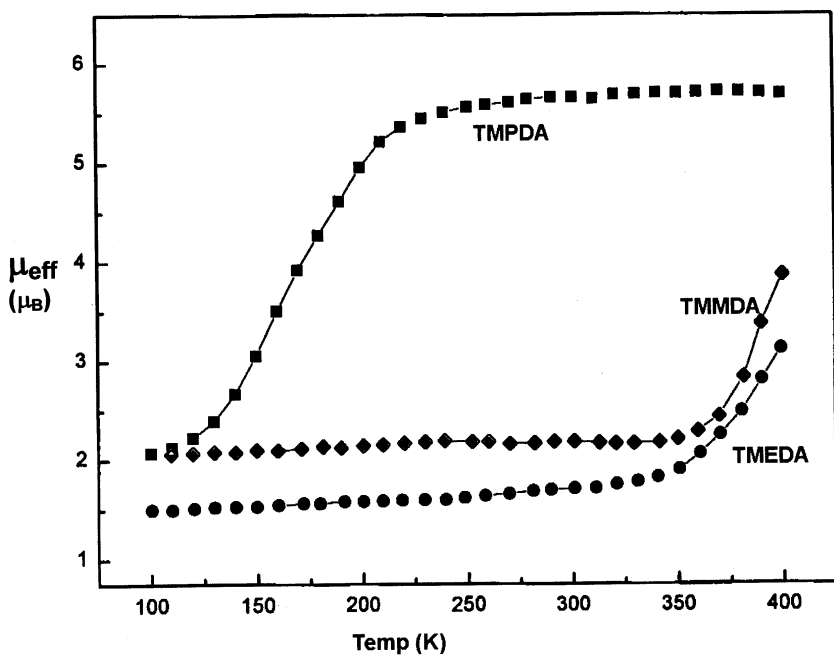


Fig. 12 Temperature-dependent magnetic data for complexes of the $[\text{Co}(\text{Me}_2\text{N}(\text{CH}_2)_n\text{NMe}_2)(3,6\text{-DBQ})_2]$ series, where $n=1$ is tmmda, $n=2$ is tmeda, and $n=3$ is tmpda

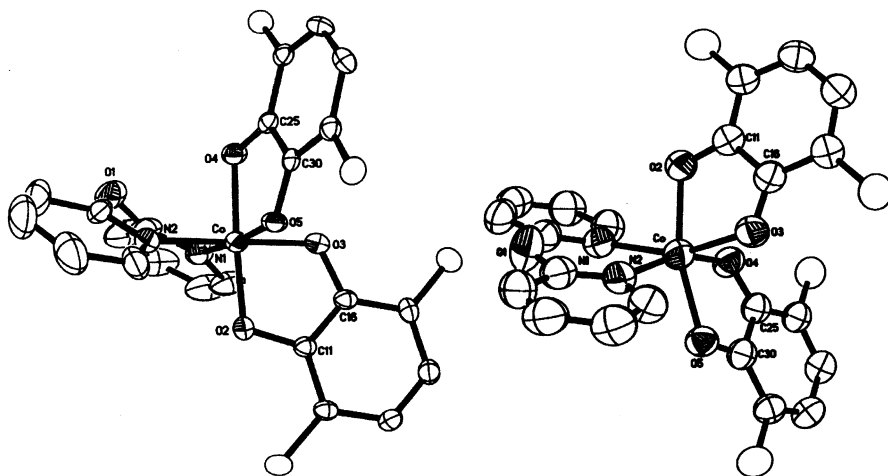
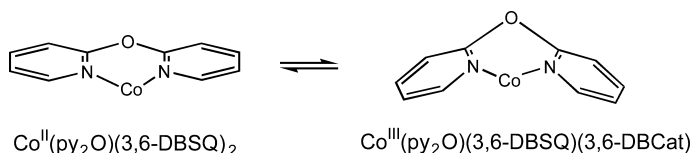


Fig. 13 View showing the folded structure of the py_2O ligand in $[\text{Co}^{\text{III}}(\text{py}_2\text{O})(3,6\text{-DBSQ})(3,6\text{-DBCat})]$ (left) and the planar structure in $[\text{Co}^{\text{II}}(\text{py}_2\text{O})(3,6\text{-DBSQ})_2]$. Both structure determinations were carried out at room temperature. Crystals of the Co(III) redox isomer were obtained from acetone solution, crystals of the Co(II) isomer were grown in toluene. Neither of the crystals was found to be solvated

methylene group in the N-donor chelate ring [28]. Donation properties of the nitrogen atoms are the same for the two complexes, and the large difference in transition temperature is thought to result from an entropic effect associated with the increase in conformational flexibility for the six-membered chelate ring.

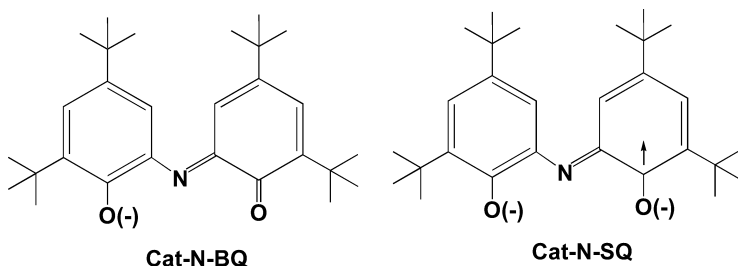
With interests in switching applications, complexes that show hysteresis in the forward and reverse electron transfer steps have been studied. The bis(pyridine)ether ligand is known to be able to adjust chelate ring dimensions by coordinating with metal ions in either planar or folded structures. Structural characterization on $[\text{Co}^{\text{II}}(\text{py}_2\text{O})(3,6\text{-DBSQ})_2]$, Fig. 13, has shown that with the relatively large radius of HS-Co(II), the py_2O ligand is planar, while for the $[\text{Co}^{\text{III}}(\text{py}_2\text{O})(3,6\text{-DBSQ})(3,6\text{-DBCat})]$ redox isomer, with Co-N bond lengths that are roughly $0.2 \text{ \AA}$ shorter, the ligand is in a folded structure [31].



The planar/folded change in structure for the py_2O ligand contributes to a large hysteresis in the forward and reverse electron transfer steps. It has been possible to structurally characterize both redox isomers in the solid

state at the same temperature for crystals formed under slightly different conditions of recrystallization [31].

Observations on valence tautomerism for the quinone complexes of cobalt are centered about thermodynamic changes that result from the transfer of charge to and from antibonding orbitals directed at ligands, the $d\sigma e_g$ orbitals of the octahedral complex. *tert*-Butyl substituents of the ligands encapsulate the complex, reducing, but not eliminating, solvent effects. All complexes of cobalt that have been reported to exhibit VT have been prepared with either 3,5- or 3,6-di-*tert*-butylcatecholate or semiquinonate ligands. Dei has observed VT for a cobalt complex containing a ligand obtained by Schiff base condensation of two 3,5-DBCat ligands with ammonia [32]. As with the quinones, the tridentate ligand resulting from condensation may exist in several charged forms. The two forms that appear most commonly are the Cat-N-BQ anion and the Cat-N-SQ radical dianion [33].



Structural, spectral, electrochemical, and magnetic properties of this complex, Fig. 14, have indicated that in the solid state at room temperature the metal is Co(III) as a complex containing mixed charge ligands, [Co (Cat-N-BQ)(Cat-N-SQ)] [33]. Dei has reported spectral changes in toluene solution over the temperature range between 295 and 360 K that have been interpreted as indicating an equilibrium between Co(III) and Co(II) redox isomers, similar to the VT equilibria of the [Co(N-N)(SQ)(Cat)] series [32].

Neuwahl and Dei have recently described the results of photoexcitation experiments on $[\text{Co}^{\text{II}}(\text{Me}_4\text{cyclam})(3,5\text{-DBSQ})]^+$ with resolution on the femtosecond time scale [34]. Excitation was carried out at 400 nm, close to a transition at 402 nm assigned as a MLCT with the objective of resolving steps in the transition from HS- $\text{Co}^{\text{II}}(\text{SQ})$ to LS- $\text{Co}^{\text{III}}(\text{Cat})$. Two sequential steps were resolved, one on the 140–200 fs time scale, and a second on the time scale of several picoseconds. The second step was associated with the appearance of a transition at 650 nm that is associated with the diamagnetic $[\text{Co}^{\text{III}}(\text{Me}_4\text{cyclam})(3,5\text{-DBCat})]^+$ redox isomer. The form of the short-lived intermediate species is unclear, but it may be either a LS- $\text{Co}^{\text{II}}(\text{SQ})$ or HS- $\text{Co}^{\text{III}}(\text{Cat})$ species formed upon initial excitation, leading to the LS- $\text{Co}^{\text{III}}(\text{Cat})$ product.

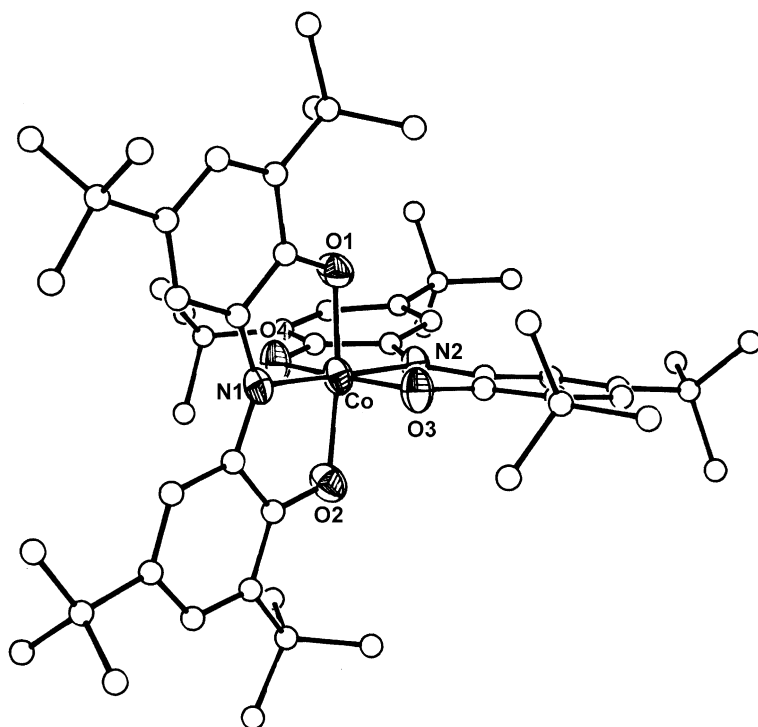


Fig. 14 View of the $[\text{Co}^{\text{III}}(\text{Cat-N-BQ})(\text{Cat-N-SQ})]$ molecule

In 1996 Hashimoto and coworkers described a unique photomagnetic effect for a cobalt-iron cyanide Prussian blue, $\text{C}_x[\text{Co}_4[\text{Fe}(\text{CN})_6]_y] \cdot n\text{H}_2\text{O}$ [35]. The effect is associated with a $\text{LS-Fe}^{\text{II}} \rightarrow \text{LS-Co}^{\text{III}}$ electron transfer that gives a ferrimagnetic $\text{Fe}^{\text{III}}\text{-C}\equiv\text{N-Co}^{\text{II}}$ product containing LS-Fe(III) and HS-Co(II) . The process is similar to the $\text{Cat} \rightarrow \text{Co(III)}$ electron transfer step that occurs for systems that exhibit VT, with LS-Fe(II) as the electron donor in place of the catecholate ligand. Subsequent study of these compounds by Hashimoto and Verdager has emphasized the importance of solid-state effects associated with cation and hydrate composition that provide lattice flexibility to accommodate the changes in bond length at the cobalt center [36, 37]. Hashimoto has assigned a transition at 550 nm as the symmetry forbidden $\text{Fe}^{\text{II}}(t_{2g}) \rightarrow \text{Co}^{\text{III}}(e_g)$ MM'CT transition across the cyanide bridge within an "efficient $\text{Fe}^{\text{II}}\text{-C}\equiv\text{N-Co}^{\text{III}}$ pair" that leads to the change in charge distribution and cobalt spin state [36, 38]. Both Hashimoto and Verdager have studied photoinduced magnetization by irradiating samples at low temperature while monitoring magnetic properties [36, 39]. Light sources with energies extending across the visible region have been used to affect electron transfer, and the process has been observed to be thermally reversible.

6

Valence Tautomerism in Copper-Quinone Complexes

Copper complexes containing quinone ligands may exist in the form of two isoelectronic redox isomers, $[L_nCu^{II}(Cat)]$ and $[L_nCu^I(SQ)]$. Charge distribution is defined by the donor properties of the ancillary ligands [40]. Phosphine ligands result in a $Cu^I(SQ)$ charge distribution with a tetrahedral coordination geometry and a complicated radical EPR spectrum containing hyperfine coupling with the ^{31}P , $^{63,65}Cu$, and semiquinone ring protons. Hard nitrogen donor ligands increase valence orbital energy of the metal resulting in a shift in charge distribution to the $[(N\text{-donor})_2Cu^{II}(Cat)]$ redox isomer. Four coordinate complexes of $Cu(II)$ are generally square planar, although tetrahedral structures are known, and, in this redox isomer, spin is concentrated on the metal resulting in EPR spectral anisotropy and strong $^{63,65}Cu$ hyperfine coupling [40]. It has been of interest to prepare copper-quinone complexes at the point where metal and quinone orbital energies are balanced so that shifts in charge distribution may be induced thermally. Structural characterization on d^{10} $[(Ph_3P)_2Cu^I(SQ)]$ and d^9 $[(bpy)Cu^{II}(Cat)]$ complexes indicate that the Cu-O bond length of the $Cu(I)$ isomer is roughly 0.15 Å longer than values observed for $Cu(II)$ redox isomers. Changes in entropy and enthalpy that define transition temperature for the complexes of cobalt may result in temperature-dependent equilibria for $[L_nCu^{II}(Cat)]$ and $[L_nCu^I(SQ)]$ redox isomers. The strong preference of $Cu(I)$ for a tetrahedral geometry and the tendency for $Cu(II)$ to form planar complexes may present a barrier to electron transfer, but the significance of this effect is undetermined. Observations by Dooley and coworkers on EPR spectra for the reduced Cu-topaquinoxone (TPQ) site of amine oxidase indicated a change in hyperfine coupling that would be consistent with an equilibrium between $Cu^I(TPQ^{SQ})$ and $Cu^{II}(TPQ^{Cat})$ species for the reduced and radical semiquinone forms of TPQ [41]. The reduced $Cu(I)$ center provides a site for dioxygen binding in the mechanism for oxidation to the active form of the enzyme.

Observations on equilibria between Cu-quinone redox isomers have been demonstrated in recent publications. Abakumov described observations on the solvent-dependent EPR spectra of a $[(N\text{-}N)Cu(Cat)]$ complex prepared with 4-chloro-3,6-di-*tert*-butylcatechol and with di-*tert*-butyl-1,4-diazabutadiene as the ancillary ligand [42]. Changes in EPR spectrum were interpreted as indicating the existence of an equilibrium mixture of redox isomers. However, crystallographic characterization indicated that the complex consisted of separate $[Cu^I((t\text{-}Bu)_2C_2H_2)_2]^+$ cations and $[Cu^{II}(SQ)(Cat)]^-$ anions [43]. In early work we had found, by EPR, that a bidentate phosphorus-nitrogen ligand gave only $[(P\text{-}N)Cu^I(3,5\text{-}DBSQ)]$ species [39], but, recently, Kaim described temperature-dependent shifts in the EPR spectrum of a copper complex of 3,5-di-*tert*-butylcatechol containing a nitrogen-sulfur coli-

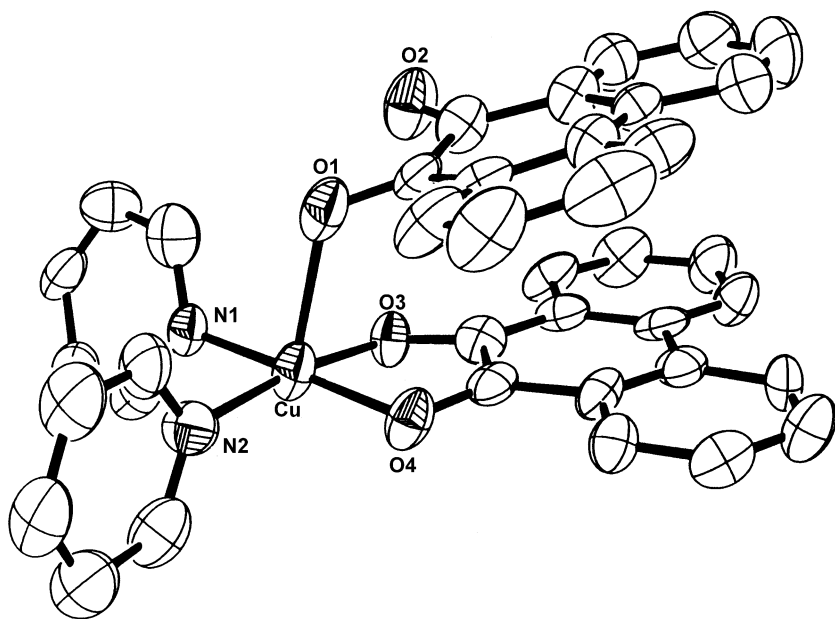


Fig. 15 View of the $[\text{Cu}^{\text{II}}(\text{py})_2(\text{PhenCat})(\text{PhenBQ})]$ molecule

gand [45]. We recently published the results of an investigation on copper complexes of 9,10-phenanthrenequinone that exhibit the equilibrium between redox isomers associated with valence tautomerism [46]. This observation is significant not only as an example of VT for a copper-quinone system, but it is the first complex of any metal to show VT for a quinone ligand that is not of the DBBQ family.

Metallic copper reacts with 9,10-phenanthrenequinone (PhenBQ) and pyridine to give $[(\text{py})_2\text{Cu}(\text{PhenQ})_2]$ [47]. Crystallographic characterization, Fig. 15, has shown that the copper is square pyramidal with pyridine and 9,10-phenanthrenediolate (PhenCat) ligands coordinated in the basal plane. An unreduced PhenBQ ligand is weakly coordinated through one quinone oxygen at the apical site and paired with the planar PhenCat ligand. Optical spectra indicate that the benzoquinone ligand dissociates in solution, and EPR spectra recorded on solid samples of $[(\text{py})_2\text{Cu}^{\text{II}}(\text{PhenCat})(\text{PhenBQ})]$ show that spin is localized on the metal as a complex of $\text{Cu}(\text{II})$. EPR spectra recorded on the complex in solution show dependence upon both solvent and temperature, Fig. 16. In pyridine solution, spectral changes show the existence of an equilibrium between $\text{Cu}^{\text{II}}(\text{Cat})$ and $\text{Cu}^{\text{I}}(\text{SQ})$ species with a clear shift in the magnitude of copper hyperfine coupling with a change in paramagnetic center from metal to ligand at higher temperatures [47]. As toluene is added to a pyridine solution the temperature range of the equilibrium drops, and in 10:1 toluene/pyridine glass the equilibrium appears with a

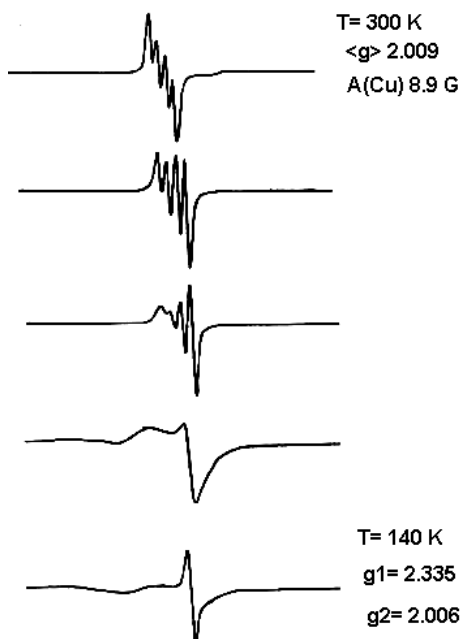


Fig. 16 Temperature-dependent changes in the EPR spectrum of $[\text{Cu}(\text{py})_2(\text{PhenQ})]$ with the shift in charge distribution from $[\text{Cu}^{\text{I}}(\text{py})_2(\text{PhenSQ})]$ (top), to $[\text{Cu}^{\text{II}}(\text{py})_2(\text{PhenCat})]$ (bottom)

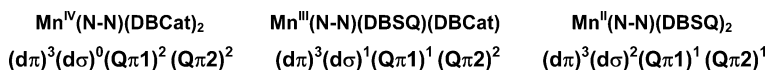
transition temperature just above 77 K. Since there is little mobility in the glass, copper-quinone ET occurs intramolecularly as an equilibrium between $[(\text{py})_2\text{Cu}^{\text{II}}(\text{PhenCat})]$ and $[(\text{py})_2\text{Cu}^{\text{I}}(\text{PhenSQ})]$ redox isomers.

These observations show that VT is possible for metal-quinone ligand combinations other than the Co-DBQ systems studied in initial projects. Together with observations by Dooley on the amine oxidase copper-TPQ center, VT may occur as a general property of metal-quinone systems, including systems of bioinorganic interest.

7

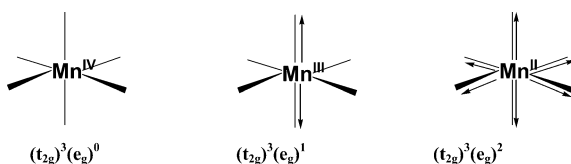
Valence Tautomerism in Manganese-Quinone Complexes

Manganese commonly forms complexes as hs-d^5 Mn(II) and hs-d^4 Mn(III), and less commonly as d^3 Mn(IV).



Changes in occupancy of $d\sigma$ orbitals follow the pattern of HS-Co(II), LS-Co(II), and LS-Co(III), and the quinone complexes of manganese exhibit valence tautomerism [3]. Octahedral complexes of each Mn ion typically have structural features characteristic of charge and d-configuration. Consequently, the quinone complexes of manganese have been of interest in extending the scope of VT to new metal ions, and structural investigations have provided insight on charge distribution. Octahedral d^3 Mn(IV) with high positive charge and an unpopulated $d\sigma$ level forms strong bonds with O- and N-donor ligands. This high oxidation state is generally observed for complexes containing O-donor ligands that provide charge to the metal through strong π -donation. Alkoxo and catecholate ligands are strong π donors, and $[\text{Mn}^{\text{IV}}(3,5\text{-DBCat})_3]^{2-}$ was one of the early examples of Mn(IV) [48]. It resembles LS-Co(III) in forming complexes with strong metal-ligand bonds, and with a rigidly octahedral geometry. In its coordination properties, Mn(II) is the antithesis of Mn(IV). It is generally high-spin with a $t_{2g}^3 e_g^2$ configuration. Two electrons are directed at ligand bonding sites similar to HS-Co(II), and the Mn(II) ion has a flexible coordination geometry. The reaction between $[\text{Mn}_2(\text{CO})_{10}]$ and 3,5-DBBQ was found to give the $[\text{Mn}^{\text{II}}(3,5\text{-DBSQ})_2]_4$ tetramer [49], with a structure very similar to that of the related Co(II) tetramer [9]. Similarities between Mn(IV) with Co(III) and Mn(II) with Co(II) are clear; the intermediate oxidation state of manganese, Mn(III) is obviously different. However, even this ion with its $t_{2g}^3 e_g^1$ configuration resembles the LS-Co(II) ion ($t_{2g}^3 e_g^1$) that is formed upon ET to LS-Co(III) prior to spin transition as a short-lived intermediate.

The addition of pyridine to $[\text{Mn}^{\text{II}}(3,5\text{-DBSQ})_2]_4$ was found to give *trans*- $[\text{Mn}^{\text{IV}}(\text{py})_2(3,5\text{-DBCat})_2]$, Fig. 2, and related reactions carried out with 3,6-DBBQ have been used to form $[\text{Mn}^{\text{IV}}(2,2'\text{-bpy})(3,6\text{-DBCat})_2]$ and *trans*- $[\text{Mn}^{\text{IV}}(\text{Bu-py})_2(3,6\text{-DBCat})_2]$ [11, 29, 50]. Bond lengths to the Mn centers in all three molecules are short, and of values expected for Mn(IV). Studies on polymeric complexes have produced the pyrazine-bridged polymer $[\text{Mn}^{\text{III}}(\mu\text{-pyz})(3,6\text{-DBSQ})(3,6\text{-DBCat})]_n$, the *trans*- $[\text{Mn}^{\text{III}}(4,4'\text{-bpy})_2(3,6\text{-DBSQ})(3,6\text{-DBCat})]$ monomer, and *trans*- $[\text{Mn}^{\text{III}}(\text{thf})_2(3,6\text{-DBSQ})(3,6\text{-DBCat})]$ as a potential polymer precursor [50–52]. Bond lengths to the metals in each case show axial lengthening as a signature of the tetragonally distorted Mn(III) ion. As with the complexes of Co, weak N-donor ligands lead to Mn(II). This was found for $[\text{Mn}^{\text{II}}(3,5\text{-DBSQ})_2]_4$ where weak bridging interactions from SQ oxygens link adjacent Mn(II) centers that are nearly five-coordinate [11], and for $[\text{Mn}^{\text{II}}(\text{NO}_2\text{-phen})(3,6\text{-DBSQ})_2]$ where long Mn-O and Mn-N distances and a trigonal prismatic coordination geometry indicate HS-Mn(II) [50]. With this series of complexes coligand-dependent shifts in Mn-quinone charge distribution have been defined, pointing to the existence of three stable redox isomers:



Observations on VT for the complexes of Mn have been made from electronic spectral changes in solution and in the solid state. Changes in magnetism that occur with shifts in charge distribution have not been of use in the Mn series because the $\text{Mn}^{\text{IV}}(\text{Cat})_2$, $\text{Mn}^{\text{III}}(\text{SQ})(\text{Cat})$, and $\text{Mn}^{\text{II}}(\text{SQ})_2$ redox isomers all have $S=3/2$ spin ground states due to antiferromagnetic Mn-SQ coupling [50]. Observations on changes in optical spectra are complicated by the appearance of a strong Cat $\rightarrow$ Mn LMCT band at 880 nm that results in spectral similarity in the visible region for the $[(\text{N-donor})_2\text{Mn}^{\text{IV}}(\text{Cat})_2]$ and $[(\text{N-donor})_2\text{Mn}^{\text{III}}(\text{SQ})(\text{Cat})]$ redox isomers. Changes in the intensity of a low-energy LL'CT transition between Cat and SQ ligands of the $\text{Mn}^{\text{III}}(\text{SQ})(\text{Cat})$ isomer in the 2000–2200 nm region have permitted observations on VT in the solid state. Electronic spectra of the $\text{Mn}^{\text{II}}(\text{SQ})_2$ redox isomers consist of relatively weak transitions at 420 and 750 nm. Observations on the shift from the Mn(III) isomer to Mn(II) are best observed in the solid state as a decrease in intensity in the 2100 nm region with increasing temperature, and the shift from Mn(IV) to Mn(III) as an intensity increase in this region [50, 52].

Initial observations on VT for the Mn complexes came from the solution behavior of $[\text{Mn}^{\text{IV}}(\text{py})_2(3,5\text{-DBCat})_2]$ [11]. Reversible changes in color, from the intense red-purple of $[\text{Mn}^{\text{IV}}(\text{py})_2(3,5\text{-DBCat})_2]$ and $[\text{Mn}^{\text{III}}(\text{py})_2(3,5\text{-DBSQ})(3,5\text{-DBCat})]$ to the pale green-brown of $[\text{Mn}^{\text{II}}(\text{py})_2(3,5\text{-DBSQ})_2]$ pointed to an equilibrium similar to that of $[\text{Co}(\text{bpy})(3,5\text{-DBSQ})(3,5\text{-DBCat})]$. In subsequent studies, solid state spectra recorded on *trans*- $[\text{Mn}^{\text{IV}}(\text{Bu-py})_2(3,6\text{-DBCat})_2]$ at the temperature used for crystallographic characterization showed the expected transitions at 520 and 880 nm for the Mn(IV) redox isomer, but a weak transition at 2123 nm [29]. The intensity of this low energy transition was observed to increase reversibly with increasing temperature with the shift to the Mn(III) isomer. Similar observations have been made for $[\text{Mn}^{\text{IV}}(2,2'\text{-bpy})(3,6\text{-DBCat})_2]$ in the solid state indicating a shift to $[\text{Mn}^{\text{III}}(2,2'\text{-bpy})(3,6\text{-DBSQ})(3,6\text{-DBCat})]$. In toluene solution at room temperature both complexes give spectra of the Mn(II) isomer and show a return to the intense red-purple color of Mn(III) (or Mn(IV)) upon cooling in liquid N_2 [50–52].

Observations on shifts from the Mn(III) to the Mn(II) redox isomer in the solid state have been made for both $[\text{Mn}^{\text{III}}(4,4'\text{-bpy})_2(3,6\text{-DBSQ})(3,6\text{-DBCat})]$ and the $[\text{Mn}^{\text{III}}(\mu\text{-pyz})(3,6\text{-DBSQ})(3,6\text{-DBCat})]_n$ polymer [50, 52]. Intense Cat $\rightarrow$ SQ transitions appear at 2170 and 2090 nm, respectively, for the compounds in the solid state. The intensities of both transitions were observed to decrease with increasing temperature, as would accompany the

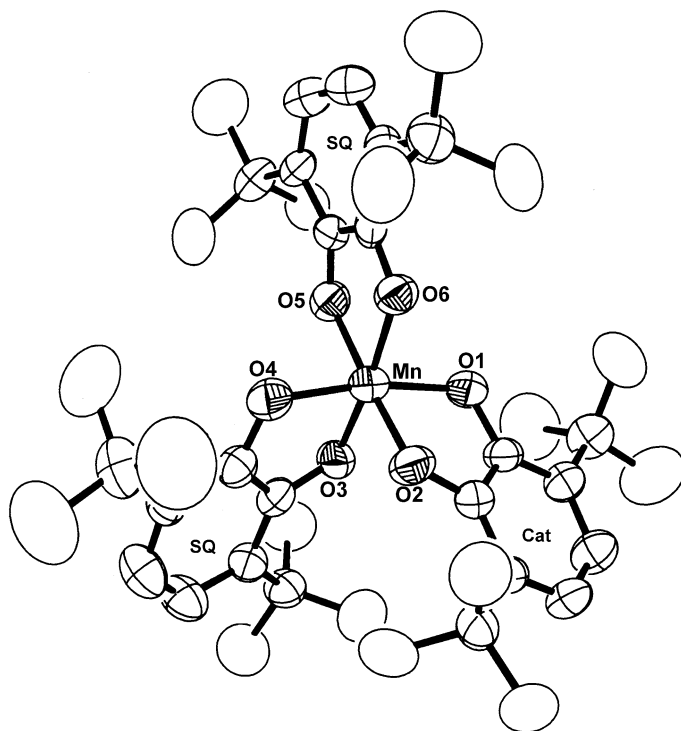


Fig. 17 View of the $[\text{Mn}^{\text{IV}}(3,6\text{-DBSQ})_2(3,6\text{-DBCat})]$ molecule

shift to the Mn(II) isomer. Magnetic measurements recorded on samples of all three redox isomers show a slight temperature dependence, with magnetic moment dropping from a value near $4.0 \mu_{\text{B}}$ at temperatures near room temperature to approximately $3.7 \mu_{\text{B}}$ at 25 K. In no case was there an abrupt change in magnetic moment associated with an isomeric shift, as for the Co complexes.

Spectral changes that occur in solution and in the solid state for the Mn quinone complexes indicate a two-step shift in charge distribution that follows the pattern of effects of weakened M-L bonds with population of the $d\sigma$ orbital proposed to account for observations on the Co series. An important difference with Mn lies in the relative stability of the Mn(III) redox isomer compared with the LS-Co(II) isomer that rapidly undergoes spin transition to HS-Co(II). Otherwise, Co equilibria would occur in separate observable ET and ST steps.

As with Co, it has been of interest to extend observations on VT to complexes other than members of the $[\text{Mn}(\text{N-N})(\text{DBQ})_2]$ series. Dei has reported that $[\text{Mn}(\text{CTH})(3,5\text{-DBQ})]^+$ may be isolated in the solid state in the form of green $[\text{Mn}^{\text{III}}(\text{CTH})(3,5\text{-DBCat})]^+$ and yellow $[\text{Mn}^{\text{II}}(\text{CTH})(3,5\text{-DBSQ})]^+$ re-

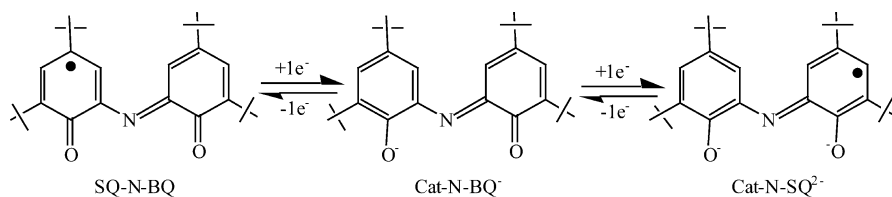
dox isomers [53]. Thermal equilibria were observed for the compound in the solid state and in solution. We have reported that while the reaction between $\text{Mn}_2(\text{CO})_{10}$ and 3,5-DBBQ gives the $[\text{Mn}^{\text{II}}(3,5\text{-DBSQ})_2]_4$ tetramer, reactions carried out with 3,6-DBBQ give $[\text{Mn}(3,6\text{-DBQ})_3]$ [51]. Structural and spectral characterization of the complex in the solid state at room temperature are consistent with a $[\text{Mn}^{\text{IV}}(3,6\text{-DBSQ})_2(3,6\text{-DBCat})]$ charge distribution, Fig. 17. The complex exhibits an intense transition at 2300 nm in accord with the mixed-charge ligand formulation. Spectral changes that occur in the solid state with increasing temperature have been interpreted as indicating a shift to the $[\text{Mn}^{\text{III}}(3,6\text{-DBSQ})_3]$ redox isomer. This electronic form of the complex resembles $[\text{Co}^{\text{III}}(3,6\text{-DBSQ})_3]$, extending the similarity between Co and Mn in their quinone coordination chemistry.

8

Dual Mode Valence Tautomerism

Cobalt valence tautomeric complexes can be interconverted in solution or in the solid state by means of different external stimuli such as temperature, pressure [54], or irradiation between a high-spin $[\text{Co}^{\text{II}}(\text{SQ})_2(\text{N-N})]$ or a low-spin $[\text{Co}^{\text{III}}(\text{Cat})(\text{SQ})(\text{N-N})]$ form with appreciable changes in electronic absorption spectra and magnetic properties. Recently, Ruiz et al. [55] showed that it is possible to electrochemically reduce each of the above complexes to give the $[\text{Co}^{\text{II}}(\text{SQ})(\text{Cat})(\text{N-N})]^-$ and $[\text{Co}^{\text{III}}(\text{Cat})_2(\text{N-N})]^-$ species, respectively. It was quite interesting to find that these two singly-reduced monoanionic complexes are also involved in a valence tautomerism. In this manner it was possible to establish a “dual-mode switching array”, as depicted in Fig. 18. There are four different forms of the complex that are in equilibrium. Switching between the four forms is possible by means of temperature and electrochemistry.

Even more recently Ruiz-Molina et al. [56] showed that such a dual-mode switching array could be constructed for a cobalt complex where an oxidation process was employed. In this case the interesting ligand ((2-hydroxy-3,5-di-*tert*-butyl-1-phenyl)imino)-3,5-di-*tert*-butyl-1,2-benzoquinone ligand was employed. This ligand has the following redox states:



Very recently, these same workers [57] showed that a switching array could be constructed employing $[\text{Mn}^{\text{IV}}(\text{Cat-N-SQ})_2]$ and $[\text{Mn}^{\text{III}}(\text{Cat-N-Q})_2]$

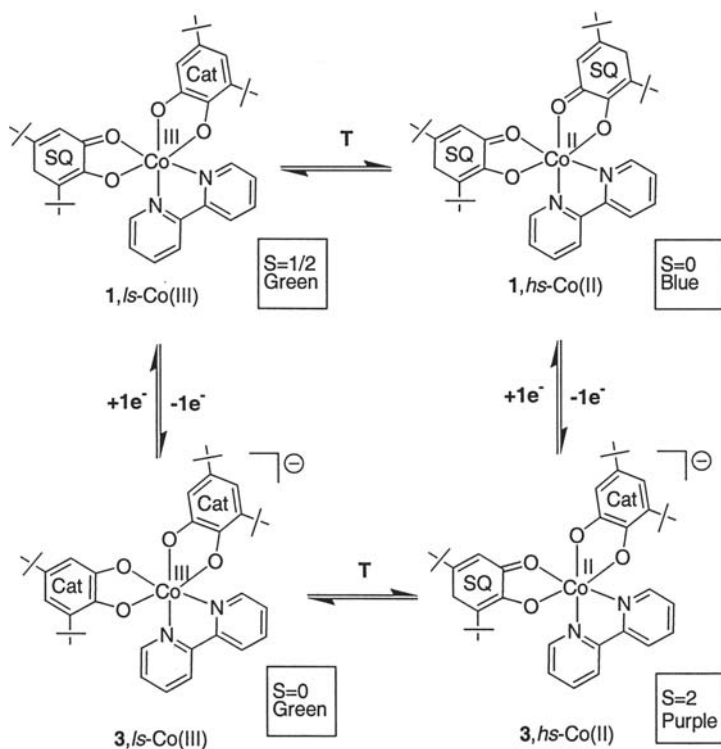


Fig. 18 Diagram of a dual-mode switching array. Complexes 1 and 3 each undergo a valence tautomeric interconversion and the tautomers of complex 3 are obtained reversibly by one-electron reduction of the tautomers of complex 1. An array four different states with different optical and magnetic ground states is then obtained

[BF₄] that has six states with different optical and magnetic properties that interconvert reversibly either thermally or by a reversible oxidation process.

9

Future Directions

It is always difficult to predict the future, however there are certain experiments that clearly should be carried out on valence tautomeric complexes. First, in reference to Fig. 9, it would be interesting to prepare a valence tautomeric cobalt complex that in the solid state exhibits considerable hysteresis. This would be manifested in the heating and cooling magnetic moment (μ_{eff}) vs temperature curves. If there was not a superimposability of the heating and cooling curves, then there would be a thermal hysteresis. Obviously, appreciable hysteresis has been found for certain spin-crossover com-

plexes. It is probably important to establish some type of *intermolecular* interactions between valence tautomeric complexes in the solid state in order to develop such a thermal hysteresis. Second, it is interesting to discover whether a valence tautomeric cobalt complex could be found that exhibits the LIESST effect. The factors that influence the “barrier thickness” for quantum mechanical tunneling between the LS-Co^{III} and HS-Co^{II} states need to be better understood.

Since the valence tautomeric cobalt complexes exhibit appreciably different electronic absorption spectra and magnetic properties between the different tautomeric forms, applications of the complexes should be investigated. Cobalt complexes could be appended to electrically conducting polymers to examine whether electrochromic devices result. The optical switching properties could provide an avenue for application. Q-switched lasers employ rare earth laser light in the near-IR region. The switching is implemented by inserting a mixed-valence organic dye into the laser beam. The high energy laser light causes a near-IR electronic transition in the organic dye. The electronic state population inversion in the organic dye modulates the laser light to give light consisting of pulses occurring at regular intervals. The LS-Co^{III} tautomer has an electronic transition (2500 nm) in the near-IR. A polymer film of such a LS-Co^{III} tautomer could be employed as a saturable dye in a Q-switched laser. The advantage here is that a second laser pulse in the visible region could be used to switch the cobalt absorber between the LS-Co^{III} and HS-Co^{II} tautomers.

References

1. Pierpont CG, Buchanan RM (1981) *Coord Chem Rev* 38:45
2. Pierpont CG, Lange CW (1994) *Prog Inorg Chem* 41:331
3. Pierpont CG (2001) *Coord Chem Rev* 216/217:99
4. Pierpont CG (2001) *Coord Chem Rev* 219/221:415
5. Gütllich P, Dei A (1997) *Angew Chem Int Ed Engl* 37:2734
6. Pierpont CG, Attia AS (2001) *Collect Czech Chem Commun* 66:33
7. Buchanan RM, Pierpont CG (1980) *J Am Chem Soc* 102:4951
8. Shultz DA (2001) Valence tautomerism in dioxolene complexes of cobalt. In: Miller JS, Drillon M (eds) *Magnetism: molecules to materials II*. Wiley-VCH, New York
9. Buchanan RM, Pierpont CG (1979) *Inorg Chem* 18:3439
10. Lynch MW, Buchanan RM, Pierpont CG, Hendrickson DN (1981) *Inorg Chem* 20:1038
11. Lynch MW, Hendrickson DN, Fitzgerald BJ, Pierpont CG (1981) *J Am Chem Soc* 103:3961
12. Adams DM, Hendrickson DN (1996) *J Am Chem Soc* 118:11,515
13. Hendrickson DN, Adams DM, Wu CC (1996) Magnetism: a supramolecular function. In: Kahn O (ed) *Nato ASI Series*. Kluwer Publishing Co., Dordrecht, The Netherlands, pp 357–382

14. (a) Day P (1981) *Int Rev Phys Chem* 1:149; (b) Creutz C (1983) *Prog Inorg Chem* 30:1; (c) Richardson DE, Taube H (1984) *Coord Chem Rev* 60:107; (d) Hendrickson DN (1991) Mixed valence systems: applications in chemistry, physics, and biology. In: Prassides K (ed) NATO ASI Series. Kluwer Publishing Co., Dordrecht, The Netherlands, pp 67–90
15. (a) Beattie JK (1988) *Adv Inorg Chem* 32:1; (b) König E (1987) *Prog Inorg Chem* 35:527; (c) Rao CNR (1985) *Int Rev Phys Chem* 4:19; (d) Gülich P (1981) *Struct Bonding* (Berlin) 44:83; (e) Bacci M (1988) *Coord Chem Rev* 86:245; (f) Maeda Y, Takashima Y (1988) *Comments Inorg Chem* 7:41; (g) Toftlund H (1989) *Coord Chem Rev* 94:67; (h) Zarembowitch J (1992) *New J Chem* 16:255; (g) Kahn O (1993) *Molecular magnetism*. VCH Publishers, New York, pp 52–85
16. Kahn O, Launay JP (1988) *Chemtronics* 3:140; (b) Kahn O, Kröber J, Jay C (1992) *Adv Mater* 4:718; (c) Launay JP (1987) *Molecular electronic devices II*. Carter FL (ed) Marcel Dekker, New York; (d) Joachim C, Launay JP (1990) *J Mol Electron* 6:37; (e) Hush NS, Wong AT, Bacskey GP, Reimers JR (1990) *J Am Chem Soc* 112:4192; (f) Aviram A (1992) *Int J Quant Chem* 42:1615; (g) Lazarev PI (ed) (1991) *Molecular electronics: materials and methods*. Kluwer Academic Publishers, Dordrecht, The Netherlands; (f) Sienick K (ed) (1994) *Molecular electronics and molecular electronic devices*. CRC Press, Boca Raton, FL
17. (a) Gülich P, Hauser A, Spiering H (1994) *Angew Chem Int Ed Engl* 33:2024; (b) Gülich P, Hauser A (1990) *Coord Chem Rev* 97:1
18. (a) Jay C, Grolière F, Kahn O, Kröber J (1993) *J Mol Cryst Liq Cryst* 234:255; (b) Kröber J, Codjovi E, Kahn O, Grolière F (1993) *J Am Chem Soc* 115:9810; (c) Kahn O, Kröber J, Jay C (1992) *Adv Mater* 4:718
19. (a) Hauser A (1993) *Chem Phys Lett* 202:173; (b) Hauser A (1991) *Coord Chem Rev* 111:275
20. (a) Adams DM, Dei A, Rheingold AL, Hendrickson DN (1993) *Angew Chem Int Ed Engl* 32:880; (b) Adams DM, Dei A, Rheingold AL, Hendrickson DN (1993) *J Am Chem Soc* 115:8221
21. (a) Hauser A (1995) *Comments Inorg Chem* 17:17; (b) Hauser A, Vef A, Adler PJ (1991) *J Chem Phys* 95:8710
22. Adams DM, Li B, Simon JD, Hendrickson DN (1995) *Angew Chem Int Ed Engl* 34:1481
23. Buhks E, Navon G, Bixon M, Jortner J (1980) *J Am Chem Soc* 102:2918
24. Adams DM, Noodleman L, Hendrickson DN (1997) *Inorg Chem* 36:3966
25. Newton MD (1991) *J Phys Chem* 95:30
26. Adams DM, Hendrickson DN. Unpublished results
27. Jung O-S, Pierpont CG (1994) *Inorg Chem* 33:2227
28. Jung O-S, Jo DH, Lee Y-A, Sohn YS, Pierpont CG (1998) *Inorg Chem* 37:5875
29. Attia AS, Jung O-S, Pierpont CG (1994) *Inorg Chim Acta* 226:91
30. Jung O-S, Pierpont CG (1994) *J Am Chem Soc* 116:2229
31. Jung O-S, Jo DH, Lee Y-A, Conklin BJ, Pierpont CG (1997) *Inorg Chem* 36:19
32. Caneschi A, Cornia A, Dei A (1998) *Inorg Chem* 37:3419
33. Larsen SK, Pierpont CG (1988) *J Am Chem Soc* 110:1827
34. Neuwahl FVR, Righini R, Dei A (2002) *Chem Phys Lett* 352:408
35. Sato O, Iyoda T, Fujishima A, Hashimoto K (1996) *Science* 272:704
36. Shimamoto N, Ohkoshi S, Sato O, Hashimoto K (2002) *Inorg Chem* 41:678
37. Escax V, Bleuzen A, Moulin CC, Villain F, Goujon A, Varret F, Verdaguer M (2001) *J Am Chem Soc* 123:12,536
38. Sato O, Einaga Y, Fujishima A, Hashimoto K (1999) *Inorg Chem* 38:4405

39. Moulin CC, Villain F, Bleuzen A, Arrio M-A, Saintavit P, Lomenech C, Escax V, Baudelet F, Dartyge E, Gallet J-J, Verdaguer M (2000) *J Am Chem Soc* 122:6653
40. Speier G, Tisza S, Tyeklar Z, Lange CW, Pierpont CG (1994) *Inorg Chem* 33:2041
41. Dooley DM (1999) *J Biol Inorg Chem* 4:1
42. Abakumov GA, Gamov VA, Nevodchikov VI, Cherkasov VK (1989) *Dokl Akad Nauk SSSR* 304:107
43. Zakharov LN, Sa'fyanov YN, Struchkov YT, Abakumov G, Cherasov VK, Garnov VA (1990) *Koord Khim* 16:802
44. Buchanan RM, Wilson-Blumenberg C, Trapp C, Larsen SK, Greene DL, Pierpont CG (1986) 25:3070
45. Rall J, Wanner M, Albrecht M, Homung FM, Kaim W (1999) *Chem Eur J* 5:2802
46. Speier G, Tyeklar Z, Szabo L, Toth P, Pierpont CG, Hendrickson DN (1993) Evidence for substrate activation of copper catalyzed intradiol cleavage in catechols. In: Barton HD, Martel AE, Sawyer DT (eds) *The activation of dioxygen and homogeneous catalytic oxidation*. Plenum, New York, p 423
47. Speier G, Tyeklar Z, Toth P, Speier E, Tisza S, Rothenbauer A, Whalen AM, Alkire N, Pierpont CG (2001) *Inorg Chem* 40:5653
48. Magers KD, Smith CG, Sawyer DT (1980) *Inorg Chem* 19:492
49. Lynch MW, Hendrickson DN, Fitzgerald BJ, Pierpont CG (1984) *J Am Chem Soc* 106:2041
50. Attia AS, Pierpont CG (1995) *Inorg Chem* 34:1172
51. Attia AS, Pierpont CG (1997) *Inorg Chem* 36:6184
52. Attia AS, Pierpont CG (1998) *Inorg Chem* 37:3051
53. Caneschi A, Dei A (1998) *Angew Chem Int Ed Engl* 37:3005
54. Roux C, Adams DM, Itié JP, Polian A, Hendrickson DN, Verdaguer M (1996) *Inorg Chem* 35:2846; Caneschi A, Dei A, Fabrizi de Biani F, Gütlich P, Ksenofontov V, Levchenko G, Hoefer Renz F (2001) *Chem Eur J* 7:3926
55. Ruiz D, You J, Guzei IA, Rheingold AL, Hendrickson DN (1998) *Chem Commun* 2089
56. Ruiz-Molina D, Veciana J, Wurst K, Hendrickson DN, Rovira C (2000) *Inorg Chem* 39:617
57. Ruiz-Molina D, Wurst K, Hendrickson DN, Rovira C, Veciana J (2002) *J Adv Funct Mater* 12:347

Structural Aspects of Spin Crossover. Example of the $[\text{Fe}^{\text{II}}\text{L}_n(\text{NCS})_2]$ Complexes

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Dedicated to Professor Philipp Gütllich on the occasion of his 70th birthday.

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Abstract The interplay between the spin crossover and the structural properties of the complexes in the solid state is still under investigation. In particular the following questions may be asked. What are the structural modifications of the metal coordination sphere at the spin crossover? How are the dimensions and the symmetry of the crystallographic unit cell affected by the spin crossover? Conversely, how may structural properties influence the spin crossover behavior? Do intramolecular parameters account for the features of the spin crossover? What are the relevant characteristics of the crystal packing for the cooperativity? Do the above questions have general answers that can be used for

all the spin crossover compounds? This contribution tries to give answers to these questions. The discussion is based on a large structural data set provided in the literature for the six-coordinated iron(II) mononuclear complexes of general formula $[\text{FeL}_n(\text{NCS})_2]$. The effects of temperature, light and pressure on the X-ray diffraction crystal structures are reviewed. The structural modifications due to the spin crossover are first estimated, these include the expansion and the distortion of the FeN_6 octahedron, the isotropic and the anisotropic changes of the unit cell. The influence of the structural properties on the features of the spin crossover is then discussed. For example, intramolecular properties such as Fe-N bond lengths are in general not relevant to account for the spin crossover features. In contrast, hydrogen bonds play a paramount role in the propagation of the spin conversion throughout the crystal lattice.

Keywords Spin crossover · Crystal structure · Thermal expansion · Octahedron · Hydrogen bond

List of Abbreviations

abpt	4-Amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole
AzA	4-(Phenylazo)aniline
BiA	4-(Aminobiphenyl)aniline
bpy	2,2'-Bipyridine
bpym	2,2'-Bipyrimidine
bt	2,2'-Bi-2-thiazoline
btz	2,2'-Bi-4,4-dihydrothiazine
DiyA	4-(Phenylbutadiyne)aniline
dmp	2,9-Dimethyl-1,10-phenanthroline
dpea	(2-Aminoethyl)bis(2-pyridylmethyl)amine
dpp	Dipyrido[3,2- <i>a</i> :2',3'- <i>c</i>]phenazine
dppa	(3-Aminopropyl)bis(2-pyridyl-methyl)amine
dpq	2,3-Bis-(2'-pyridyl)-quinoxaline
HS	High spin
LS	Low spin
LIESST	Light-Induced Excited Spin-State Trapping
mtz	Methyltetrazole
PeA	4-(Phenylethynyl)aniline
phen	1,10-Phenanthroline
PM	<i>N</i> -(2'-Pyridylmethylene)
pic	Picolylamine (2-aminomethyl-pyridine)
ptz	1-Propyltetrazole
py	Pyridine
tap	1,4,5,8-Tetraazaphenanthrene
SCO	Spin crossover
stpy	4-Styrylpyridine
tap	Bis(1,4,5,8-tetraazaphenanthrene)
TeA	4-(Aminoterphenyl)aniline
TheA	4-(Thienylethynyl)aniline
TIA	<i>N</i> - <i>o</i> -Tolyl-2-imidazolalidine

1 Introduction

The determination of the crystal structure by X-ray diffraction is undoubtedly an essential step in the course of the characterization of a new spin crossover (SCO) complex. Apart from a determination of the molecular geometry, preferably performed for both the high spin and low spin states, a careful analysis of the structural properties gives relevant information on the spin crossover phenomenon itself. In particular, the description of the crystal packing of a complex allows one to define the intermolecular interactions that may potentially favor the propagation of the spin conversion over the molecules, which is known as the cooperative effect. In general, crucial information has been obtained to date via such characterization. For example, early studies of the structural properties of spin crossover complexes proved that there are only two discrete structures that correspond to the two different spin states, the high spin (HS) and low spin (LS) isomers of the complex [1, 2]. Likewise the determination of the atomic coordinates gave experimental proof of the decrease of the metal-ligand distances with a transition from HS to LS [3–5]. Moreover, for instance, the temperature dependence of the cell parameters has revealed unit cell modifications at the spin crossover [1, 6, 7]. However, the relationship between magnetic and structural properties is still not clearly formulated. Examples of some points that could be debated or that at least need to be clarified are illustrated by the following questions. What are all the structural modifications of the metal coordination sphere at the spin crossover? Are all crystallographic unit cells affected in a similar way by the spin crossover? Conversely, how may structural properties influence the nature of the spin crossover? What is the role of the intramolecular structural parameters in determining the features of the spin crossover? What are the relevant characteristics of the crystal packing for the cooperativity? Do the above questions have general answers for all the spin crossover compounds? What are the differences from a structural point of view between thermal, pressure and light-induced spin crossover phenomena? These points could be elucidated by the comparison of the structural properties of a range of spin crossover compounds. Reviews on the structural properties of spin crossover complexes have been published previously [1, 5]. However, only a relatively small number of accurate crystal structures was then available in the literature. Since then, the number and the accuracy of structural data have significantly increased and a large number of crystal structures of spin crossover complexes are now known. Thus a re-examination of the structural properties on the basis of a large set of crystal structures is now appropriate. This is the topic of this paper. The aim is to confirm or invalidate the current beliefs and incidentally to show general trends of the relationship between structural and magnetic properties.

We shall restrict our attention to the six-coordinated mononuclear iron (II) complexes of general formula $[\text{FeL}_n(\text{NCS})_2]$. This is primarily because the structural and magnetic properties of a large number of these complexes have been investigated in detail over the last 30 years. In particular, many crystal structures of the $[\text{FeL}_n(\text{NCS})_2]$ complexes have been determined in both the HS and LS states. Moreover, limited structural information is also available at high pressure or under light irradiation. In addition, in the last five years we have studied in a systematic way the $[\text{Fe}(\text{L})_2(\text{NCS})_2]$ ($\text{L}=\text{PM-X}$) complexes [8–14], which, apart from their chemical similarity, display a large range of structural and magnetic behavior.

This chapter is organized as follows. The next section deals with some selected data of the $[\text{FeL}_n(\text{NCS})_2]$ complexes. Then, in the following section details of the structural modifications due to the spin crossover are considered. In particular, the comparative effects of the thermal, pressure and light-induced spin crossover phenomena on the structural properties are analyzed. Finally, in the next section, the influence of the structural properties on the spin crossover features is discussed.

2 Overview of the $[\text{FeL}_n(\text{NCS})_2]$ Complexes

2.1 Thermal Spin Crossover

The main magnetic features of the thermal spin crossover of the $[\text{FeL}_n(\text{NCS})_2]$ complexes (Fig. 1) are summarized in Table 1. Despite all these complexes being in the HS state at room temperature, the diversity of the temperature dependence of their magnetic behavior justifies our interest in this particular family of spin crossover complexes. Indeed, all the possible kinds of spin transition are present, from very abrupt to very gradual, complete to incomplete. For example, the $[\text{Fe}(\text{PM-X})_2(\text{NCS})_2]$ complexes for which the main difference, from a chemical point of view, is the length of the conjugated diimine ligand, show very different spin crossover features. Moreover, the range of critical $T_{1/2}$ is quite large, from 110 K to 215 K, and wide hysteresis loops are found (up to 40 K). In addition, some of these complexes show polymorphism with drastically different magnetic features for each phase. For example $[\text{Fe}(\text{dppa})(\text{NCS})_2]$ may crystallize in three polymorphs (denoted A, B, and C), A undergoes a gradual spin crossover, B does not show any spin crossover and C exhibits an abrupt spin transition.

The magnetic study of the thermal spin crossover in the $[\text{FeL}_n(\text{NCS})_2]$ complexes has been accompanied by numerous single crystal X-ray diffraction investigations. From a survey based principally on information from the Cambridge Structural Data Base (June 2002), the crystal structures of 26

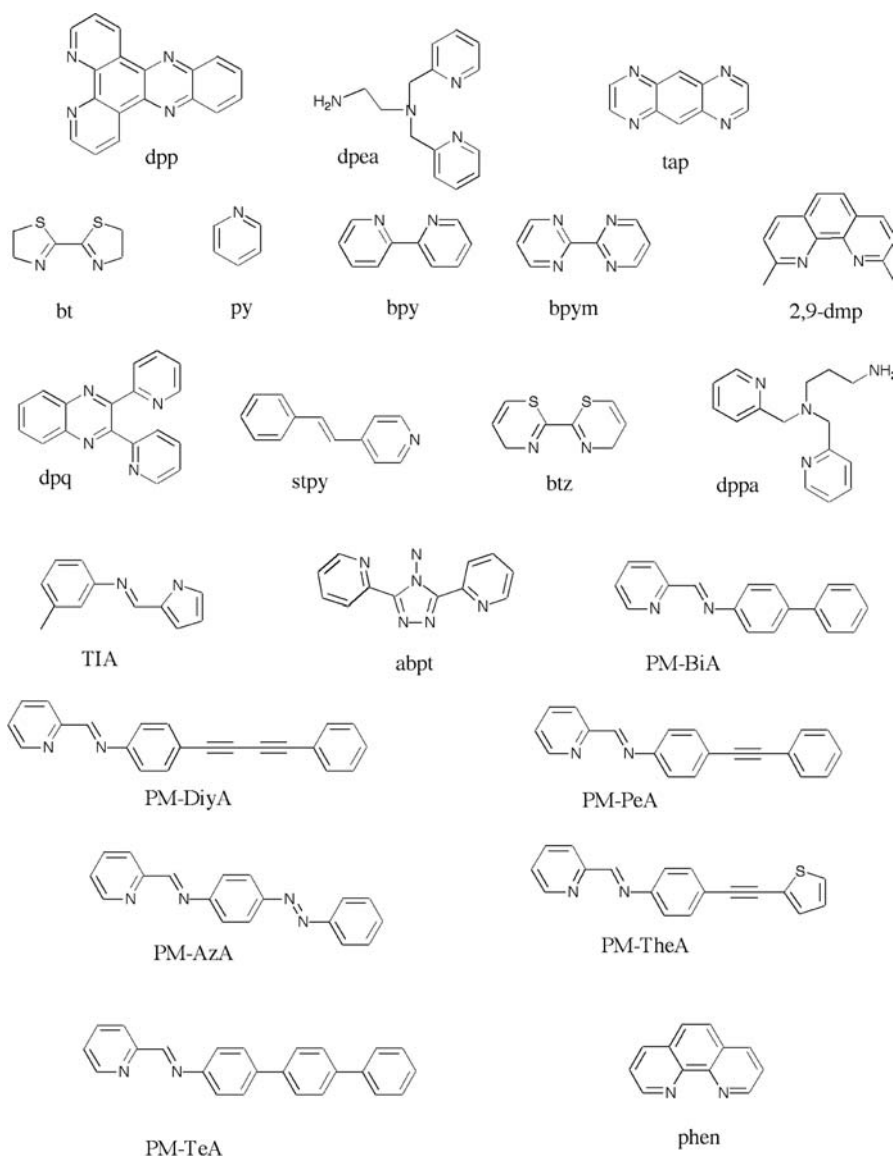


Fig. 1 L ligands in the $[\text{FeL}_n(\text{NCS})_2]$ complexes discussed in this chapter. See also the list of abbreviations

$[\text{FeL}_n(\text{NCS})_2]$ complexes have been determined in the HS state and the crystal structures of 10 of these complexes have also been determined in the LS state (see Table 2 for references). It is also worth noting that, in some cases, X-ray absorption spectroscopy studies have been carried out in order to ob-

Table 1 Summary of the magnetic properties of spin crossover in $[\text{FeL}_n(\text{NCS})_2]$ complexes. The nature of the transition is indicated by *A* for abrupt, *S* for smooth, *VS* for very smooth, and *I* for incomplete. $T_{1/2\downarrow}$ is the temperature for which there is 50% HS when cooling down. The hysteresis width is characterized with $\Delta T_{1/2}$ that is the difference between $T_{1/2\downarrow}$ and $T_{1/2\uparrow}$ the temperature for which there is 50% HS when warming up. $T(\text{LIESST})$ is the reference temperature for the LIESST effect. Note that some known $[\text{FeL}_n(\text{NCS})_2]$ complexes are not included in this chapter because their crystal structures are not available in the literature

Label	Compounds	References	Kind of SCO	$T_{1/2\downarrow}$	$\Delta T_{1/2}$	$T(\text{LIESST})$
1	$[\text{Fe}(\text{btz})_2(\text{NCS})_2]$	15	S, I	215	0	
2	$[\text{Fe}(\text{bpy})_2(\text{NCS})_2]$	16, 17	A	213	0	
3	$[\text{Fe}(\text{PM-TheA})_2(\text{NCS})_2]\text{-I}$	18	S	208	29 ^a	
4	$[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\text{-II}$	19	VS	190	0	34
5	$[\text{Fe}(\text{PM-AzA})_2(\text{NCS})_2]$	12	VS	189	0	46
6	$[\text{Fe}(\text{PM-PeA})_2(\text{NCS})_2]$	8	S	188	40	^b
7	$[\text{Fe}(\text{abpt})_2(\text{NCS})_2]$	20	VS, I	180	0	40
8	$[\text{Fe}(\text{phen})_2(\text{NCS})_2]$	4, 21–23	A, I	176	0.3	62
9	$[\text{Fe}(\text{dppa})(\text{NCS})_2]\text{-A}$	24	S	176	0	
10	$[\text{Fe}(\text{bt})_2(\text{NCS})_2]\text{-A}$	25–27	A	171	10	
11	$[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\text{-I}$	9	A	168	5	78
12	$[\text{Fe}(\text{tap})_2(\text{NCS})_2]\cdot\text{CH}_3\text{CN}$	28	VS	168	0	52
13	$[\text{Fe}(\text{dpea})(\text{NCS})_2]$	29	S	138	0	
14	$[\text{Fe}(\text{PM-TeA})_2(\text{NCS})_2]\cdot 0.5\text{CH}_3\text{OH}$	12	VS, I	125	0	
15	$[\text{Fe}(\text{dpp})_2(\text{NCS})_2]\cdot\text{py}$	30	S	123	40	
16	$[\text{Fe}(\text{py})_2\text{bpym}(\text{NCS})_2]\cdot 0.25\text{py}$	31	A	114	3	60
17	$[\text{Fe}(\text{dppa})(\text{NCS})_2]\text{-C}$	24	A	112	8	
18	$\text{cis-}[\text{Fe}(\text{stpy})_4(\text{NCS})_2]$	32	S	110	0	
19	$\text{trans-}[\text{Fe}(\text{stpy})_4(\text{NCS})_2]$	32	no SCO			
20	$[\text{Fe}(\text{PM-DiyA})_2(\text{NCS})_2]$	18	no SCO			
21	$[\text{Fe}(\text{bt})_2(\text{NCS})_2]\text{-B}$	25–27	no SCO			
22	$[\text{Fe}(2,9\text{-dmp})_2(\text{NCS})_2]\cdot 0.25\text{H}_2\text{O}$	33	no SCO			
23	$[\text{Fe}(\text{dpq})_2(\text{NCS})_2]\cdot\text{COCH}_3$	34	no SCO			
24	$[\text{Fe}(\text{py})_4(\text{NCS})_2]$	35	no SCO			
25	$[\text{Fe}(\text{dppa})(\text{NCS})_2]\text{-B}$	24	no SCO			
26	$[\text{Fe}(\text{TIA})_2(\text{NCS})_2]$	36	no SCO			

^a This is not a true hysteresis as it corresponds to an irreversible structural change to another polymorph

^b No photomagnetic effect observed

tain preliminary information or to supplement the structural data obtained from X-ray single crystal diffraction studies. For example, EXAFS investigations [37] of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ revealed information on the temperature dependence of the Fe-N bond lengths in this complex when the room temperature crystal structure was of only average quality and the low temperature one was not known. It is also the case that some crystal structures determined before the 1980s were of relatively poor quality and have been recently re-investigated; this applies, for instance, to $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, $[\text{Fe}(\text{bpy})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{py})_4(\text{NCS})_2]$. In this chapter we have chosen to discuss the relationship between the structural properties and three of the spin cross-

Table 2 Fe-N bond lengths (Å) in the HS state at room temperature for all the $[\text{Fe}^{\text{II}}_n(\text{NCS})_2]$ complexes for which crystal structures are available. Reference of the atomic coordinates is given for each complex through the corresponding publication as well as its Cambridge Structural Data bank code, noted CSD. Columns number 1 and 2 refer to Fe-NCS bond lengths. Standard deviations are in the range [0.001 Å–0.005 Å]

$[\text{Fe}^{\text{II}}_n(\text{NCS})_2]$ complexes	CSD	Ref	1	2	3	4	5	6
$[\text{Fe}(\text{btz})_2(\text{NCS})_2]$	PASGOF	15	2.064	2.064	2.165	2.165	2.176	2.176
$[\text{Fe}(\text{bpy})_2(\text{NCS})_2]$	FEBCYC04	4, 17	2.053	2.053	2.181	2.181	2.166	2.166
$[\text{Fe}(\text{PM-TeA})_2(\text{NCS})_2]\text{-I}$	-	18	2.054	2.071	2.172	2.190	2.253	2.267
$[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\text{-II}$	RONPIT06	19	2.066	2.076	2.153	2.177	2.241	2.250
$[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\text{-I}$	RONPIT	9	2.041	2.041	2.230	2.230	2.251	2.251
$[\text{Fe}(\text{PM-AzA})_2(\text{NCS})_2]$	XECNAV	12	2.060	2.059	2.172	2.157	2.270	2.246
$[\text{Fe}(\text{PM-PeA})_2(\text{NCS})_2]$	NOWBIK	8	2.056	2.055	2.164	2.167	2.246	2.227
$[\text{Fe}(\text{abpt})_2(\text{NCS})_2]$	QAHVOK	20	2.120	2.120	2.120	2.120	2.205	2.205
$[\text{Fe}(\text{Phen})_2(\text{NCS})_2]$	KEKVIF	4, 60	2.057	2.057	2.213	2.213	2.199	2.199
$[\text{Fe}(\text{dppa})(\text{NCS})_2]\text{-A}$	NUMBEC01	24	2.084	2.103	2.209	2.284	2.182	2.182
$[\text{Fe}(\text{dppa})(\text{NCS})_2]\text{-C}$	NUMBEC02	24	2.067	2.112	2.213	2.266	2.208	2.197
$[\text{Fe}(\text{dppa})(\text{NCS})_2]\text{-B}$	NUMBEC	24	2.061	2.128	2.251	2.250	2.162	2.208
$[\text{Fe}(\text{bt})_2(\text{NCS})_2]\text{-B}$	GAKKOS01	61	2.082	2.082	2.214	2.232	2.216	2.225
$[\text{Fe}(\text{bt})_2(\text{NCS})_2]\text{-A}$	GAKKOS	61	2.061	2.079	2.173	2.242	2.195	2.197
$[\text{Fe}(\text{tap})_2(\text{NCS})_2]\text{-CH}_3\text{CN}$	POHLUT	28	2.059	2.056	2.180	2.198	2.225	2.253
$[\text{Fe}(\text{dpea})(\text{NCS})_2]$	NEFSIA	29	2.115	2.155	2.186	2.177	2.231	2.215
$[\text{Fe}(\text{PM-TeA})_2(\text{NCS})_2]\cdot 0.5\text{CH}_3\text{OH}$	XECMIB	12	2.082	2.082	2.181	2.181	2.259	2.259
$[\text{Fe}(\text{dpp})_2(\text{NCS})_2]\text{-py}$	POWSID	30	2.090	2.104	2.165	2.186	2.237	2.237
$[\text{Fe}(\text{py})_2\text{bpy}(\text{NCS})_2]\cdot 0.25\text{py}$	-	31	2.098	2.115	2.212	2.224	2.242	2.228
cis- $[\text{Fe}(\text{stpy})_4(\text{NCS})_2]$	WIGBAP	32	2.072	2.072	2.251	2.251	2.256	2.256
trans- $[\text{Fe}(\text{stpy})_4(\text{NCS})_2]$	WIFZUG	32	2.108	2.103	2.198	2.222	2.215	2.234
$[\text{Fe}(\text{PM-DiyA})_2(\text{NCS})_2]$	-	18	2.047	2.047	2.185	2.185	2.264	2.264
$[\text{Fe}(2,9\text{-dmp})_2(\text{NCS})_2]\cdot 0.25\text{H}_2\text{O}$	PAGXAW	33	2.058	2.076	2.233	2.331	2.301	2.233
$[\text{Fe}(\text{dpq})_2(\text{NCS})_2]\cdot \text{COCH}_3$	LOQPAL	34	2.013	2.033	2.307	2.177	2.425	2.153
$[\text{Fe}(\text{py})_4(\text{NCS})_2]$	FETPYR	31, 62	2.106	2.106	2.241	2.241	2.260	2.260
$[\text{Fe}(\text{TIA})_2(\text{NCS})_2]$	POGMED	36	2.096	2.096	2.133	2.133	2.318	2.318

over features: $T_{1/2}$, the presence of hysteresis and the abruptness of the transition.

2.2

Light Irradiation Effects

The possibility for a conversion from LS to HS induced by light irradiation, was discovered in 1984 [38] and is commonly known as the LIESST effect (Light-Induced Excited Spin-State Trapping). Extensive studies of the LIESST effect have been carried out [39–47] and today different methods can be used to compare the photomagnetic properties of a series of spin crossover materials [19, 39, 46]. In this chapter we have decided to use the $T(\text{LIESST})$ value defined as the temperature for which the light-induced HS information is erased [46]. The $T(\text{LIESST})$ of some of the $[\text{FeL}_n(\text{NCS})_2]$ complexes have been determined [46] (Table 1). Up to now, most known spin crossover complexes exhibit very low $T(\text{LIESST})$ values. A current challenge in the spin crossover research field is the design of materials with $T(\text{LIESST})$ within the temperature range of potential applications. In this respect, structural studies of complexes in the light-induced HS state would provide crucial information. However, until recently, structural data concerning the effect of light on spin crossover complexes were limited to the study of the unit cell parameters determined by X-ray powder diffraction [6] and single crystal diffraction at low temperature [48]. The determination of the crystal structures of complexes in a light induced metastable HS state, noted HS-2, has now been achieved. At the time of writing this chapter, three crystal structures [49–51] of spin crossover complexes in HS-2 have been published one of which belongs to the family of iron(II) complexes of the title of this chapter. Indeed, the crystal structure of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ in HS-2 at 30 K has been recently published and compared to the LS crystal structure at the same temperature and the HS crystal structure at room temperature [50]. This study showed, for instance, that the crystal packing of the complex in HS-2 is different from the crystal structures of the complex in LS and in HS states.

Elsewhere, the possibility to change the spin state using irradiation by soft X-rays has been discovered for the $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ complex and called the SOXIESST effect (Soft X-Ray Induced Excited Spin-State Trapping) [52]. To date, no other observation of such a phenomenon has been reported and no structural data relative to the SOXIESST effect are available.

2.3

High Pressure Effects

An entire chapter of this issue is dedicated to the spin crossover under high pressure; thus we will not go into further comments on that point. Let us just

say here that the pressure induced spin crossover phenomenon was first investigated a long time ago [53] even if it is only recently that the amount of available magnetic data has significantly increased. Within this context, the study under high pressure of some of the $[\text{FeL}_n(\text{NCS})_2]$ complexes has been very informative. For example, the magnetic study of the $[\text{Fe}(\text{PM-X})_2(\text{NCS})_2]$ complexes have proved that, contrary to what was expected, high pressure may increase as well as decrease the transition temperature and the hysteresis width [54, 55]. For $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ -I, $T_{1/2}$ increases and $\Delta T_{1/2}$ decreases with increasing pressure while on the contrary $T_{1/2}$ decreases and $\Delta T_{1/2}$ increases with increasing pressure for $[\text{Fe}(\text{PM-PeA})_2(\text{NCS})_2]$. Another very interesting example is the study of $[\text{Fe}(\text{py})_4(\text{NCS})_2]$ which does not undergo a thermal spin crossover but undergoes a spin transition under high pressure at room temperature [56]. At least three other complexes of this family exhibit a spin crossover under high pressure at room temperature, $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, $[\text{Fe}(\text{btz})_2(\text{NCS})_2]$ [57] and $[\text{Fe}(\text{py})_2\text{bpym}(\text{NCS})_2]$ [56]. Note that for these complexes the transition appears at pressure values within the range 5–7 kbar.

The explanation of the effects of pressure described above and, in a general way, the understanding of the interplay between the temperatures and the pressures of spin crossover require structural data under pressure. Unfortunately, information relating to the determination of the crystal structures of spin crossover systems under high pressure is very rare. Up to now, to our knowledge, the structural properties of only three spin crossover complexes have been studied under pressure at room temperature by X-ray diffraction. They all concern iron complexes of the $[\text{FeL}_n(\text{NCS})_2]$ family: $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, $[\text{Fe}(\text{btz})_2(\text{NCS})_2]$ [57–59], and $[\text{Fe}(\text{PM-TeA})_2(\text{NCS})_2]$ [11]. Moreover, no structural investigation of a spin crossover complex under high pressure at low temperature has been reported so far.

3

Structural Modifications Due to Spin Crossover

3.1

Geometry of the FeN_6 Octahedron

The main structural modification due to the spin transition concerns the geometry of the FeN_6 octahedron. Indeed, when the electrons go from the antibonding e_g orbital to the slightly bonding t_{2g} orbital, i.e., when the $\text{Fe}(\text{II})$ ion goes from HS to LS, the electronic repulsion strongly decreases. The first and more obvious consequence is the shortening of the Fe-N bond lengths. The N-Fe-N angles are also strongly affected. The aim of this section is to characterize these modifications. The following discussions refer to Tables 3 and 4.

Table 3 FeN₆ octahedron geometry for [FeL_n(NCS)₂] complexes for which both HS and LS crystal structures are available. d_{FeL} is the average of the six Fe-N bond lengths at room temperature in the HS state. Δr is the variation of d_{FeL} at the SCO. Σ is the distortion parameter in the HS and $\Delta\Sigma$ its variation from HS to LS. θ_{NCS} is another parameter to characterize the distortion (see text for definitions). Complexes are ordered by decreasing Δr

Compound	Ref	T _{1/2}	d_{FeL}	Δr	Σ	$\Delta\Sigma$	θ_{NCS}	$\Delta\theta_{\text{NCS}}$
[Fe(PM-BiA) ₂ (NCS) ₂]-I	9	168	2.174	0.235	87	-39	30.4	+14.3
[Fe(PM-TheA) ₂ (NCS) ₂]-I	18	208	2.168	0.207	85	-29	35.1	+7.2
[Fe(PM-PeA) ₂ (NCS) ₂]	8	188	2.159	0.204	85	-29	35.0	+12.1
[Fe(PM-BiA) ₂ (NCS) ₂]-II	19	190	2.160	0.200	80	-37	37.3	+9.3
[Fe(tap) ₂ (NCS) ₂]-CH ₃ CN	28	168	2.162	0.194	80	-43	42.2	+8.6
[Fe(PM-AzA) ₂ (NCS) ₂]	12	189	2.160	0.193	83	-36	36.7	+8.7
[Fe(bpy) ₂ (NCS) ₂]	17	213	2.133	0.174	65	-20	47.0	+8.5
[Fe(phen) ₂ (NCS) ₂]	60	176	2.156	0.173	64	-29	50.7	+1.2
[Fe(bt) ₂ (NCS) ₂]	15	215	2.135	0.170	83	-34	43.6	+9.0
[Fe(PM-TeA) ₂ (NCS) ₂]. 0.5CH ₃ OH	12	125	2.171	0.150	90	-32	38.9	+0.9

Table 4 FeN₆ octahedron geometry for [FeL_n(NCS)₂] complexes for which only the HS crystal structure is available (see Table 3 for legend). Calculation of d_{FeL} , Σ and θ_{NCS} were made from the atomic coordinates retrieved from the CSD cifs, see Table 2 for CSD references. Complexes are ordered by decreasing d_{FeL}

Compound	References	T _{1/2}	d_{FeL}	Σ	θ_{NCS}
[Fe(2,9-dmp) ₂ (NCS) ₂].0.25H ₂ O	33	No	2.205	93	39.1
[Fe(py) ₄ (NCS) ₂]	31	No	2.202	14	56.7
cis-[Fe(stpy) ₄ (NCS) ₂]	32	110	2.194	16	55.8
[Fe(py) ₂ bpy(NCS) ₂].0.25py	31	114	2.186	54	42.8
[Fe(dpq) ₂ (NCS) ₂].CO(CH ₃) ₂	34	No	2.184	78	32.3
[Fe(TIA) ₂ (NCS) ₂]	36	No	2.183	76	46.4
trans-[Fe(stpy) ₄ (NCS) ₂]	32	No	2.180	25	54.1
[Fe(dpea)(NCS) ₂]	29	138	2.179	90	40.5
[Fe(dppa)(NCS) ₂]-B	24	No	2.176	69	45.9
[Fe(bt) ₂ (NCS) ₂]-B	61	No	2.175	80	29.4
[Fe(dppa)(NCS) ₂]-A	24	176	2.174	68	45.6
[Fe(tap) ₂ (NCS) ₂].1/2CH ₃ CN	28	No	2.171	86	29.1
[Fe(dpp) ₂ (NCS) ₂].py	30	123	2.168	76	49.9
[Fe(PM-DiyA) ₂ (NCS) ₂]	18	No	2.165	84	37.0
[Fe(dppa)(NCS) ₂]-C	24	112	2.163	63	38.3
[Fe(bt) ₂ (NCS) ₂]-A	61	171	2.158	80	31.2
[Fe(abpt) ₂ (NCS) ₂]	20	180	2.148	71	42.2
[Fe(abpt) ₂ (NCSe) ₂]	20	224	2.142	72	42.5

3.1.1

Fe-N Bond Lengths

Table 2 reports the six Fe-N bond lengths for all the $[\text{FeL}_n(\text{NCS})_2]$ complexes for which data are available at room temperature (HS state). One of the features that first emerges is the differences between the two Fe-NCS bond lengths on the one hand and the other Fe-N bond lengths on the other hand. Indeed, in HS, the Fe-NCS bond lengths range from 2.013 Å to 2.155 Å while the others are longer and fall within the range 2.120 Å to 2.425 Å. Consequently the distribution of the Fe-N bond lengths is quite large for these complexes. For the same complex the difference between the minimum and the maximum of the Fe-N bond lengths may be very large and even up to 0.41 Å for $[\text{Fe}(\text{dpq})_2(\text{NCS})_2]\cdot\text{COCH}_3$. Nevertheless, in the literature, the discussion on the Fe-N bond lengths is generally based on their average, denoted d_{FeL} in this paper and very often denoted r in the literature.

The statistical distribution of d_{FeL} for all the Fe(II) complexes found with in the literature (Fig. 2) shows a large range from 1.890 Å to 2.274 Å but with two zones centered around two maxima at 1.96 Å and 2.18 Å. These two zones correspond respectively to the low spin state and to the high spin state of the Fe(II) ion. The proportion of low temperature data is very small in the histogram. Consequently, this histogram shows that at room temperature the LS state is more common than the HS state in the six coordinated iron(II) complexes that are structurally characterized. The statistical distribution of d_{FeL} for the Co(II) complexes appears very similar to that of Fe(II) as it also shows a large range from 1.887 Å to 2.258 Å with two zones centered around two maxima at 1.98 Å and 2.14 Å. The ratio LS to HS is almost the same for the iron and the cobalt complexes. In contrast, for the Mn(II) complexes the HS state that corresponds to the maximum centered around 2.25 Å seems more prevalent than the LS state at room temperature. However, in the case of Mn(II) complexes the number of available crystal structures (169) is much less than for Co(II) (787) or Fe(II) complexes (589).

For the $[\text{FeL}_n(\text{NCS})_2]$ complexes the room temperature HS d_{FeL} values are reported in Tables 3 and 4. These values differ significantly from one complex to another and lay within the range 2.135 Å–2.205 Å with standard deviation of the order of magnitude of 0.001 Å. Let us introduce first the variation of d_{FeL} at the spin crossover.

Such a variation is defined as the difference between the HS and the LS Fe-N bond lengths average, $r_{\text{HS}} - r_{\text{LS}}$, and is usually denoted Δr .

Let us first pay attention to the effect of temperature on the magnitude of Δr . Indeed, most of the low spin investigations are not performed at exactly the same temperature. Variable temperature crystal structure determinations have demonstrated that even if Δr is mainly a function of the spin state it is also slightly dependent on temperature. For example, for $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\cdot\text{I}$, the calculated Δr value (0.218 Å) from 293 K (HS) to 140 K (LS)

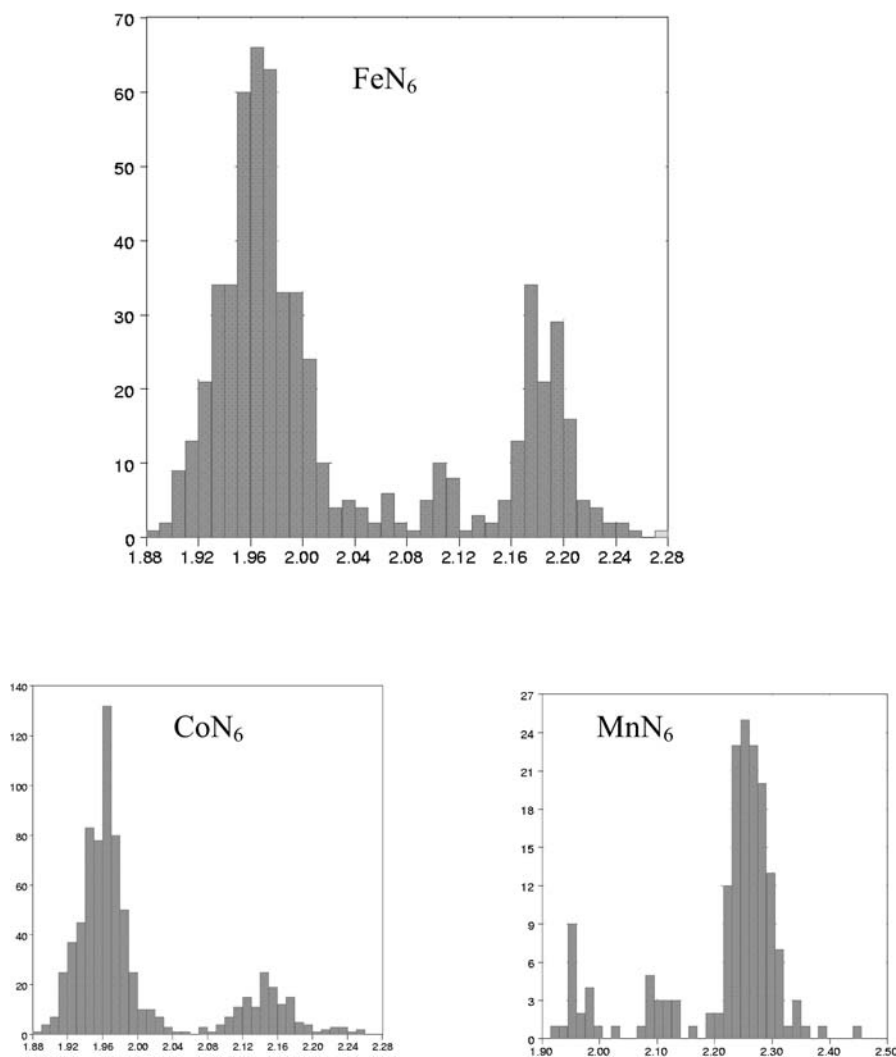


Fig. 2 Histograms of the average of the six M-N bond lengths (Å) (M=Fe, Co, Mn), denoted d_{FeL} in the text, from a Cambridge Structural Data Base investigation (June 2002)

is smaller than the calculated value (0.235 Å) from 293 K (HS) to 30 K (LS). The same comment may apply for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, $\Delta r = 0.164$ Å from 293 K to 130 K and $\Delta r = 0.173$ Å from 293 K to 30 K. These differences are probably affected by a possible low fraction of one of the two spin states remaining at the temperature under study. Thus depending on the actual temperature, comparison of very small Δr differences must be taken with caution.

The effect of pressure on Δr cannot be discussed due to the lack of a sufficient number of data for the LS state at high pressure. However, it is interesting to note that, in absence of spin crossover, the Fe-N bond lengths are almost insensitive to the applied pressure, as previously predicted [63]. Indeed, the high pressure dependence of the crystal structure of $[\text{Fe}(\text{PM-TeA})_2(\text{NCS})_2] \cdot \text{CH}_3\text{OH}$ shows that the Fe-N bond lengths vary by less than 0.01 under a pressure of less than 1.0 GPa when there is no spin crossover.

For Fe(II) ions in general, theoretical calculations have estimated that the Δr variation due to the SCO phenomenon is 0.16 Å [64]. The first multi-temperature single crystal X-ray diffraction studies have confirmed this trend [1, 4]. However, we now know that Δr may significantly differ from one complex to another. Indeed, the Fe-N shortening strongly depends on the ability of the complex to re-organization, because of intramolecular constraints, i.e., on the nature of the ligands, and also on the intermolecular environment. In the $[\text{FeL}_2(\text{NCS})_2]$ family Δr may differ from 0.170 Å for $[\text{Fe}(\text{btz})_2(\text{NCS})_2]$ to 0.235 Å for $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\text{-I}$. Even within the $[\text{Fe}(\text{PM-X})_2(\text{NCS})_2]$ series, where intramolecular and intermolecular constraints are similar for all the complexes, Δr differs significantly from one complex to another, from 0.193 Å for $[\text{Fe}(\text{PM-AzA})_2(\text{NCS})_2]$ to 0.235 Å for $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\text{-I}$. This shows the sensitivity of Δr to small environment modifications. Interestingly, Table 3 shows that the decrease of Δr almost follows the decrease of d_{FeL} in HS. In other words, it is the room temperature HS value of d_{FeL} which mainly differs from one complex to another and not the LS d_{FeL} value. As a result, on the hypothesis that the larger d_{FeL} in HS the larger should be Δr , some comments may be added on the complexes for which only the HS crystal structure is known (Table 4). The *cis*- and *trans*- forms of $[\text{Fe}(\text{stpy})_4(\text{NCS})_2]$ exhibit different HS d_{FeL} values showing the influence of the complex conformation on the Δr values. The $[\text{Fe}(\text{dppa})_2(\text{NCS})_2]$ complex offers an interesting feature as it crystallizes in three polymorphs. Although they are chemically equivalent they display different HS d_{FeL} values. Similarly, the HS d_{FeL} values are quite different for the two polymorphs of $[\text{Fe}(\text{bt})_2(\text{NCS})_2]$. These examples illustrate the influence of the constraint imposed by the crystal packing on the Fe-N bond lengths and thus on the Δr values.

3.1.2

Octahedron Distortion

The spin state transition from LS to HS also corresponds to the deformation of the FeN_6 octahedron. Such a deformation of the FeN_6 octahedron is usually evident in the literature from the list of the N-Fe-N angles. A few parameters have already been proposed to characterize the deformation of an octahedron [65–69]. However, we will discuss below only two of them recently

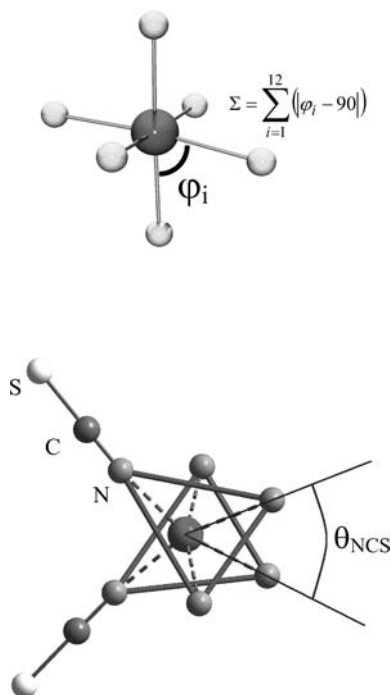


Fig. 3 Definition of the structural parameters used to characterize the distortion of the FeN_6 octahedron. Σ is calculated from the 12 *cis* angles. For the calculation of θ_{NCS} , the two triangles represented here are taken in a projection on the same plane

proposed to explore the spin crossover phenomenon and previously tested on the $[\text{Fe}(\text{PM-X})_2(\text{NCS})_2]$ series [10, 11, 50].

The first parameter proposed, denoted Σ , derives from the N-Fe-N angles as it is the sum of the deviations from 90° of the 12 *cis* N-Fe-N angles in the coordination sphere (Fig. 3). Σ is equal to 0 for an ideal octahedron and increases with the deformation. In the $[\text{FeL}_2(\text{NCS})_2]$ complexes the HS Σ values are relatively high and similar from one complex to the other. The FeN_6 deformation obviously depends on the nature of L. For example in the $[\text{Fe}(\text{PM-X})_2(\text{NCS})_2]$ series they are all very close with an average value of $85(5)^\circ$. This value is smaller for complexes with L of more symmetric nature such as $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ or $[\text{Fe}(\text{bpy})_2(\text{NCS})_2]$ where Σ is 65° . Not surprisingly the $[\text{FeL}_4(\text{NCS})_2]$ complexes show a smaller deformation. Elsewhere, unlike the Fe-N bond lengths, Σ is almost unaffected by the structural environment of the complex. This is illustrated by the identical Σ value for the two $[\text{Fe}(\text{bt})_2(\text{NCS})_2]$ polymorphs and the very close values for the three polymorphs of $[\text{Fe}(\text{dppa})_2(\text{NCS})_2]$.

The variation at the spin crossover, $\Delta\Sigma$, appears greater than 30% for all the complexes and may even reach 55%. This large variation allows the use

of the Σ parameter to characterize the spin state. This assumption is confirmed by the relative independence of Σ on the applied temperature and pressure. For example, Σ is identical for $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ -I for the LS state at 140 K and at 30 K as well as for $[\text{Fe}(\text{PM-AzA})_2(\text{NCS})_2]$ for the LS state at 110 K and at 30 K. Likewise, in $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, Σ is identical for the LS state at 130 K, at 30 K and at 1.0 GPa (293 K). Σ is also identical for this complex for the HS state at 293 K and in the light induced high spin state at 30 K.

Table 3 clearly indicates that there is neither a relationship between the $\Delta\Sigma$ and Δr values nor between the Σ and d_{FeL} values. These two parameters and their variations are thus complementary in characterizing the structural modification due to the spin crossover in a complex. We assume that such a means of estimating the deformation of the metal environment could be successfully extended to all spin crossover systems.

Another way to consider the distortion is for example the trigonal twist angle derived as shown in Fig. 3. There are six such angles with 60° as the value for a regular octahedron. We have chosen to investigate the angle which is opposite to the NCS ligands. The so defined angle, noted θ_{NCS} , is therefore a characteristic of only the $[\text{FeL}_n(\text{NCS})_2]$ complexes, unlike Σ which is a parameter that may be calculated in all the six coordinate metal spin crossover compounds. With the exception of the $n=4$ complexes, all the θ_{NCS} values (Tables 3 and 4) are lower than 60° and indicate a strong distortion of the HS octahedron in the $[\text{FeL}_n(\text{NCS})_2]$ complexes. The difference between the pure LS and the pure HS values, denoted $\Delta\theta_{\text{NCS}}$, is positive for each complex, confirming that the LS octahedron is less distorted. However, contrary to the observation made on the Σ parameter, the HS values of θ_{NCS} may differ significantly from one complex to another even within the $[\text{Fe}(\text{PM-X})_2(\text{NCS})_2]$ series. Moreover, $\Delta\theta_{\text{NCS}}$ may be very small and even almost zero. The comparison of both distortion parameters shows that the highest values of Σ do not necessary correspond to the lowest values of θ_{NCS} and vice versa. Therefore each of these two parameters yields complementary information. θ_{NCS} might be relevant to account for differences in the magnetic properties; this point will be discussed later.

3.1.3

Octahedron Volume

It is only recently that the volume of the FeN_6 octahedron, denoted V_p , has been calculated [10, 50]. Such a calculation was done using a general method particularly suitable for distorted polyhedra [70]. The V_p values of all the $[\text{FeL}_n(\text{NCS})_2]$ complexes are virtually identical, differences being within the standard deviation. This volume is $13.0(2) \text{ \AA}^3$ for the HS state and $10.0(1) \text{ \AA}^3$ for the LS state. The volume contraction along the HS $\rightarrow$ LS transition is then equal to $3.0(3) \text{ \AA}^3$, which corresponds to a decrease of around 25%.

On the basis of the study of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, it seems that the modification of V_p is identical for the thermal spin crossover, the photo-induced spin crossover and the high pressure spin crossover. This statement, however, has to be verified by further experiments.

Such an octahedron volume contraction together with the modification of the distortion should obviously affect significantly the topology of the crystallographic unit cell. The following paragraph reports on this aspect.

3.2

Crystallographic Unit Cells

The distribution of the unit cell symmetry in the $[\text{FeL}_n(\text{NCS})_2]$ complexes is sharp. Indeed, of the complexes studied so far, 11 crystallize in a monoclinic space group ($P2_1/c$ or $C2/c$), 9 in an orthorhombic space group ($Pccn$, $Pbcn$, or $Pbca$), 5 in the triclinic $P-1$ space group and 1 in the quadratic space group $I4_1/a$. The iron ion is in a general position in the triclinic and monoclinic unit cells while it lies on a twofold axis in the orthorhombic unit cells. The comparison of the HS and the LS unit cell symmetries in the $[\text{FeL}_n(\text{NCS})_2]$ complexes definitively proves that a sharp transition does not imply a change of space group.

The description of the lattice deformation is meaningful because the correlation between the mechanism of interaction among HS and LS molecules and the deformation of the crystal is still an active topic in spin crossover research [71–73]. In particular the volume change caused by the spin crossover as well as the anisotropy of the lattice deformation are used in the calculation of the interaction energy between the molecules [6, 49]. The purpose of the following description is to comment within this context on these structural parameters in the $[\text{FeL}_n(\text{NCS})_2]$ complexes.

3.2.1

Isotropic Contraction: ΔV_{SC}

It is well established now that the temperature dependence of the unit cell volume is strongly correlated to the nature of the spin crossover [1, 44]; a smooth spin crossover gives rise to a smooth unit cell volume modification while an abrupt spin crossover transition gives rise to an abrupt volume change. The difference between the pure HS and the pure LS unit cell volumes will be named hereafter $\Delta V_{SC}(T)$, $\Delta V_{SC}(P)$, or $\Delta V_{SC}(L)$ for respectively the thermal, the pressure, and the light induced spin crossover.

The determination of only the two HS and LS crystal structures is not adequate to obtain $\Delta V_{SC}(T)$. This must be extracted from the temperature dependence of the unit cell parameters determined over a large temperature range either by powder or single crystal X-ray diffraction. Indeed, this volume modification can only be determined by taking into account the contri-

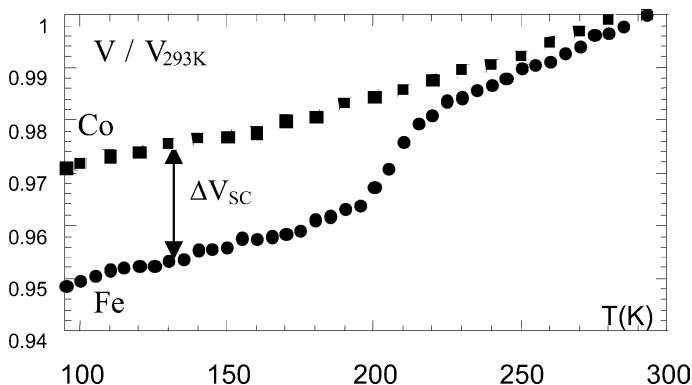


Fig. 4 Comparison of the temperature dependence of the relative unit cell volume for the isostructural $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\text{-II}$ (circle) and $[\text{Co}(\text{PM-BiA})_2(\text{NCS})_2]$ (square) complexes that shows the volume variation, noted ΔV_{SC} , due to the spin crossover only [10]

bution of the normal thermal contraction. In a first approach $\Delta V_{\text{SC}}(T)$ may be approximately determined by subtracting the pure LS (at low temperature) from the pure HS (at high temperature) unit cell volume temperature dependence. Such a method gave $\Delta V_{\text{SC}}(T)$ in the range $70 \text{ \AA}^3$ to $90 \text{ \AA}^3$ for the complexes of the $[\text{Fe}(\text{PM-X})_2(\text{NCS})_2]$ series [11, 12], $44 \text{ \AA}^3$ for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, and $47 \text{ \AA}^3$ for $[\text{Fe}(\text{btz})_2(\text{NCS})_2]$ [59]. Interestingly all these $\Delta V_{\text{SC}}(T)$ values correspond to the similar percentage of the corresponding room temperature volume: $\sim 2\%$. A more accurate study of $\Delta V_{\text{SC}}(T)$ has been performed for $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\text{-II}$ using the volume temperature dependences of this complex and that of its Co(II) analogue which is isostructural with the Fe(II) complex at room temperature but does not display a spin crossover [10]. The $\Delta V_{\text{SC}}(T)$ value ($70(2) \text{ \AA}^3$) corresponds to 2.0% of the room temperature HS volume and confirms the previous results (Fig. 4). A similar value is obtained in the tetrazole spin crossover complexes, $[\text{Fe}(\text{mtz})_6](\text{PF}_6)_2$ and $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$, even though the structural properties are very different from those of the present family [6]. In general, it would not be surprising, however, to observe larger $\Delta V_{\text{SC}}(T)$ when a structural phase transition occurs.

Are $\Delta V_{\text{SC}}(P)$, $\Delta V_{\text{SC}}(L)$, and $\Delta V_{\text{SC}}(T)$ identical for a same complex? The pressure dependence of the unit cell allows the determination of $\Delta V_{\text{SC}}(P)$, once again by distinguishing the pure compressibility contribution from the effect of the spin crossover. Unfortunately, too few high pressure structural data are available to estimate the decrease of $\Delta V_{\text{SC}}(P)$ in general. In the case of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{btz})_2(\text{NCS})_2]$, $\Delta V_{\text{SC}}(P)$ is found approximately $10 \text{ \AA}^3$ larger than the corresponding $\Delta V_{\text{SC}}(T)$ [59]. The way to obtain a true value of the unit cell volume reduction due to the spin crossover without any correction is to compare the HS and LS structural data of a complex at

the same temperature and under the same pressure. The unit cell volumes of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ in HS-2 and LS at 30 K (1 atm) give a $\Delta V_{\text{sc}}(\text{L})$ of $24 \text{ \AA}^3$. This value is about twice as small as $\Delta V_{\text{sc}}(\text{T})$ estimated from the unit cell temperature dependence. The powder X-ray investigations [6] of a tetrazole spin crossover complex, $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$, have yielded an identical result, $\Delta V_{\text{sc}}(\text{L})$ being two times smaller than $\Delta V_{\text{sc}}(\text{T})$. On the basis of these results, it seems that the unit cell volume reduction due solely to spin crossover is different for the thermal, the pressure and the light induced spin crossovers. The comparison of the volume reductions gives $\Delta V_{\text{sc}}(\text{T})$ slightly smaller than $\Delta V_{\text{sc}}(\text{P})$ and almost twice as large as $\Delta V_{\text{sc}}(\text{L})$. Further experimental work under high pressure or light-irradiation should be performed to confirm this observation.

3.2.2

Anisotropy

The anisotropy of the thermal unit cell contraction is a general feature in molecular materials as they often crystallize in low symmetry space groups. In the study of spin crossover complexes, one has to distinguish the cell parameter changes due to the classical thermal effects from the cell parameter modifications due to the spin crossover only. For example, the temperature dependence of the unit cell parameters of $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\text{-II}$ has shown that from 300 to 90 K the *b* and *c* parameters decrease while the *a* parameter and the β angle increase but the study of the isostructural $[\text{Co}(\text{PM-BiA})_2(\text{NCS})_2]$ complex proved that the increase of β is a purely thermal effect.

In a first approach the anisotropy of the unit cell contraction may be analyzed through the temperature dependence of the unit cell parameters within a large temperature range that includes the spin crossover. Such an investigation performed on $[\text{FeL}_n(\text{NCS})_2]$ complexes has shown the diversity of the behavior. For example, $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ displays a high anisotropy while $[\text{Fe}(\text{btz})_2(\text{NCS})_2]$ shows a quasi isotropic behavior. Such a difference has been directly connected to the difference in crystal packing [59]. The $[\text{Fe}(\text{PM-X})_2(\text{NCS})_2]$ series also confirms the diversity of the behavior. The lattice temperature dependence of $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\text{-I}$ and $[\text{Fe}(\text{PM-PeA})_2(\text{NCS})_2]$ shows that of the three cell parameters, one increases, one decreases and one remains nearly constant at the spin crossover [12, 13]. In contrast, all the unit cell parameters for $[\text{Fe}(\text{PM-TeA})_2(\text{NCS})_2] \times \text{CH}_3\text{OH}$ and $[\text{Fe}(\text{PM-AzA})_2(\text{NCS})_2]$ decrease [11].

A further characterization of the anisotropy of the unit cell can be achieved with the calculation of the expansion tensors from the unit cell temperature dependence. In this case, the results must however be interpreted keeping in mind that the elements of the tensor are very sensitive to the choice of the temperature region used for the calculation. First this tensor

allows the calculation of the bulk modulus that reflects the ability of the unit cell to deform. Very few data are available [10, 59] and the only general comment that may be made is that bulk modulus values for the studied spin crossover complexes are of the same order of magnitude as the values obtained for molecular material. Then, the direction of the main and least expansion may be determined. For example in $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ -II the thermal expansion tensor suggests that the intermolecular space corresponding to π - π interactions is more affected by the temperature than the hydrogen contact direction. Moreover, it is clear from all the available tensors calculated for the $[\text{FeL}_n(\text{NCS})_2]$ family that, in general, the thermal expansion is not the same in both high spin and low spin phases. This result is not in conflict with the possibility of finding in some particular cases similar thermal expansion in the two spin states [7]. In general, however, this result should be taken into account in any attempts to correlate spin crossover features with the deformation of the lattice.

4

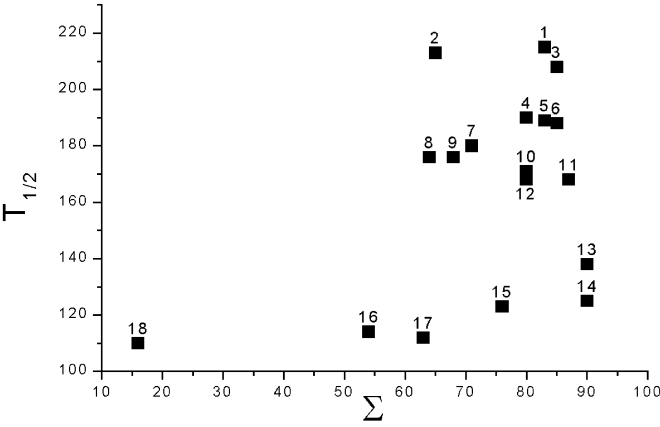
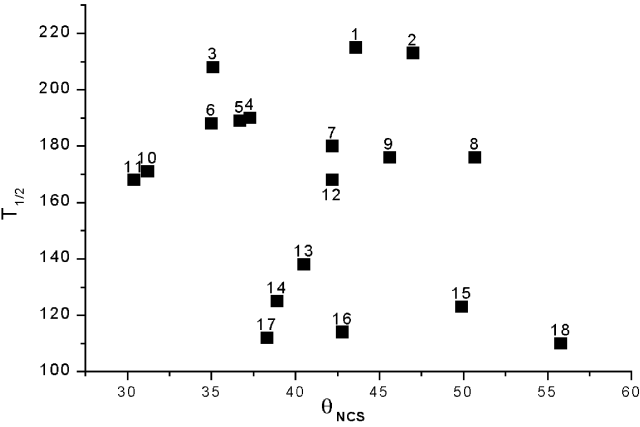
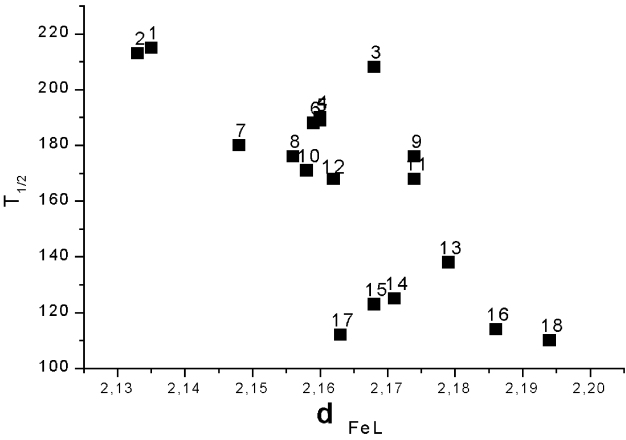
Structural vs Magnetic Features

We have focused on some structural features and their modifications at the spin crossover. The aim of the following discussion is now to show the influence of the structural properties on the magnetic features of the spin crossover.

4.1

Temperatures of Spin Crossover

Is there a structural reason to explain why the spin crossover occurs in some complexes and not in others? Regarding the intermolecular interactions the answer seems to be negative. Indeed, $[\text{FeL}_n(\text{NCS})_2]$ complexes with similar crystal packing may or may not display spin crossover. This is, for example, the case with the $[\text{Fe}(\text{PM-X})_2(\text{NCS})_2]$ series. It has also been shown that the existence of spin crossover is not altered by the absence of hydrogen bonds [44] although the features are affected by their presence, as discussed below. In contrast, intramolecular structural features may be involved in the failure of a complex to undergo spin crossover. For example, long Fe-N bond lengths weaken the crystal field. This reason is put forward to explain why the complexes $[\text{Fe}(\text{dppa})(\text{NCS})_2]$ -B, $[\text{Fe}(2,9\text{-dmp})_2(\text{NCS})_2]$, or $[\text{Fe}(\text{py})_4(\text{NCS})_2]$ do not show a spin crossover even when cooled to very low temperature. However, a contradiction of such an assumption is, for example, shown by longer Fe-N bond lengths in *cis*- $[\text{Fe}(\text{stpy})_4(\text{NCS})_2]$ than in *trans*- $[\text{Fe}(\text{stpy})_4(\text{NCS})_2]$. The distortion of the FeN_6 octahedron, either measured with Σ or θ_{NCS} , does not seem to be connected with the failure to undergo



spin crossover. Indeed, similar values are found in complexes with opposite behaviors.

The temperature of the thermal transition, noted $T_{1/2}$, may be very different in complexes showing a similar octahedron geometry. The dispersion of the expansion and distortion parameters over the $T_{1/2}$ range does not show any strict correlation (Fig. 5). Indeed, similar Fe-N bond lengths may correspond either to high or low $T_{1/2}$. Similar anisotropy of the Fe-N bond lengths leads to different $T_{1/2}$ and vice versa. Likewise relatively strong distortion may also either correspond to high or low $T_{1/2}$. The variations at the spin crossover of this octahedron geometry estimated from Δr , $\Delta\Sigma$, or $\Delta\theta_{\text{NCS}}$ also display no correlation with the transition temperature. To sum up, the investigation of a large structural data set like that for the $[\text{FeL}_n(\text{NCS})_2]$ family shows that obvious relationships between the octahedron geometry and $T_{1/2}$ do not exist in a rigorous way. The only general tendency concerns d_{FeL} . Despite exceptions, it seems that, to a first approximation, the higher d_{FeL} the lower $T_{1/2}$. The octahedron geometry therefore plays a role but is not the predominant characteristic to account for $T_{1/2}$.

Let us now examine the influence of the octahedron geometry on the $T(\text{LIESST})$ value. It is first important to note that up to now only seven $T(\text{LIESST})$ values have been recorded in the $[\text{FeL}_n(\text{NCS})_2]$ family. Any statistical analysis is then to be viewed with caution. Figure 6 indicates that there is no evident correlation between $T(\text{LIESST})$ and the geometry of the octahedron in the room temperature HS state. It would however be better to compare $T(\text{LIESST})$ with the geometry of the octahedron in the light-induced HS state. At present, the lack of structural information for the HS-2 prevents such an ideal approach.

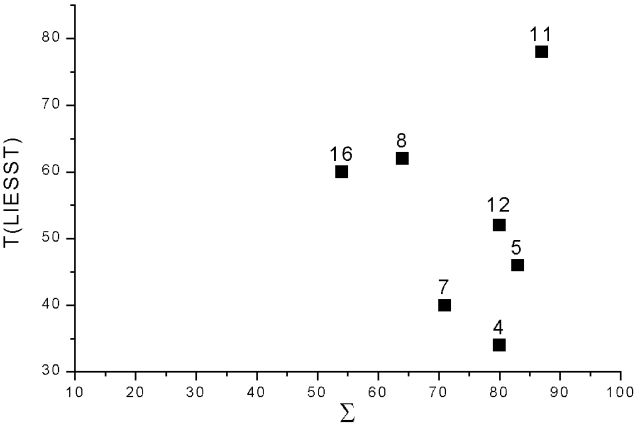
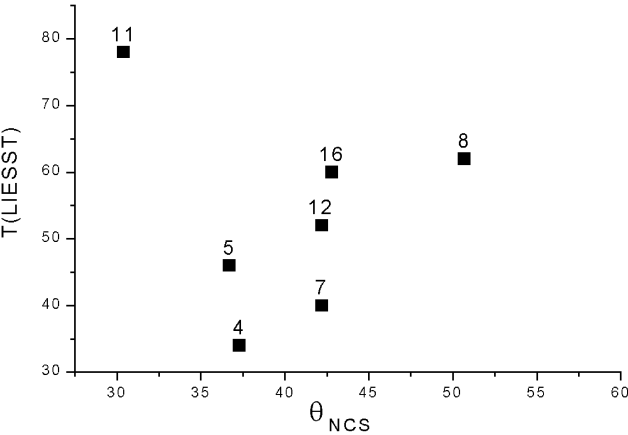
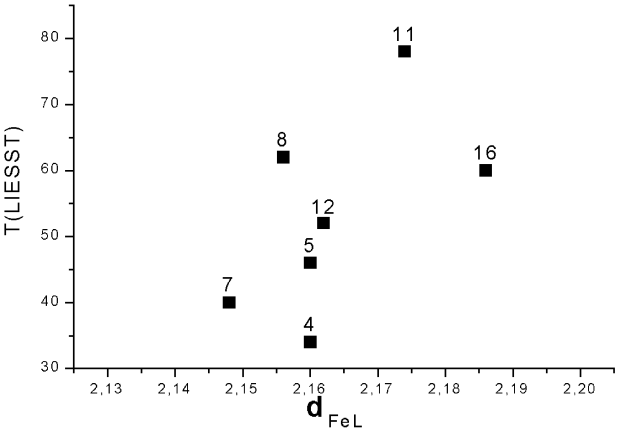
4.2

Hysteresis

It may happen that the temperature of transition is higher in the warming mode than in the cooling mode, i.e., that there is an hysteresis loop. Some of the complexes of the $[\text{FeL}_n(\text{NCS})_2]$ family show such a feature (Table 1) and two of them, $[\text{Fe}(\text{PM-PeA})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{dpp})_2(\text{NCS})_2]\cdot\text{py}$, even exhibit an unusually large hysteresis. The magnetic feature in $[\text{Fe}(\text{PM-PeA})_2(\text{NCS})_2]$ was related to a very short intermolecular interaction [12] involving the



Fig. 5 Plot for the $[\text{FeL}_n(\text{NCS})_2]$ complexes of the temperature at which 50% of the molecular complex is in HS, noted $T_{1/2}$, vs the different parameters that characterize the octahedron geometry in the HS state: the average of the six Fe-N bond lengths, d_{FeL} (Å) (*top*), the distortion parameter θ_{NCS} (°) (*middle*), and the distortion parameter Σ (°) (*bottom*). See Table 1 for labels



carbon-carbon triple bond of the PEA ligand. Similarly, the hysteresis in $[\text{Fe}(\text{dpp})_2(\text{NCS})_2]\cdot\text{py}$ has been associated with strong π - π interaction networks [30].

The presence of a hysteresis loop does not necessarily mean that a structural phase transition occurs. One of the most studied spin crossover compounds, $[\text{Fe}(\text{2-pic})_3]\text{Br}_2\cdot\text{EtOH}$, provides experimental proof of such an assertion [7]. Examples are also given within the $[\text{FeL}_n(\text{NCS})_2]$ family by $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\cdot\text{I}$ or $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ for which the unit cell symmetry is identical whatever the spin state of the iron ion is. However, in the case of a very large hysteresis, one may expect to observe a change in the unit cell symmetry. Unfortunately, the crystal structure of the LS form of only one of the $[\text{FeL}_n(\text{NCS})_2]$ complexes showing a large hysteresis, $[\text{Fe}(\text{PM-PeA})_2(\text{NCS})_2]$, has been determined. In this case, a structural phase transition accompanies the spin crossover and the crystal packing is less symmetric in HS (monoclinic $\text{P2}_1/\text{c}$) than in LS (orthorhombic Pccn). The iron atoms are aligned in LS while they form a zigzag in HS. In the case of $[\text{Fe}(\text{bt})_2(\text{NCS})_2]$, the authors mention that the single crystals do not survive the HS $\rightarrow$ LS transition which could also be seen as the consequence of a large structural rearrangement. In general, discussions on which of the structural phase transition or the spin transition triggers the hysteresis leads to a “hen and egg” like problem, and the question remains, therefore, unsolvable. In particular cases, however, the question may be investigated. To this end classical X-ray diffraction cannot allow the observation of the structural phase transition separately from the spin crossover, time dependent X-ray diffraction and spectroscopic studies would certainly be much more relevant. They have been used to show that, in $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$, the hysteresis originates in the crystallographic phase transition [76–78].

4.3

Abruptness of Transition

4.3.1

Intramolecular Parameters

For a long time, the Δr value had been considered by some workers as the main parameter that governs the abruptness of the transition. However,



Fig. 6 Plot for the $[\text{FeL}_n(\text{NCS})_2]$ complexes of T(LIESST), the temperature that characterizes the LIESST effect, vs the different parameters that characterize the octahedron geometry in the HS state: the average of the six Fe-N bond lengths, d_{FeL} (Å) (*top*), the distortion parameter θ_{NCS} (°) (*middle*), and the distortion parameter Σ (°) (*bottom*). See Table 1 for labels

some preliminary studies based on the comparison of only two complexes seemed to contradict this assumption [15]. Here, with the large amount of data now available, we confirm that the Δr value is not a relevant parameter to account for the difference in abruptness of the spin crossover. Indeed, direct comparison of magnetic spin crossover features (Table 1) and Δr values (Table 3) shows that there is no link between Δr and the abruptness of the transition. One can argue that, due to the sensitivity of the spin crossover to small changes, slight differences in Δr could lead to distinct magnetic features. However, the $[\text{FeL}_n(\text{NCS})_2]$ complexes demonstrate that Δr values related to a smooth transition may be smaller or larger than those related to very abrupt transition complexes. For example, Δr for complexes showing smooth transition, such as $[\text{Fe}(\text{PM-AzA})_2(\text{NCS})_2]$, $[\text{Fe}(\text{bt})_2(\text{NCS})_2]$, or $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\text{-II}$, may be either larger or smaller compared to Δr for complexes presenting an abrupt transition such as $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, $[\text{Fe}(\text{btz})_2(\text{NCS})_2]$, or $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\text{-I}$. The same comment can be made by looking at the Fe-N bond lengths in detail (Table 2). Indeed, comparison of all the Fe-N bond lengths of the $[\text{FeL}_n(\text{NCS})_2]$ complexes shows no correlation between the abruptness of the transition and the maximum length or the spread (anisotropy) of the values for the Fe-N bonds. Consequently, it is clear that other structural features that do not concern the octahedron expansion might be predominant.

Let us consider the influence of the octahedron distortion on the abruptness of the transition. The parameter Σ may be identical for complexes showing very different spin crossover features. It is for instance identical (80°) in $[\text{Fe}(\text{bt})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{tap})_2(\text{NCS})_2]\cdot\text{CH}_3\text{CN}$ that, respectively, exhibit an abrupt and a very smooth spin transition. The role of this parameter is then limited. In contrast, the θ_{NCS} parameter seems to be more sensitive to the shape of the spin transition as the values of θ_{NCS} are different from one complex to the other. However, it is rather difficult to correlate these values directly with the magnetic features for all the $[\text{FeL}_n(\text{NCS})_2]$ complexes. In the particular case of the $[\text{Fe}(\text{PM-X})_2(\text{NCS})_2]$ series, the smaller θ_{NCS} , the more abrupt the transition. At this point, it is worth noting that the θ_{NCS} angle we have defined depends on the geometry of the NCS ligand. As the latter is strongly involved in the cohesion of the crystal packing, this remark strengthens the assumption that intermolecular interactions must play a predominant role in determining the abruptness of the spin crossover.

4.3.2

Crystal Packing

The same molecular complex may crystallize in various symmetries resulting in very different spin crossover features (Table 1). For instance, the orthorhombic form of $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ undergoes a very abrupt transi-

tion while the monoclinic form shows a smooth spin crossover. However, the comparison of the structural and magnetic properties of all the polymorphs within the $[\text{FeL}_n(\text{NCS})_2]$ family shows that there is no correlation between the symmetry of the unit cell and the sharpness of the transition. In the same way, the comparative study of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{btz})_2(\text{NCS})_2]$, later confirmed by the study of the two phases of $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$, had clearly established that the amplitude of the unit cell volume reduction does not explain the sharpness of the transition. In contrast, our study confirms that the anisotropy of the unit cell contraction is a relevant parameter to take into account for the abruptness of the transition. Indeed, the main differences between complexes that undergo an abrupt transition like $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ or $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ -I and those that undergo a smooth spin crossover like $[\text{Fe}(\text{btz})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{PM-AzA})_2(\text{NCS})_2]$ come from the lattice anisotropy. The latter is linked to the crystal packing that defines how the unit cell contraction is distributed over the different directions in space. Consequently, features of the crystal packing can be expected to influence the nature of the spin transition.

In the $[\text{FeL}_n(\text{NCS})_2]$ complexes the crystal packing is driven by π - π interactions as well as by intermolecular hydrogen contacts. It is to be expected that, in general, strong intermolecular interactions will enhance the cooperativity [1, 44, 79–81]. The study of the $[\text{Fe}(\text{PM-X})_2(\text{NCS})_2]$ complexes has provided a clear proof that the topology of the π - π interactions is important in accounting for the abruptness of the transition. Within this series, the transition is more abrupt when these interactions are found in all directions and, in particular, the inclusion of a solvent molecule that blocks the π - π interactions concomitantly results in a smooth spin crossover. The same statement on the role of the π - π interactions has been made in the comparative study of $[\text{Fe}(\text{btz})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$. In addition, in solid state spin crossover materials, hydrogen bonds are suspected to play an important role in the propagation of the information about the change of the spin state and thus the abruptness of a transition [44, 79]. Evidence for the influence of hydrogen bonding had been first given in the study of $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2\cdot\text{Sol}$ ($\text{Sol}=\text{EtOD}$, MeOD) where the replacement of hydrogen by deuterium affects the spin crossover features [82]. In almost all the $[\text{FeL}_n(\text{NCS})_2]$ complexes studied, short $\text{S}\cdots\text{H-C}$ intermolecular hydrogen bonds are found. For instance, in all the complexes of the $[\text{Fe}(\text{PM-X})_2(\text{NCS})_2]$ series the NCS ligands are involved in hydrogen bonding (Fig. 7). In this series where each complex displays different magnetic spin crossover behavior, one of the main distinctions in the crystal packing of the complexes concerns the length of intermolecular $\text{S}\cdots\text{H-C}$ contacts. Figure 8 shows a direct correlation between the length of this contact in the room temperature HS crystal packing and the abruptness of the transition deduced from the magnetic curves. The shorter the $\text{S}\cdots\text{C}$ distances the more abrupt the spin crossover. Such a result constitutes a direct experimental proof of the correlation between structural and

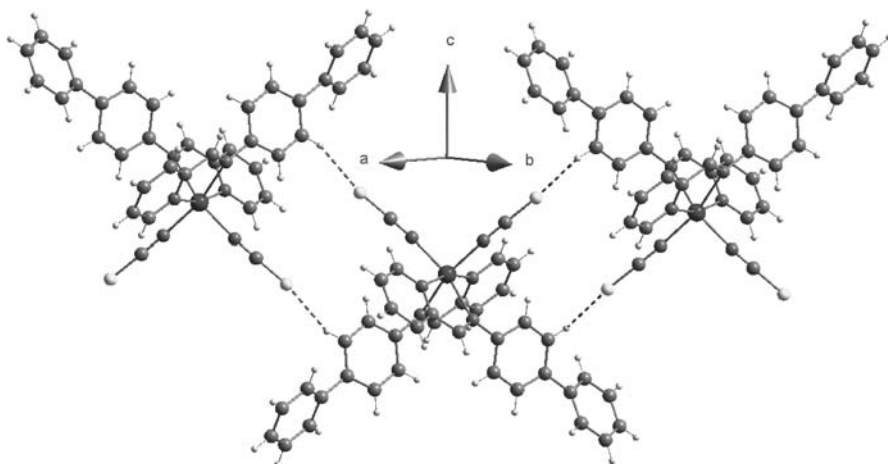


Fig. 7 View of the S...H-C hydrogen bond in $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]\cdot\text{I}$

magnetic features. It demonstrates further the paramount role of hydrogen bonding on the spin crossover features. Hydrogen bonding had also been taken into consideration to explain for example the presence of a more abrupt transition in polymorph C of $[\text{Fe}(\text{dppa})(\text{NCS})_2]$ than in polymorphs

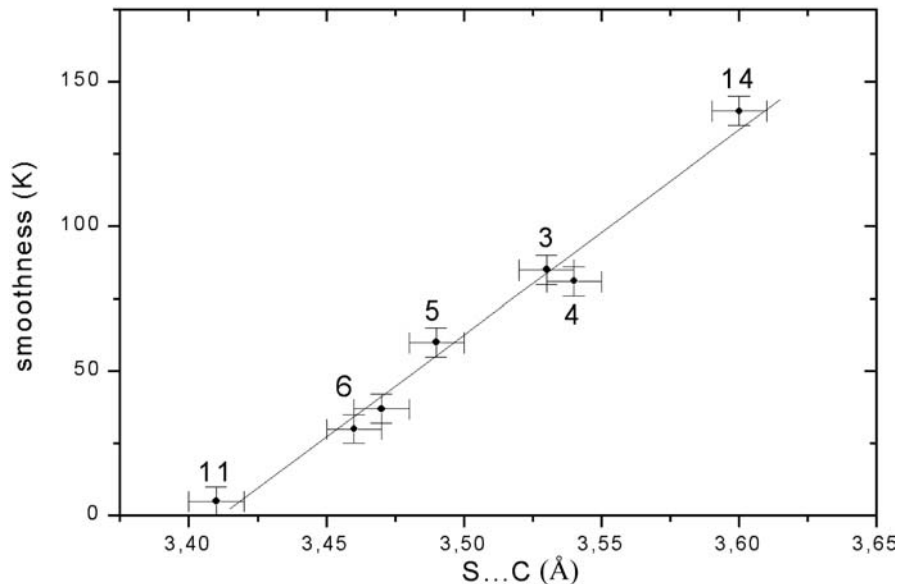


Fig. 8 Plot of the smoothness of the transition, here defined as the difference in the temperatures for which 80% and 20% of the molecular complexes are in HS, vs the length of the shortest S...C intermolecular distances within the crystal packing of the $[\text{Fe}(\text{PM-X})_2(\text{NCS})_2]$ complexes. See Table 1 for labels

A and B [24]. The role of the hydrogen bond network has also been shown elsewhere in the study of salicylidene based iron(II) complexes for which modifications of such a network directly trigger the features of the spin crossover [83].

5 Conclusion

On the basis of the X-ray diffraction study of 26 iron(II) complexes of the $[\text{FeL}_n(\text{NCS})_2]$ family, general trends of the spin crossover phenomenon have been shown and some previous correlations have been confirmed and others have been invalidated. We assume that most of the results discussed in this chapter for the $[\text{FeL}_n(\text{NCS})_2]$ complexes family may be extended to other spin crossover complexes, especially mononuclear compounds. These results can be summarized as follows:

- Contrary to what was previously believed, the transitions are not more abrupt when Δr values are larger. The Δr parameter and in general the Fe-N bond lengths are not a predominant structural property to account for the features of the spin crossover.
- The distortion of the FeN_6 octahedron is a more complex structural feature because of the large number of ways in which it can be characterized. For example, the Σ parameter accounts only for the spin state while the θ_{NCS} parameter seems to be correlated somewhat with the abruptness of the transition. Nevertheless, in any case, the LS octahedron is less distorted than the HS octahedron.
- The decrease of the FeN_6 octahedron volume from HS to LS is typically 25%.
- The reduction of the unit cell volume, $\Delta V_{\text{SC}}(T)$, due to the thermal spin crossover only—the pure thermal contraction being subtracted—is of the order of 2% of the room temperature volume. Besides, for the same complex, the effects of the thermal, the pressure and the light induced spin crossovers on the unit cell volume do not appear to be necessarily identical. Further investigations are however required to confirm this assumption.
- Differences in the amplitude of $\Delta V_{\text{SC}}(T)$ from one complex to another do not account for differences in the abruptness of the transition. In contrast, the anisotropy of the lattice deformation must be considered in accounting for the abruptness of a transition.
- Hydrogen bonds play a paramount role in the propagation of the spin state change from one complex to the other, i.e., on the cooperativity of the system. The more efficient the hydrogen bond network the more abrupt the transition.

To conclude, we would like to make a few general comments on this chapter. First, throughout the discussion, we have pointed out that small changes in the crystal packing may influence intramolecular properties, such as the

Fe-N bond lengths for instance. Consequently, the intramolecular properties must always be kept in mind along with the intermolecular features. This confirms the assumption that in the solid state the magnetic properties of spin crossover compounds must be interpreted with care in the absence of structural data. Second, some structural features have not been discussed here, thermal motion for example. We have investigated the temperature dependent displacement parameters of the atomic position in some $[\text{FeL}_n(\text{NCS})_2]$ complexes [11] but we have been unable to detect any significant difference of behavior with non-spin crossover material and consequently we have not considered such data to be relevant here. It is worth pointing out that classical X-ray diffraction is probably not the most appropriate technique to account for this feature which can be investigated by spectroscopy techniques or well described with very accurate X-ray diffraction such as a charge density determination. The influence of crystal quality is also not discussed in this paper due to a lack of experimental data. Without doubt, crystal defects of any nature in the crystal must influence the propagation of the spin change.

This chapter highlights the need for structural data under varying conditions. In particular detailed study of the effects of high pressure on the structural properties must be undertaken prior to any industrial application (for example as pressure sensors) involving high pressure induced spin crossover compounds. To achieve this aim, structural data under high pressure are required. Finally, classical X-ray diffraction as discussed in this chapter has shown its limitations since it explores structure, not mechanism. However, the rapid development of time resolved X-ray crystallography now allows the study of time dependent structural changes of, for example, excited states [84, 85]. Exploration of spin crossover compounds using such a technique would undoubtedly contribute to greater understanding and control of this fascinating phenomenon.

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Note Added in Proof

While this article is in press, a large number of significant results based on the structural studies of mononuclear Fe(II) spin crossover complexes have been obtained and published. Some of them echo the questions raised in the conclusion of the present review and relevant points are elucidated. Selected results can be summarized as follows.

- the modification of the unit cell volume due to the SCO, named ΔV_{SC} , does not depend on the manner to obtain the HS state. This has been clearly demonstrated by the description of the crystal structures of some Fe(II) complexes either in photo-induced [86, 87] or in thermal trapped HS metastable states [88].

– the crystal structures of the same complex in a metastable HS state and in the stable room temperature HS state show very significant differences in the crystal packing, *i.e. in the cooperativity*, but not in the geometry of the Fe intramolecular environment [86,88]. This confirms the assumption developed in the present review.

– the strong influence of the intermolecular hydrogen bonds on the SCO abruptness in $[\text{FeL}_n(\text{NCS})_2]$ complexes has been confirmed [89, 90] and extended to $[\text{FeL}_n(\text{NCSe})_2]$ complexes [86].

– the distortion of the FeN_6 octahedron is clearly correlated to the spin crossover features. Indeed, it has been shown, using a new structural parameter derived from the *twist* angle, that $T(\text{LIESST})$ increases and $T_{1/2}$ decreases linearly when the octahedron distortion increases [91]. This result suggests that the more the HS $\text{Fe}(\text{II})$ coordination sphere is distorted the more $T(\text{LIESST})$ is close to the room temperature. The role of this distortion deserves thus to be examined in details. To our mind, an interesting route has been recently opened by the notion of Continuous Symmetry applied to the spin crossover complexes [92].

To finish we would like to mention an interesting result that deals with the structural aspects of the SCO. Two research teams have shown independently that, in the SCO $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ complex, when half of the complexes are in the HS state and half in the LS state, there is no diffuse scattering but well shaped Bragg peaks [87,93]. Collet et al. have evidenced the coexistence of the Bragg peaks corresponding to the HS state and to the LS state during the photo-induced HS state to LS state relaxation [87]. Bürgi et al. have observed the occurrence of an intermediate phase at $T_{1/2}$ characterized by additional Bragg peaks [93]. Both results are interpreted by the authors as a failure of the mean field approach generally used in models to describe the SCO features and particularly the photomagnetism. Indeed, this approach considers the SCO as an homogeneous process and therefore predicts diffuse scattering in the above experiments. Consequently, the mechanism itself of the SCO is questioned here and thus this should attract attention from the SCO community.

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References

1. König E (1987) *Prog Inorg Chem* 35:527
2. König E, Ritter G, Kulshreshtha SH (1985) *Chem Rev* 85:219
3. König E, Madeja K (1966) *Chem Commun* 3:61
4. König E, Watson KJ (1970) *Chem Phys Lett* 6:457
5. Gülich P (1981) *Struct Bond* 44:83
6. Wiehl L, Spiering H, Gülich P, Knorr K (1990) *J Appl Cryst* 23:151

7. Wiehl L, Kiel G, Köhler CP, Spiering H, Gütlich P (1986) *Inorg Chem* 25:1565
8. Létard JF, Guionneau P, Codjovi E, Lavastre O, Bravic G, Chasseau D, Kahn O (1997) *J Am Chem Soc* 119:10861
9. Létard JF, Guionneau P, Rabardel L, Howard JAK, Goeta A, Chasseau D, Kahn O (1998) *Inorg Chem* 37:4432
10. Guionneau P, Marchivie M, Bravic G, Létard JF, Chasseau D (2002) *J Mater Chem* 12:2546
11. Guionneau P, Brigouleix C, Barrans Y, Goeta A, Létard JF, Howard JAK, Gaultier J, Chasseau D (2001) *C R Acad Sci Ser IIc Chim* 161
12. Guionneau P, Létard JF, Yufit DS, Chasseau D, Bravic G, Goeta A, Howard JAK, Kahn O (1999) *J Mater Chem* 9:985
13. Daubric H, Kliava J, Guionneau P, Chasseau D, Létard JF, Kahn O (2000) *J Phys Condens Matter* 12:5481
14. Gaudry JB, Capes L, Langot P, Marcén S, Kollmannsberger M, Lavastre O, Freysz E, Létard JF, Kahn O (2000) *Chem Phys Lett* 324:321
15. Real JA, Gallois B, Granier T, Suez-Panama F, Zarembowitch J (1992) *Inorg Chem* 31:4972
16. König E, Madeja K, Watson J (1968) *J Am Chem Soc* 90:1146
17. Konno M, Mikami-Kido M (1991) *Bull Chem Soc Jpn* 64:339
18. Marchivie M, Kollmannsberger M, Guionneau P, Létard JF, Chasseau D. To be published
19. Létard JF, Chastanet G, Nguyen O, Marcén S, Marchivie M, Guionneau P, Chasseau D, Gütlich P (2003) *Monatsh Chem* 134:165
20. Moliner N, Muñoz C, Létard S, Létard JF, Solans X, Burriel R, Castro M, Kahn O, Real JA (1999) *Inorg Chim Acta* 291:279
21. Baker WA, Bobonich HM (1964) *Inorg Chem* 3:1184
22. Müller EW, Spiering H, Gütlich P (1982) *Chem Phys Lett* 93:567
23. Lee JJ, Sheu HS, Lee CR, Chen JM, Lee JF, Wang CC, Huang CH, Wang Y (2000) *J Am Chem Soc* 122:5742
24. Matouzenko GS, Bousseksou A, Lecocq S, van Koningsbruggen PJ, Perrin M, Kahn O, Collet A (1997) *Inorg Chem* 36:5869
25. Bradley G, McKee V, Nelson SM (1979) *J Chem Soc Dalton Trans* 533
26. König E, Ritter G, Irlér W, Nelson SM (1979) *Inorg Chim Acta* 37:169
27. Müller EW, Spiering H, Gütlich P (1983) *J Chem Phys* 79:1439
28. Real JA, Muñoz MC, Andrès E, Granier T, Gallois B (1994) *Inorg Chem* 33:3587
29. Matouzenko GS, Bousseksou A, Lecocq S, van Koningsbruggen PJ, Perrin M, Kahn O, Collet A (1997) *Inorg Chem* 36:2975
30. Zhong ZJ, Tao JQ, Dum CY, Liu YJ, You XZ (1998) *J Chem Soc Dalton Trans* 327
31. Claude R, Real JA, Zarembowitch J, Kahn O, Ouahab L, Grandjean D, Boukheddaden K, Varret F, Dworkin A (1990) *Inorg Chem* 29:4442
32. Roux C, Zarembowitch J, Gallois B, Granier T, Claude R (1994) *Inorg Chem* 33:2273
33. Figg DC, Herber RH, Potenza JA (1992) *Inorg Chem* 31:2111
34. Moliner N, Muñoz C, van Koningsbruggen PJ, Real JA (1998) *Inorg Chim Acta* 274:1
35. Little BF, Long GJ (1978) *Inorg Chem* 17:3401
36. Shue CF, Lee ZC, Wei HH, Cheng MC, Wang Y (1994) *Polyhedron* 13:2259
37. Cartier C, Thuery P, Verdaguer M, Zarembowitch J, Michalowicz A (1992) *J Phys C* 47:563
38. Decurtins S, Gütlich P, Hasselbach KM, Hauser A, Spiering H (1985) *Inorg Chem* 24:2174
39. Hauser A (1991) *Coord Chem Rev* 111:275

40. Decurtins S, Gülich P, Köhler CP, Spiering H (1985) *J Chem Soc Chem Commun* 340
41. Hauser A (1984) *Chem Phys Lett* 105:1
42. Hauser A (1986) *Chem Phys Lett* 124:543
43. Hauser A (1995) *Comm Inorg Chem* 17:17
44. Gülich P, Jung J, Goodwin HA (1996) Spin transition in iron(II) complexes. In: Coronado et al. (eds) *Molecular magnetism: from molecular assemblies to the devices*. NATO Advance Study Institute Series E321, Plenum, New York, p 327
45. Hauser A, Jęftic J, Romstedt H, Hinek R, Spiering H (1999) *Coord Chem Rev* 471
46. Létard JF, Capes L, Chastanet G, Moliner N, Létard S, Real A, Kahn O (1999) *Chem Phys Lett* 313:115
47. Herber R, Casson LM (1986) *Inorg Chem* 25:847
48. Kusz J, Spiering H, Gülich P (2000) *J Appl Cryst* 33:201
49. Kusz J, Spiering H, Gülich P (2001) *J Appl Cryst* 34:229
50. Marchivie M, Guionneau P, Howard JAK, Goeta AE, Chastanet G, Létard JF, Chasseau D (2002) *J Am Chem Soc* 124:194
51. Money VA, Radosavljevic Evans I, Halcrow MA, Goeta AE, Howard JAK (2003) *Chem Commun* 1:158
52. Collison D, Garner D, McGrath C, Mosselmans JFW, Roper MD, Seddon JMW, Sinn E, Young NA (1997) *J Chem Soc Dalton Trans* 4371
53. Fischer DC, Drickamer HG (1971) *J Chem Phys* 54:4825
54. Ksenofontov V, Levchenko G, Spiering H, Gülich P, Létard JF, Bouhedja Y, Kahn O (1998) *Chem Phys Lett* 294:545
55. Levchenko GG, Ksenofontov VK, Stupakov AV, Spiering H, Garcia Y, Gülich P (2002) *Chem Phys Lett* 277:125
56. Roux C, Zarembowitch J, Itié JP, Polian A, Verdaguer M (1996) *Inorg Chem* 35:574
57. Granier T, Gallois B, Gaultier J, Real JA, Zarembowitch J (1993) *Inorg Chem* 32:5305
58. Gaultier J, Granier T, Gallois B, Real JA, Zarembowitch J (1991) *High Press Res* 7:336
59. Granier T, Gallois B, Suez-Panama F, Gaultier J, Real JA, Zarembowitch J (1992) *Bull Soc Cat Cièn XIII*:293
60. Gallois B, Real JA, Hauw C, Zarembowitch J (1990) *Inorg Chem* 29:1152
61. Ozarowski A, McGarvey BR, Sarkar AB, Drake JE (1988) *Inorg Chem* 27:628
62. Sotofe I, Rasmussen SE (1967) *Acta Chem Scand* 21:2028
63. Hauser A (1992) *Chem Phys Lett* 192:65
64. Shannon RD, Prewitt CT (1969) *Acta Cryst* B25:925
65. Purcell KF (1979) *J Am Chem Soc* 101:5147
66. Musher JI (1972) *Inorg Chem* 11:2335
67. Drew MGB, Harding CJ, McKee V, Morgan CG, Nelson J (1995) *J Chem Soc Chem Commun* 1035
68. Makovicky E, Balic-Zunic T (1998) *Acta Cryst* B54:766
69. McCusker JK, Rheingold AL, Hendrickson DN (1996) *Inorg Chem* 35:2100
70. Balic Zunic T, Vickovic I (1996) *J Appl Cryst* 29:305
71. Spiering H, Meissner E, Köppen H, Müller EW, Gülich P (1982) *Chem Phys* 68:65
72. Meissner E, Köppen H, Spiering H, Gülich P (1983) *Chem Phys Lett* 95:163
73. Adler P, Wiehl L, Meissner E, Köhler CP, Spiering H, Gülich P (1987) *J Phys Chem Solids* 48:517
74. Gülich P, Hauser A, Spiering H (1994) *Angew Chem Int Ed Engl* 33:2024
75. Wiehl L (1993) *Acta Cryst* B49:289
76. Jęftic J, Romstedt H, Hauser A (1996) *J Phys Chem Solids* 57:1743
77. Jęftic J, Matsarski M, Hauser A, Goujon A, Codjovi E, Linares J, Varret F (2001) *Polyhedron* 20:1599

78. Jung J, Schmitt G, Wiehl L, Hauser A, Knorr K, Spiering H, Gütllich P (1996) *Z Phys B Condens Matter* 100:523
79. Kahn O (1993) *Molecular magnetism*. VCH, New York
80. Real JA, Andréz E, Muñoz MC, Julve M, Granier T, Bousseksou A, Varret F (1995) *Science* 268:265
81. Zarembowitch J, Roux C, Boillot ML, Claude R, Itie JP, Polian A, Boltec M (1993) *Mol Cryst Liq Cryst* 234:247
82. Gütllich P, Köppen H, Steinhäuser HG (1980) *Chem Phys Lett* 74:3
83. Salmon L, Donnadieu B, Bousseksou A, Tuchagues JP (1999) *C R Acad Sci Ser IIC Chim* 305
84. Kim CD, Pillet S, Wu G, Fullagar WK, Coppens P (2002) *Acta Cryst A* 58:133
85. Moffat K (2001) *Chem Rev* 101:1569
86. MacLean EJ, McGrath CM, O'Connor CJ, Sangregorio C, Seddon JMW, Sinn E, Sowrey FE, Teat SJ, Terry AE, Vaughan GBM, Young NA (2003) *Chem. Eur. J.* 9:21:5314
87. Huby N, Guérin L, Collet E, Toupet L, Ameline JC, Cailleau H, Roisnel T, Tayagaki T, Tanaka K (2003) *Phys. Rev. B* 69:020101
88. Marchivie M, Guionneau P, Létard JF, Chasseau D, Howard JAK (2004) *J. Phys. Chem. Sol.* 65:17
89. Real JA, Gaspar AB, Niel V, Munoz MC (2003) *Coord. Chem. Rev.* 236:121.
90. Marchivie M, Guionneau P, Létard JF, Chasseau D (2003) *Acta Cryst. B* 59:479
91. Marchivie M (2003) PhD, University Bordeaux I, N° 2746. Marchivie M, Guionneau P, Létard JF, Chasseau D (2004) submitted to *Acta Cryst. B*.
92. Alvarez S (2003) *J. Am. Chem. Soc.* 125:6795
93. Chernyshov D, Hostettler M, Törnroos KW, Bürgi HB (2003) *Angew. Chem. Int. Ed.* 42:3825.

Structural Investigations of Tetrazole Complexes of Iron(II)

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Dedicated to Professor Hans Bock on the occasion of his 75th birthday.

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Abstract The results of X-ray diffraction studies of spin crossover complexes of iron(II) with R=1-propyl- (ptz), 1- methyl- (mtz) and 1-ethyltetrazole (etz) ligands, [Fe(Rtz)₆](BF₄)₂, as a function of temperature (down to 10 K) and after light-induced conversion to long-lived metastable spin states (LIESST) are reviewed. Not only has the most prominent member of this class of spin crossover compounds, viz. [Fe(ptz)₆](BF₄)₂, been studied very extensively, particularly in relation to its photophysical properties and cooperative interactions in solids, but this general class of spin crossover complexes has also attracted much interest from a crystallographic point of view. [Fe(ptz)₆](BF₄)₂ has only one type of lattice site for the iron(II) centres, but it is possible to generate five different phases depending on the rate of cooling the sample on the one hand and on irradiation with light on the other. The methyl and ethyl-tetrazole derivatives, also being mononuclear systems, show the peculiarity that the iron(II) ions occupy two different lattice sites (A and B), with ratio 1:1 in the mtz complex and 2:1 in the etz complex, where only A site

ions undergo thermal spin transition but B site ions remain in the high spin state at all temperatures under study. The LIESST phenomenon has been verified at A and B lattice sites generating metastable HS states at A sites with green light and metastable LS states at B sites. Three possible phases created this way in the case of the mtz complex have been structurally characterised.

Keywords Spin crossover · Crystal structure · Lattice expansion · Phase transition · LIESST

List of Abbreviations

SCO	Spin crossover
HS	High spin
LS	Low spin
γ_{HS}	Molar fraction of HS molecules
LIESST	Light induced excited spin state trapping
$T_{1/2}$	Spin transition temperature (temperature of 50% conversion of all SCO-active complex molecules)
mtz	1-Methyl-tetrazole
etz	1-Ethyl-tetrazole
ptz	1- <i>n</i> -Propyl-tetrazole
pic	2-Picolylamine
phen	1,10-Phenanthroline

1

Introduction—Importance of Structural Studies in Spin Crossover Research

It is well established that thermal spin crossover (SCO) in solid transition metal compounds is always accompanied by more or less significant structural changes arising primarily from the changes in the electronic populations of the antibonding e_g and the weakly bonding t_{2g} orbitals. The charge depletion in the e_g orbitals and simultaneous increase of occupancy in the t_{2g} orbitals on going from the high spin (HS) to the low spin (LS) state act synergistically to shorten the metal-donor atom bond lengths. These bond length changes are particularly large, $\Delta r = r_{\text{HS}} - r_{\text{LS}} \approx 2.20 - 2.00 \text{ \AA} \approx 0.20 \text{ \AA}$ (ca. 10%) in the case of iron(II) SCO compounds with a total spin change of $\Delta S = 2$ resulting from the $(e_g)^2(t_{2g})^4 \leftrightarrow (e_g)^0(t_{2g})^6$ transition. The changes in Δr are somewhat smaller in iron(III) SCO compounds ($\approx 0.10 - 0.13 \text{ \AA}$), also with $\Delta S = 2$ transitions, but with one electron hole remaining in the t_{2g} orbitals: $(e_g)^2(t_{2g})^3 \leftrightarrow (e_g)^0(t_{2g})^5$. In the case of cobalt(II) SCO compounds Δr is relatively small, because only one electron is transferred between the e_g and t_{2g} orbitals in the $\Delta S = 1$ transitions: $(e_g)^2(t_{2g})^5 \leftrightarrow (e_g)^1(t_{2g})^6$. The structural changes also involve modifications of bond angles between the metal and ligand donor atoms, changes of intraligand bond lengths and angles and possibly changes of orientations of non-co-

ordinating anions and solvent molecules. All these structural changes are predominantly *displacive* but not bond breaking in nature.

It was proposed even in the early stages of SCO research that structural changes, particularly bond length changes, are expected to play an important role in the mechanism of the communication of changes of spin state from one complex molecule to another in the crystal lattice leading to *cooperative interactions*. A meaningful understanding of the nature of such cooperative interactions is possible only by following directly the positional changes of lattice atoms as a function of temperature using diffraction methods on single crystals. The first attempts to determine the crystal structures of SCO compounds at temperatures above and below the spin transition temperature were reported by König and Watson [1] and Leipoldt and Coppens [2]. The results available from temperature dependent X-ray diffraction measurements up to the mid-1980s were collected and discussed by König [3] in a comprehensive review on “Structural Changes Accompanying Continuous and Discontinuous Spin State Transitions”. Remarkable results from structural investigations on SCO complexes have been reported since then. There is, for instance, the observation of a step in the transition curve $\gamma_{\text{HS}}(T)$ for $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ [4], which is exactly mirrored in the temperature dependence of the unit-cell parameters [5]. Another remarkable observation on this system is that the bromide salt shows hysteresis in the spin transition curve, although the space group is the same in the HS and the LS phases. A similar observation was reported later by Gallois et al. [6] on a single crystal of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, for which they have found only a shortening in the Fe–N bond lengths and a noticeable variation of the N–Fe–N angles accompanying the change from HS to LS, leading to a more regular octahedral $[\text{Fe}-\text{N}_6]$ core. However, the system, for which a narrow hysteresis loop was detected in the steep spin transition curve [7], does not show a change in crystal symmetry.

It is now generally accepted that any attempt to treat theoretically spin transition phenomena, particularly for those systems with transition curves $\gamma_{\text{HS}}(T)$ revealing more or less strong deviations from simple Boltzmann population, as described in Chap. 1, must include both short-range and long-range cooperative interactions resulting from the structural changes due to spin transition. For instance, the model of Kambara is based on the Jahn-Teller coupling between the d-electrons and local distortion as the driving force for a spin transition [8]. Thermal spin transition in solid transition metal compounds is always accompanied by changes of the crystal lattice parameters, particularly in the metal-donor atom bond length. These changes have a strong impact on the whole crystal lattice, as can be seen from the pronounced temperature variation of the lattice parameters in the spin crossover region. A convincing example is the anomalous spin transition in $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$, where the step in the $\gamma_{\text{HS}}(T)$ curve is also seen in the temperature dependence of the unit-cell volume and other lattice parameters [5]. These observations have played a crucial role in the development of the

model of lattice expansion and elastic interactions [9, 10]. The theory developed by Spiering and co-workers takes as its basis changes of volume and shape of the lattice as the main factors for the cooperative interactions [10]. Within this model the elastic interaction energy between HS and LS molecules is calculated from the components of the deformation tensor, which describes the differences between the unit-cells of the lattice in the HS and the LS state, respectively. The experimental task was then to derive this deformation tensor from the temperature dependence of the lattice parameters. The lattice parameters $a_i(T)$ were found to depend linearly on the HS fraction $\gamma_{\text{HS}}(T)$ times a temperature independent deformation tensor. The results indicated that not only the volume change, represented by the trace of the tensor, but all tensor elements describing the entire deformation are necessary to account for the right magnitude of the elastic interaction energy. The “model of lattice expansion and elastic interactions” has been developed further and is described in detail by Spiering in Chap. 28.

Crystal structure analysis has received a particular boost during the last decade due to the enormous technical improvement in the experimental equipment. Rotating anode, focusing monochromator devices and CCD detectors have become standard components and reduce drastically the data acquisition time [11]. Cryogenic systems are available enabling more or less routine measurements down to ca. 10 K. Fibre optics have been mounted in the cryostats to enable the investigation of the structural changes resulting from irradiation of photomagnetic systems with light from tunable lasers; the well-known light-induced excited spin state trapping (LIESST) is an example which will be dealt with in the present article in the case of tetrazole complexes of iron(II). Special pressure cells have been developed which allow structural investigations as a function of temperature and pressure.

$[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ (ptz=1-*n*-propyl-tetrazole) is the SCO compound for which the photo-induced conversion from the stable LS state to a long-lived metastable HS state was first observed [12]. Hauser presents a detailed account on the phenomena of LIESST and reverse LIESST in Chap. 17. As the lifetime of the LIESST state is, at low temperature, sufficiently long for an X-ray diffraction experiment, it has been of particular interest to compare the lattice parameters and structural changes induced by light with those of the normal high and low temperature phases. In fact, this system may have five different phases depending on temperature, rate of cooling, and irradiation. In the following we shall discuss the results of our structural studies on all these phases.

The analogous iron(II) complexes with methyl- and ethyl-substituted tetrazole ligands show structural peculiarities in that the iron(II) ions occupy two inequivalent types of lattice sites. Only one of the lattice sites exhibits thermal spin transition, but light-induced spin state conversion can be achieved in both. We shall consider temperature dependent structural investigations on these systems before and after LIESST.

2

Crystal Structures of Iron(II) Tetrazole Complexes

A variety of tetrazole compounds were first synthesised and characterised as thermal SCO systems by Franke and co-workers [13, 14]. From X-ray powder diffraction it was concluded that the compounds with different Rtz ligands possess different structures. Thus this class of compounds appeared to be suited for studying the relationship between spin transition behaviour and structural properties. The six-coordinated iron(II) tetrazole complexes $[\text{Fe}(\text{Rtz})_6](\text{BF}_4)_2$ (Rtz=1-alkyl-tetrazole) with $\text{R} = -\text{CH}_3$ (mtz), $-\text{CH}_2\text{CH}_3$ (etz), $-\text{CH}_2\text{CH}_2\text{CH}_3$ (ptz), in which the space group changes with R, were chosen. The series provides examples of the strong interdependence of crystal structure and spin transition features.

2.1

Crystal Structures of Propyl-Tetrazole Compounds

The propyl-tetrazole compounds $[\text{Fe}(\text{ptz})_6]\text{X}_2$ ($\text{X} = \text{BF}_4^-$, ClO_4^-) crystallise in the rhombohedral space group $R\bar{3}$ ($Z=3$, hexagonal setting) with the following unit cell volumes at 300 K; $V=3423 \text{ \AA}^3$ for the BF_4^- salt and $V=3467 \text{ \AA}^3$ for the ClO_4^- [15]. The high spin Fe(II) atom is in a special position 3(a): 0,0,0 (site symmetry $\bar{3}$) and all $[\text{Fe}(\text{ptz})_6]^{2+}$ complexes are equivalent by lattice translations. All ligands are equivalent according to the $\bar{3}$ symmetry. The anions lie on the threefold axis, where B (or Cl) and one of the F (or O) atoms occupy the positions 6(c): 0,0, z and 0,0, $-z$ (site symmetry 3). The layers are perpendicular to the c axis and the order within the layers is exactly trigonal. Adjacent layers are shifted parallel to the planes according to the rhombohedral stacking. The stacking period is triple (Fig. 1). The distance between layers is ca. 11 Å.

A very similar structure has been found for $[\text{Zn}(\text{ptz})_6](\text{BF}_4)_2$ [16]. The structures of this compound at 110 and 190 K were determined by single crystal X-ray-diffraction measurements in order to investigate the possible local structural deformation, proposed from the measured gradual increase of the ortho-positronium lifetime with decreasing temperature [17]. At each temperature, the space group is $R\bar{3}$ and the zinc ion resides at the special position (0,0,0), and B and F1 atoms lie on the threefold axis. Thus all ptz ligands are equivalent according to the $\bar{3}$ symmetry. The $[\text{Zn}(\text{ptz})_6]^{2+}$ cations and the anions form the layer in the ab planes. The difference in the crystal structure between 190 and 110 K is very small except for the large thermal contraction along the c axis in $[\text{Zn}(\text{ptz})_6](\text{BF}_4)_2$ because Zn with its complete d shell cannot show a spin transition.

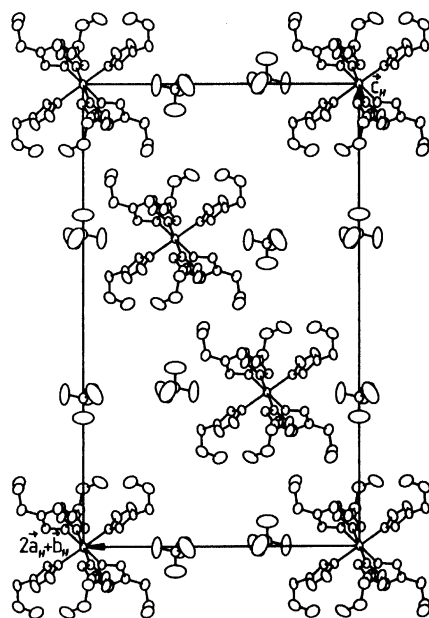


Fig. 1 Projection along the hexagonal b axis of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ at 195 K (HS state) showing only the groups with centres at zero. The structure consists of layers perpendicular to the c axis (from [15])

2.1.1

Crystal Structure of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ After Rapid Cooling (LS Super-Cooled Phase)

Ozarowski et al. [18] observed in an EPR study on a single crystal of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ doped with $\text{Mn}(\text{II})$ and $\text{Cu}(\text{II})$ that two different LS phases may be generated depending on the rate of cooling the sample through the spin transition region. On slow cooling and heating, $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ shows an abrupt and complete spin transition with hysteresis with $T_{1/2\downarrow} \sim 128 \text{ K}$, $T_{1/2\uparrow} \sim 135 \text{ K}$ [19]. From the initial X-ray powder diffraction measurements it was proposed that the spin transition is accompanied by a first-order structural phase transition [20]. Single crystal X-ray measurements showed that the low spin, low temperature crystallographic phase gives only diffuse reflections and is therefore disordered [21].

When the crystal is cooled quickly from 135 K to below 100 K, the spin transition is abrupt at $T_{1/2} = 125 \text{ K}$ without hysteresis [22]. The LS super-cooled phase belongs to the rhombohedral space group $R\bar{3}$ ($Z=3$) [23, 24], i.e. the structure of the HS-high-temperature phase is quenched by rapid cooling. These observations clearly demonstrate that the spin transition in $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ is not triggered by a structural phase change, i.e. the spin transition takes place independently of the crystallographic phase change.

Both LS phases, one after slow cooling and the other after rapid cooling of the HS-high-temperature phase, could also be generated for isomorphous mixed crystals $[\text{Fe}_x\text{Zn}_{1-x}(\text{ptz})_6](\text{BF}_4)_2$ with small concentrations of Zn [22]. Only in mixed crystals with $x > 0.44$ and with slow cooling was a first order crystallographic phase transition together with hysteresis in the spin transition curve observed. The structural phase transition induced by the spin transition in concentrated mixed crystals of $[\text{Fe}_x\text{Zn}_{1-x}(\text{ptz})_6](\text{BF}_4)_2$ can be suppressed by rapid cooling. In both the dilute single crystals ($x < 0.44$) as well as in the LS super-cooled phase of the concentrated crystal, the spin transition is complete and takes place without hysteresis [22].

Recently Moritomo et al. [25] have reinvestigated the LS super-cooled phase of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ by powder diffraction of synchrotron radiation at variable temperatures. The crystal structure was determined using the Rietveld method. The structure of the LS super-cooled phase generated by quickly cooling the sample to 90 K is similar to the structure of the HS-high-temperature phase. This means that the model for the highly symmetric rhombohedral ($R\bar{3}$, $Z=3$) structure also reproduces every small Bragg reflection of the quenched low temperature phase. This indicates that the low temperature phase shows no lowering of symmetry or enlargement of the unit-cell size (super-structure). The bond distances (ca. 2.20 Å) for the FeN_6 core in $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ are nearly independent of temperature ($T > T_{1/2}$) in the HS state, but decrease by ca. 10% to 2.00 Å in the LS state. This contraction induced by the HS-LS transition is consistent with results from a single crystal analysis [23]. The a -axis increases at temperatures above $T_{1/2} \sim 130$ K, from 10.74 Å to 10.89 Å, while the c axis decreases from 32.14 Å to 31.94 Å.

2.1.2

Crystal Structure of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ After Slow Cooling (Disordered LS Phase)

The structure of the LS phase formed by slow cooling is substantially different from the structure of the HS phase. For several single crystals of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ under study the time required for the transition to be complete was not exactly reproducible. It seems to be dependent on crystal quality and temperature fluctuations. When the sample is rapidly cooled to below $T_{1/2} = 135$ K, significant changes of the lattice parameters are observed upon the transition to the LS state, but the Bragg reflections remain sharp [23]. However, when it is cooled slowly from high temperatures to below 135 K, the lattice parameters change simultaneously with the spin transition, and then the reflections broaden slowly and split into two along the direction of c^* (Fig. 2). The time for this crystallographic phase transition is ca. 30 min. The two-dimensional q -scan and precession photograph demonstrated that diffuse scattering develops along the c^* direction. The broadening and line splitting is not observed in a^* and b^* directions. This means that correlations along the c axis are of short range nature, whereas those along

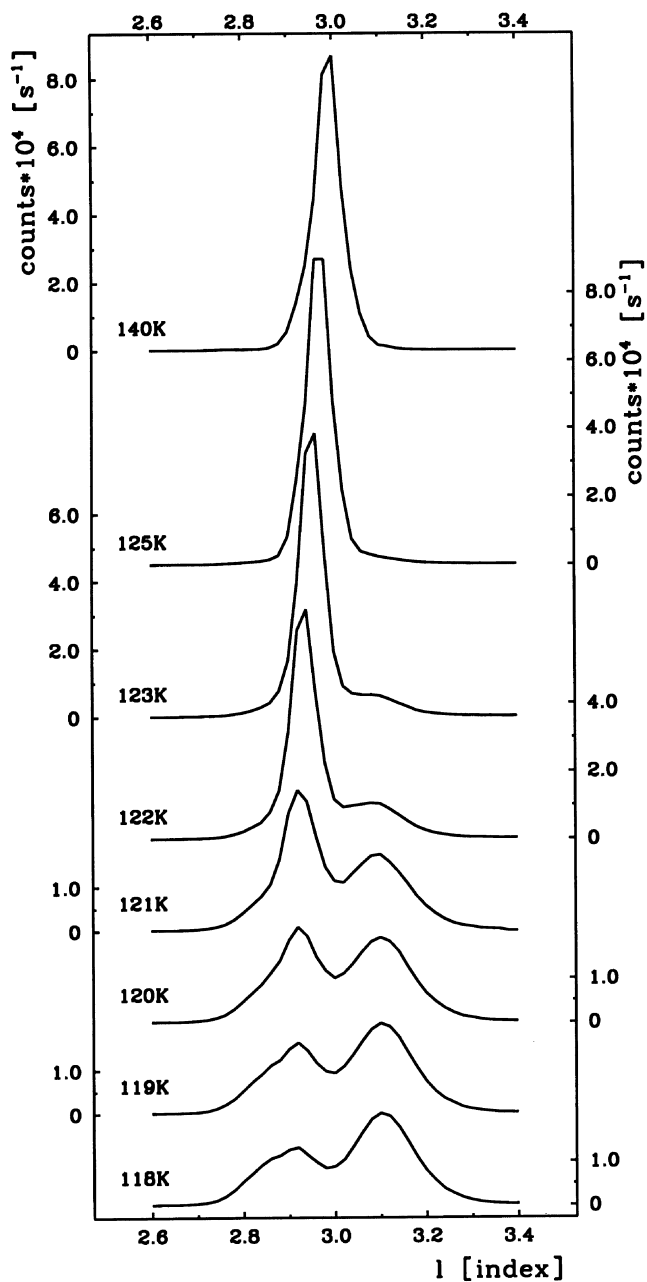


Fig. 2 Q-scan of the diffraction reflex $(1\ 1\ l)$ for $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ on cooling ([26])

the *a* and *b* axes are of long range nature. It is significant that upon warming the sample the reflections of the HS phase reappeared at ca. 135 K, i.e. the rhombohedral symmetry was fully restored [21, 26]. This whole cycle was repeated with the same crystal and the transition (both the structural and the spin transitions) proved to be fully reversible.

Franke initially pointed out that the $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ crystal at 100 K was no longer a “single crystal in the crystallographic sense” [13]. The broadening and splitting of the peaks in the single crystal X-ray diffraction pattern were previously interpreted on the basis of powder data as resulting from a structural phase transition from the rhombohedral space group ($R\bar{3}$) to the triclinic space group $P\bar{1}$ [20]. From conventional X-ray powder measurements and without Rietveld refinement it is difficult to determine whether the low temperature phase is ordered or disordered. Later, Moritomo et al. [25] confirmed from synchrotron radiation experiments and using the Rietveld method that the X-ray powder pattern of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ near $T_{1/2}$ becomes “disordered” if the exposure time is longer than 5 min. The disordered LS phase can also be generated by raising the temperature of the LS super-cooled phase to around 120 K, where the complex remains low spin, and holding it at this temperature for a sufficiently long time.

2.2

Crystal Structure of Methyl-Tetrazole Compounds

Magnetic susceptibility measurements on the methyl-tetrazole complexes $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ and $[\text{Fe}(\text{mtz})_6](\text{ClO}_4)_2$ have indicated that spin transition occurs for only 50% of all Fe(II) centres. Mössbauer spectra recorded as a function of temperature show in both cases only one quadrupole doublet, typical of Fe(II) in the HS state, at room temperature and down to ca. 160 K [27, 28]. This doublet begins to split into two doublets below ~ 160 K for the BF_4^- salt and ~ 130 K for the ClO_4^- salt. The isomer shift and quadrupole splitting values of both doublets are typical for Fe(II) in the HS state. Clearly, there are two inequivalent Fe(II) lattice sites, designated as A and B, both amounting to 50% in these complexes. On further cooling only lattice site A shows a complete HS $\rightarrow$ LS spin transition with $T_{1/2}=75$ K for $\text{X}=\text{BF}_4^-$ and 66 K for $\text{X}=\text{ClO}_4^-$. The Fe(II) ions at site B remain in the HS state down to 5 K, the lowest temperature under study. The occupancy ratio of the two sites is A:B=1:1 at 5 K, determined from the relative intensities of the doublets in the Mössbauer spectrum.

LIESST experiments on these complexes [28] have shown that lattice site A, being in the LS state at low temperature, can be converted with green light to a metastable HS state. In shorthand notation we denote this process as LIESST(LS $\rightarrow$ HS)_A. On the other hand, the lattice B site ions, showing no thermal SCO but remaining in the HS state even at temperatures as low as 5 K, are converted to a metastable LS state by irradiation with red light. We

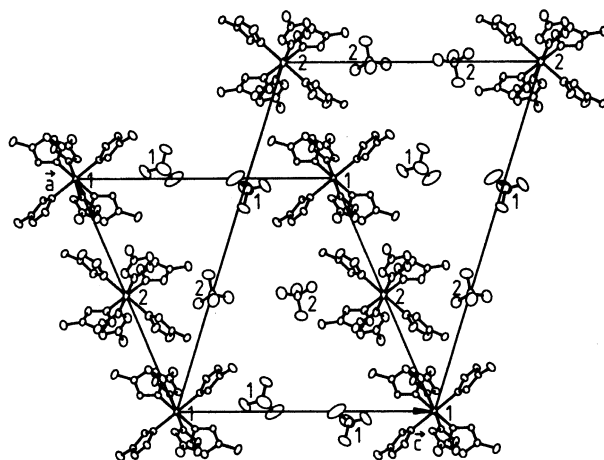


Fig. 3 Projection along the *b* axis of $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ at 157 K (HS state) showing only the groups with centres at zero. The numbers 1 and 2 indicate the two inequivalent iron(II) complex molecules and BF_4^- groups. For comparison with the analogous ptz plane, an additional cell is drawn which corresponds to the unit-cell of the ptz structure (from [15])

denote this process as $\text{LIESST}(\text{HS} \rightarrow \text{LS})_{\text{B}}$. The lifetimes of the metastable LIESST states are in both cases sufficiently long to have allowed the investigation of the structural differences accompanying these light induced spin state conversions, in comparison with the crystal structures with respective stable A and B sites.

The compounds $[\text{Fe}(\text{mtz})_6]\text{X}_2$ ($\text{X} = \text{BF}_4^-, \text{ClO}_4^-$) crystallise in the monoclinic space group $\text{P}2_1/\text{n}$ ($Z=4$) with the following unit cell volumes $V=3189 \text{ \AA}^3$ and $3089 \text{ \AA}^3$, respectively [15, 29]. The single crystal structure has been determined for fully high spin $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ at 157 and 113 K and for $[\text{Fe}(\text{mtz})_6](\text{ClO}_4)_2$ at 298 K [15]. The results clearly show that the iron(II) complexes occupy two inequivalent lattice sites (A and B) as indicated by the Mössbauer data [27, 28]. The molecular crystals consist of centrosymmetric $[\text{Fe}(\text{mtz})_6]^{2+}$ complexes with a nearly ideal octahedral FeN_6 core. The two inequivalent complexes are: $[\text{Fe1}(\text{mtz})_6]^{2+}$ with Fe1 sites at the inversion centres 2(a): 0,0,0 and 1/2,1/2,1/2, (A), and $[\text{Fe2}(\text{mtz})_6]^{2+}$ with Fe2 sites at the inversion centres 2(b): 1/2,0,0 and 0, 1/2,1/2 (B). The anions are in two different general positions. There are three non-equivalent ligands in each complex [15]. All complexes and anions are arranged in electrically neutral layers. The stacking period of these layers is double (see Fig. 3). The distance between layers is ca. 8 Å. The layers are linked together only by weak van der Waals forces and are parallel to the *bc* planes. Every second layer is rotated by 180° about the *b* direction, thus generating the twofold axis of the monoclinic structure which is missing in the rhombohedral

[Fe(ptz)₆](BF₄)₂ structure. Within the layers the pattern of cationic and anionic centres deviates only slightly from trigonal symmetry (ca. 5% elongation of *c* with respect to $\sqrt{3}b$). The monoclinic *b* and *c* axes correspond to the hexagonal [010] and [-2-10] directions of the ptz structure. Each [Fe(mt看z)₆]²⁺ complex molecule is surrounded by 12 anions, 6 in the same layer and 3 in each layer above and below. This structure does not change markedly on cooling to 113 K. A much more pronounced difference between the two inequivalent complexes [Fe1(mt看z)₆]²⁺ and [Fe2(mt看z)₆]²⁺ is found in their anisotropic displacement parameters. The U(Fe2) values from X-ray and Mössbauer measurements (Lamb-Mössbauer factor) are twice as large as those of U(Fe1) [15].

A very similar structure has been found for [Zn(mt看z)₆](BF₄)₂ and [Cu(mt看z)₆](BF₄)₂ [30]. These compounds are isomorphous with [Fe(mt看z)₆](BF₄)₂ and [Fe(mt看z)₆](ClO₄)₂ and have significant structural features in common. Significantly, like the iron complexes, there are two inequivalent complex molecules in the lattice with considerably different displacement parameters, those of the complex with the more regular octahedral (metal)N₆ core having the larger anisotropy of the displacement parameters. The six Zn-N distances in [Zn(mt看z)₆](BF₄)₂ at 293 K are very similar to the Fe-N distances in [Fe(mt看z)₆](ClO₄)₂ at 298 K [15, 30]. The choice of the anion and (metal)N₆ core seems to have no influence on these aspects of the structure of HS [Fe(mt看z)₆](BF₄)₂.

2.3

Crystal Structure of [Fe(et看z)₆](BF₄)₂

[Fe(et看z)₆](BF₄)₂ crystallises in the triclinic space group P $\bar{1}$ (Z=3) with the unit cell volume $V=2862 \text{ \AA}^3$ at 298 K. The X-ray single crystal structure determination at room temperature shows three complexes within the unit-cell occupying two non-equivalent lattice sites: site *A* without inversion symmetry and *B* with inversion symmetry [31]. Two complexes connected by the central inversion symmetry are located in general positions in the middle of the cell. The third complex is in specific positions ($\bar{1}$) on the corners of the cell and has inversion symmetry. The population ratio of the two sites is $n_A:n_B=2:1$. The BF₄⁻ groups are strongly disordered at 298 K. The complexes are stacked within electrically neutral layers parallel to the (01-1) lattice planes (Fig. 4). The stacking period of the layers is double and the distance between two adjacent layers is ca. 11 Å. There is a pseudo-trigonal symmetry axis perpendicular to each layer. The iron-nitrogen bond lengths show that the octahedral environment is nearly perfect for the two sites.

Mössbauer spectroscopy and magnetic susceptibility measurements show that iron(II) at sites *A* undergoes thermal spin transition with $T_{1/2}=105 \text{ K}$, whereas that at sites *B* remains in the HS state down to 10 K. There is no evidence for a crystallographic first-order phase transition. Application of

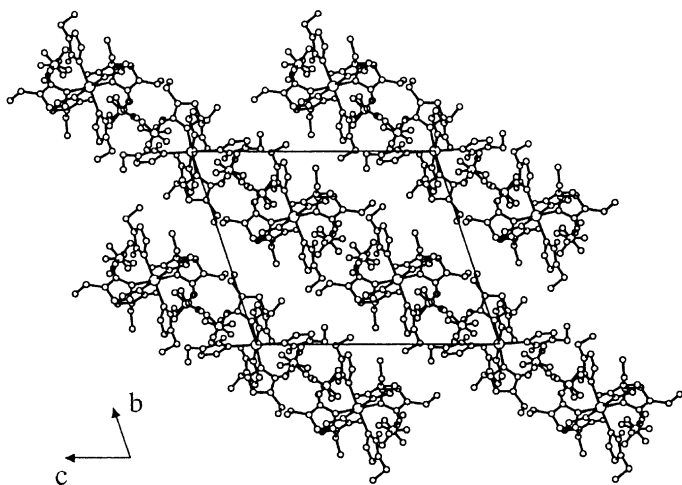


Fig. 4 Projection of the unit-cell of $[\text{Fe}(\text{etz})_6](\text{BF}_4)_2$ along the $[1\ 0\ 0]$ axis. There are layers of iron complex molecules and BF_4^- anions within the $(0\ 1\ -1)$ lattice planes with the stacking period two. The distance between layers is ca. 11 Å. (from [31])

external pressure of up to 1200 bar between 200 and 60 K does not cause any conversion to LS state on site B, but the site A spin transition is shifted to $T_{1/2}=140$ K [31].

The complexes at both lattice sites exhibit light-induced spin state conversions. Irradiation with green light ($\lambda=514.5$ nm) converts the LS state of A site molecules to the metastable HS state, this process being denoted as $\text{LIESST}(\text{LS} \rightarrow \text{HS})_A$. Irradiation with red light ($\lambda=820$ nm) leads to $\text{HS} \rightarrow \text{LS}$ conversion for B site molecules, termed $\text{LIESST}(\text{HS} \rightarrow \text{LS})_B$. The light-induced LIESST states were detected by Mössbauer and optical spectroscopy [31, 32].

3

Change of Lattice Parameters with Temperature and After LIESST

The interaction energy between SCO molecules has been estimated on the basis of elasticity theory [9]. The calculation of the interaction constants from the material properties improved considerably when the anisotropic deformation of the lattice was taken into account. The deformation has been described by two temperature independent tensors, α and ϵ . A unit-cell vector $x(T)$ at temperature T was related to the vector $x_{\text{LS}}(T_0)$ in the LS state at T_0 according to:

$$x(T) = [1 + \alpha(T - T_0) + \epsilon\gamma_{\text{HS}}(T)]x_{\text{LS}}(T_0)$$

The volume change ΔV_{HL} caused by SCO is related to the trace of the ϵ tensor by $\Delta V_{\text{HL}} = V_{\text{LS}} \text{Tr}(\epsilon)$. The temperature-dependent lattice parameters from X-ray diffraction measurements can be well parameterised with temperature-independent tensors α and ϵ [5, 23]. The observed changes of the lattice parameters as a function of temperature and after light-induced spin state conversion in the tetrazole complexes of iron(II) will be discussed in the next sections.

3.1

$[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$

The lattice parameters of single crystals of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ and the isomorphous $[\text{Zn}(\text{ptz})_6](\text{BF}_4)_2$ were measured between 300 K and 10 K [23]. For the

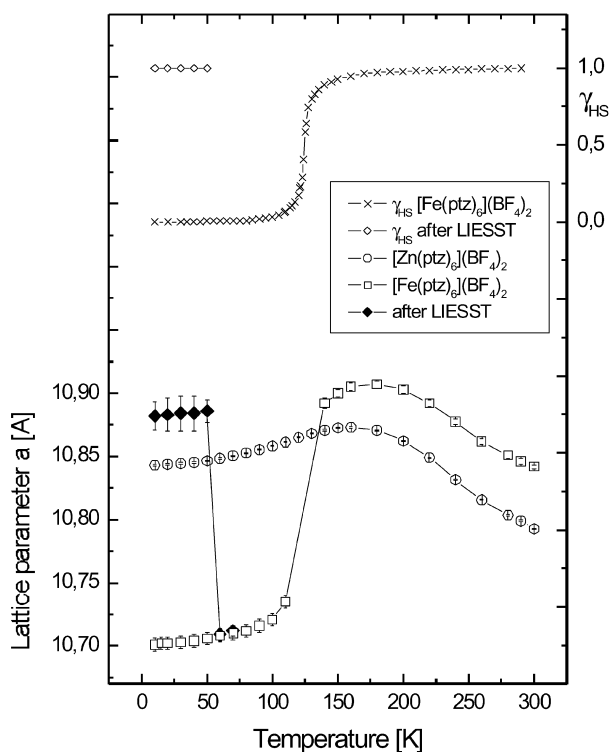


Fig. 5 The lattice parameters a of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ (open squares) and of the isomorphous zinc compound (open circles) vs temperature. At high temperature and for the LS supercooled phase the space group is $R\bar{3}$. The (filled diamonds) symbols indicate the measurements of the Fe crystal in the metastable HS state after LIESST. The spin transition curve $\gamma_{\text{HS}}(T)$ measured by optical spectroscopy is shown at the top of the figure (symbol crosses for thermal spin transition, symbol open diamonds after LIESST). The solid line is a guide for the eyes ([23])

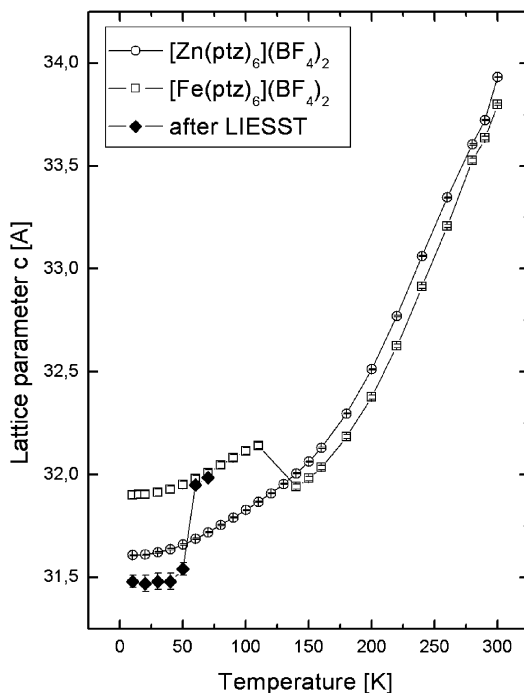


Fig. 6 The lattice parameters c of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ (open squares) and of the isomorphous zinc compound (open circles) vs temperature. At high temperature and for the low the LS super-cooled phase the space group is $R\bar{3}$. The (filled diamonds) symbols indicate the measurements of the Fe crystal in the metastable HS state after LIESST. The solid line is a guide for the eyes ([23])

iron compound the crystal was measured under slow cooling from 300 K down to 140 K (i.e. just above $T_{1/2}$). Then, in order to avoid the transition to the disordered phase, the crystal was rapidly cooled and the measurements were continued. For the Zn compound the measurements were done under slow cooling to 10 K, since the structure does not change. Only for $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ crystals did the lattice parameters change markedly near 135 K due to the spin transition. The zinc compound was chosen as a reference for the temperature dependence of the lattice parameters of the iron SCO compound, because neither of the lattice parameters $a(T)$ and $c(T)$ shows Debye-like behaviour in these compounds (Figs. 5, 6 and 7).

Using the green light (514 nm) of an argon-ion laser, the $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ crystal was quantitatively converted from the LS ($^1A_1$) state to the long-lived metastable HS ($^5T_2$) state at 10 K; its lattice parameters were measured up to 50 K, where the LIESST state begins to decay within minutes. The change of the lattice parameters can be interpreted by a superposition of a normal temperature dependence, for which the isostructural zinc compound served

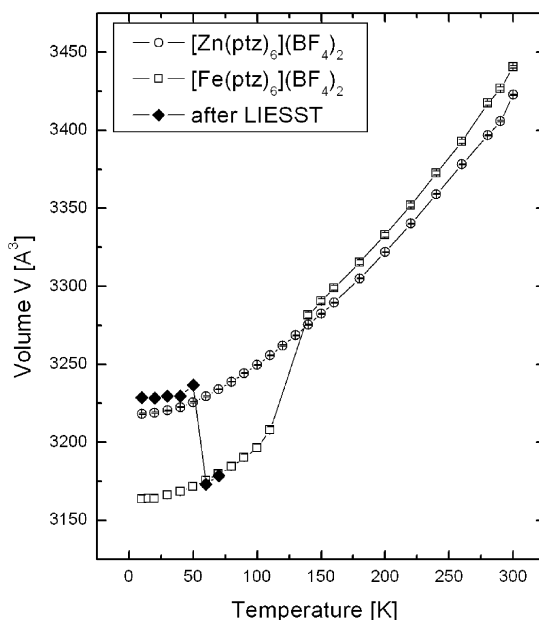


Fig. 7 The unit-cell volumes V of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ (open squares) and of the isomorphous zinc compound (open circles) vs temperature. At high temperature and for the LS super-cooled phase the space group is $R\bar{3}$. The (filled diamonds) symbols indicate the measurements of the Fe crystal in the metastable HS state after LIESST. The solid line is a guide for the eyes ([23])

as a reference, and an almost temperature-independent part which is proportional to the fraction of molecules in the HS state. At low temperatures ($T < 50$ K) a direct comparison at corresponding temperatures is possible between the lattice parameters for the thermodynamically stable LS state and those for the metastable HS state after LIESST. Direct comparison at one and the same temperature means that accurate knowledge of the temperature dependence of both the HS fraction γ_{HS} and the α tensor is not required. In Figs. 5, 6 and 7 the lattice parameters a , c and the volume of the unit-cell V of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ and $[\text{Zn}(\text{ptz})_6](\text{BF}_4)_2$ are plotted as a function of temperature and after light-induced spin state conversion, respectively. Also shown is the temperature dependence of the HS fraction γ_{HS} at the top of Fig. 5. The conversion from the LS to the HS state is accompanied by an increase of the unit-cell volume of $65 \text{ \AA}^3$.

3.2

$[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$

Precise measurements of lattice parameters for $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ in the temperature range 10–300 K [29] show dramatic changes at $T=74$ K, which are due to the spin transition at lattice sites A (Fig. 8), detected by magnetic and optical measurements at the same temperature $T_{1/2}(\text{A})=74$ K, where half of the A site molecules change spin state, whereas all B site molecules remain in the HS state over the whole temperature range. The lattice parameters in this compound also do not show Debye-like behaviour. Therefore, the isomorphous zinc compound has also been analysed as a reference for the temperature dependence of the lattice parameters of the iron compound. Except for a shift, the unit-cell parameters of the Zn compound display almost the same temperature dependence as those of the iron compound in the HS state above the transition temperature [29]. The unit-cell parameters a , b and c decrease and the angle β increases going from the HS to the LS state at site A, and correspondingly the volume of the unit-cell decreases by $62 \text{ \AA}^3$ (see Figs. 9, 10, 11, 12 and 13).

Under irradiation with green light (514 nm), the crystal was quantitatively converted by LIESST to the HS state at 10 K. Irradiation of the crystal at 10 K with red light (820 nm) converted the B site ions, being in the HS state

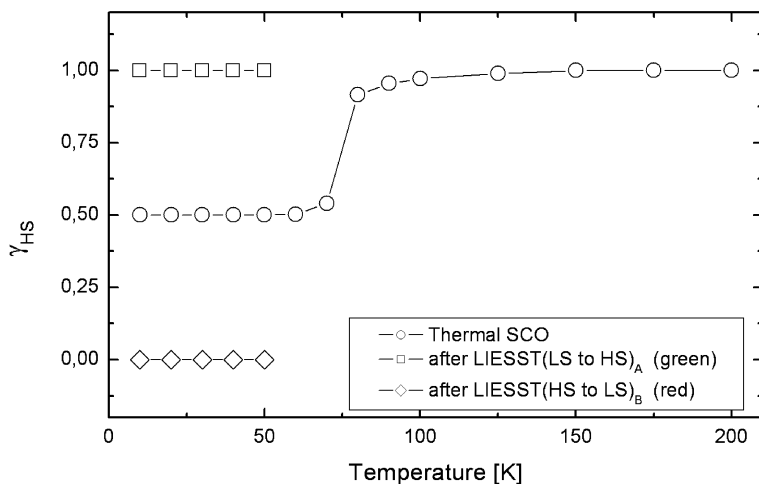


Fig. 8 The fraction of the molecules in the HS state of $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ as a function of temperature, $\gamma_{\text{HS}}(T)$, measured by optical spectroscopy (*open circles*). The $\gamma_{\text{HS}}(T)$ curve indicates that only 50% of the complex molecules (in A sites) show thermal spin transition, while the B site ions remain in the HS state at all temperatures. Irradiation with green light converts the LS(A) molecules to the metastable HS(B) state: LIESST(LS $\rightarrow$ HS)_A (*open squares*). Irradiation with red light converts the HS(B) molecules to the metastable LS(B) state: LIESST(HS $\rightarrow$ LS)_B (*open diamonds*) ([33])

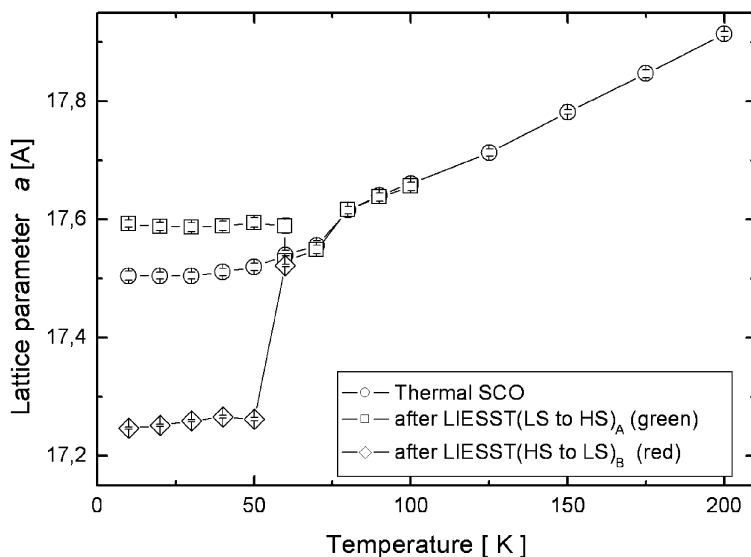


Fig. 9 The temperature dependence of the lattice parameter a of $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ after thermal spin transition (*open circles*) and after irradiation with green (*open squares*) and red light (*open diamonds*). The solid line is a guide for the eyes ([29])

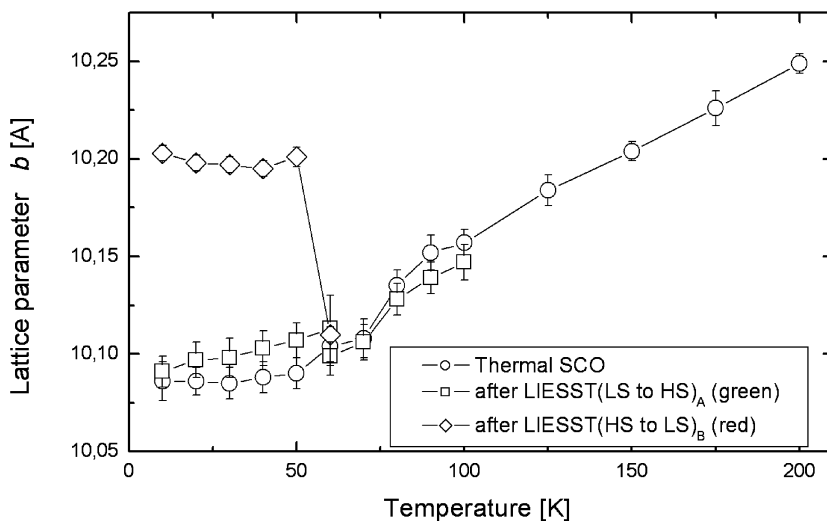


Fig. 10 The temperature dependence of the lattice parameter b of $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ after thermal spin transition (*open circles*) and after irradiation with green (*open squares*) and red light (*open diamonds*). The solid line is a guide for the eyes ([29])

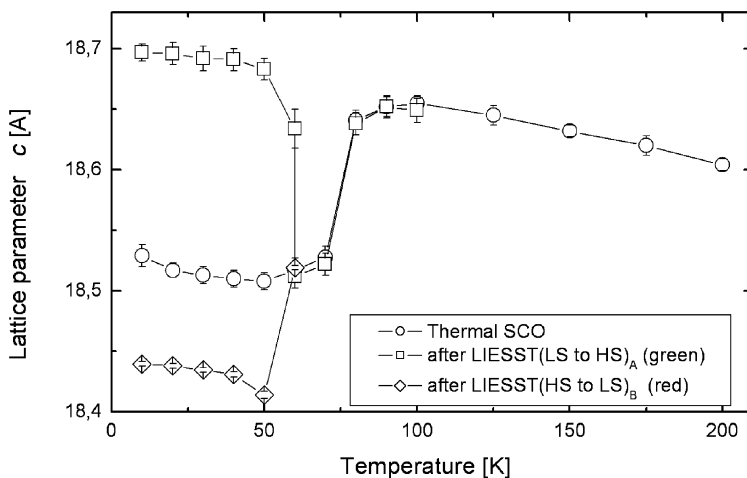


Fig. 11 The temperature dependence of the lattice parameter c of $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ after thermal spin transition (*open circles*) and after irradiation with green (*open squares*) and red light (*open diamonds*). The solid line is a guide for the eyes ([29])

at that temperature, almost completely to the LS state, while the A site ions in the LS state did not react noticeably. The lattice parameters of both photo-induced metastable states were measured up to 60 K, where they began to decay within minutes. The volume change of the crystal per complex mole-

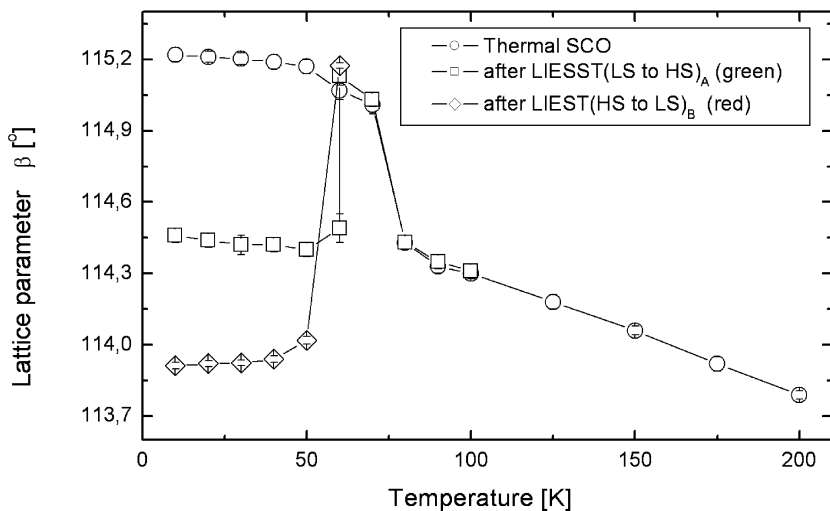


Fig. 12 The temperature dependence of the lattice parameter β of $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ after thermal spin transition (*open circles*) and after irradiation with green (*open squares*) and red light (*open diamonds*). The solid line is a guide for the eyes ([29])

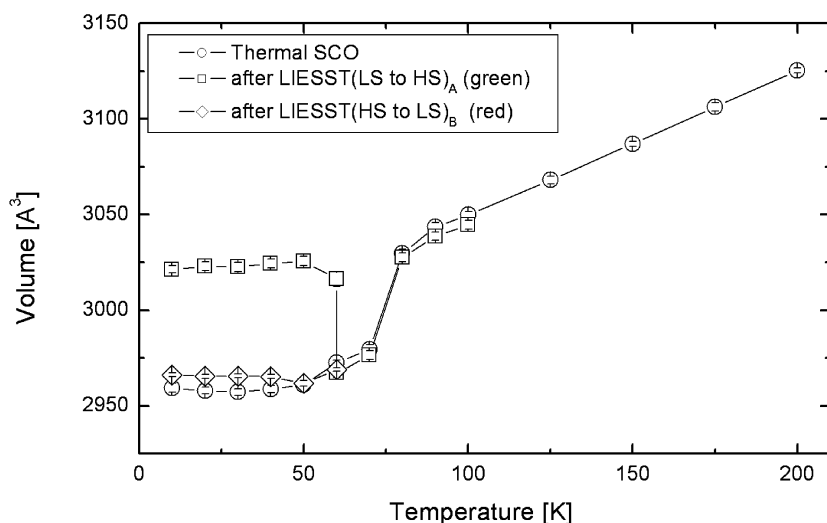


Fig. 13 The temperature dependence of the unit-cell volume V of $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ after thermal spin transition (*open circles*) and after irradiation with green (*open squares*) and red light (*open diamonds*). The *solid line* is a guide for the eyes ([29])

cule accompanying the light-induced spin transition was found to be $32 \text{ \AA}^3$ at sites A and, most surprisingly, close to zero at sites B (Fig. 13). The light-induced conversion from LS to HS at A sites with green light causes the unit-cell parameters a , b (slightly) and c to increase and the angle β to decrease. The light-induced conversion with red light from the HS to the LS state at B sites causes the unit-cell parameters a , c and the angle β to decrease and the axis b to increase. The light-induced metastable states relax at ca. 60 K, and all lattice parameters take up the values of the thermal transition curve [29].

4 Change of Crystal Structures after LIESST

The light-induced conversion from the stable LS ($^1A_1$) state to the long-lived metastable HS ($^5T_2$) state was first observed on a single crystal of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ [12]. The phenomenon has become known as LIESST (light-induced excited spin state trapping). Soon after the discovery of LIESST, Hauser demonstrated that the reverse process, i.e. restoration of the LS ground state by irradiation of the LIESST state with red light, is also possible (reverse LIESST) [34]. Later, LIESST and reverse LIESST effects have been reported for many other SCO compounds and the phenomena seem to be a general feature of compounds exhibiting thermal spin crossover. These

complexes mostly contain FeN_6 cores, i.e. the ligand molecules are coordinated via nitrogen atoms to the metallic centre, but FeN_6 core is not a prerequisite for the occurrence of thermal spin crossover and LIESST [35]. Although LIESST has mostly been observed in iron(II) SCO systems, it was recently reported to occur also in iron(III) compounds [36].

In view of the prime importance of the structural changes accompanying thermal and light-induced spin transition for the cooperative interactions in solid SCO systems, particular interest has been directed not only towards the measurement of the lattice parameters, but also the actual crystal structure of metastable states.

4.1

Structure of the Photo-Induced Metastable Phase of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)$

Photo-excitation selectively converts the complex molecules of a solid SCO system to a long-lived metastable phase. If attractive interactions with long relaxation times exist between the photo-excited units, a new type of phase transition may be observed. Recently, Moritomo et al. [25] reported the results of a structural analysis by X-ray powder diffraction of synchrotron radiation on photo-excited $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ at 91 K. After cooling the sample rapidly to 91 K, they directly determined the crystal structure of the photo-excited sample as a function of the excitation power P . The powder patterns, in the weak extinction region, showed negligible changes in comparison with the low-temperature quenched phase. They propose the formation of a novel secondary phase, when the excitation power P exceeds a critical value of 55 mW. At both $P=55$ and 70 mW the powder patterns seem to decompose into the low-temperature-like and high-temperature-like patterns. The photo-induced change of the X-ray powder pattern disappeared quickly to restore the pre-excitation pattern when the photo-excitation was stopped. This means that the structural changes are maintained only under continuous photo-excitation. The change of the powder pattern is completed in less than 1 min at 91 K. For comparison, photo-excitation (LIESST) below 50 K leads to a metastable phase, the structure of which persists after discontinuation of the photo-excitation. The powder patterns were analysed with the rhombohedral space group $R\bar{3}$ ($Z=3$). It reproduces every small Bragg reflection, indicating that no lowering of symmetry or multiplication of the unit-cell size are required. The longer bond distance $d_{\text{Fe-N}} \sim 2.1$ Å and the lattice parameter $a=10.82$ Å, indicate that this secondary phase is due to condensation of photo-excited HS molecules. The bond distance $d_{\text{Fe-N}}=2.1$ Å [24] as compared to 2.0 Å in the stable LS phase and 2.2 Å in the HS phase indicates that this secondary phase at 91 K has a fraction of photo-excited HS molecules of 0.5. A condensation of the HS molecules is likely to result, if nearest-neighbour elastic interactions increase the lifetime of the metastable HS state. In the case of high intensity excitation, the interactions between the

HS ions evolve and the effective lifetime becomes longer in regions with higher density of HS molecules than in dilute regions. This phenomenon may be regarded as a phase transition from randomly distributed small domains to larger ones of photo-excited HS molecules which develop at the critical excitation power P_c [24].

A recent single crystal structure analysis on the super-cooled phase was performed at 10 K and after LIESST. At this low temperature the light-induced spin state conversion was complete and the lifetime of the metastable LIESST state was practically infinitely long. The following metal-donor atom distances, $d_{\text{Fe-N}}$, have been found at 10 K: 2.18 Å in the HS (LIESST state) and 1.99 Å in the LS state [37]. The $d_{\text{Fe-N}}$ values determined at 80 K in the super-cooled LS phase are 1.99 Å and at 160 K 2.17 Å in the HS state [37]. These data confirm that the population of the light-induced HS state at 10 K was 100%.

4.2

Structural Modification of $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ after LIESST

The compound $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ is a fascinating system for the study of the influence of the spin state change within the cation on the lattice properties, as three different phases of the crystal can be verified at low temperatures, e.g. 10 K: Phase I=[LS(A), HS(B)], with 50% of the molecules in the LS state (A sites) and 50% in the HS state (B sites), which is the thermodynamically stable state reached by slowly cooling the crystal; Phase II=[HS(A), HS(B)], the photo-excited phase with all molecules in the HS state, generated by irradiating phase I with green light converting LS(A) molecules to HS(A) by LIESST(LS→HS)_A; Phase III=[LS(A), LS(B)], the photo-excited phase with all molecules in the LS state, generated by irradiating phase I with red light converting the HS(B) molecules to metastable LS(B) by LIESST(HS→LS)_B.

The structures of the three phases I, II and III of a single crystal of $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ were determined at 10 K, i.e. of the molecules at sites A and B in the HS state (phase II), at site A in the LS and at B in the HS state (phase I), and of both sites in the LS state (phase III). No new reflections indicating the presence of a phase other than I, II and III and no diffuse scattering were found for any of these phases [29]. The spin crossover molecules at sites A and B behave very similarly. The changes of Fe–N bond lengths going from LS to HS at sites A (by 0.187 Å) and at sites B (by 0.170 Å) do not explain the large volume change accompanying the spin transition at sites A, compared to no volume change at sites B. Furthermore, the anisotropy of the deformation tensor can be related to the bond length change, which at sites B is almost isotropic (0.176, 0.166, 0.169 Å) compared to (0.179, 0.177, 0.205 Å) at sites A. The anisotropy of the deformation is, however, larger for sites B. A simple consideration in terms of an isotropic medi-

um obviously fails completely for this compound. It is also remarkable that the increase of the Fe–N bond lengths is very isotropic, although the lattice deforms very anisotropically [29].

5 Conclusion

A detailed crystal structure determination at variable temperatures, in particular above and below the spin transition temperature, is most essential in revealing the nature of temperature- and photo-induced phase transitions in solids. Even if a suitable single crystal is not available for a complete structure determination, recording the temperature-dependent X-ray powder diffraction data can be extremely helpful in characterizing the type of spin transition (continuous or discontinuous), and determining changes of the lattice parameters, which are needed for example to understand the effect of pressure on the spin transition behaviour. The determination of the crystal structure gives important information about the metal–donor atom distances and the crystal packing, which are decisive factors in controlling the intermolecular interactions. These in turn are responsible for the spin transition behaviour, i.e. the more or less pronounced deviations from Boltzmann-like population, particularly for the appearance of abrupt transitions and hysteresis. SCO systems with such features in the room temperature region are promising candidates for practical applications (sensors, level indicators, switches). Thus, in studying the properties of newly synthesized SCO compounds, crystal structure determination, ideally as a function of temperature covering the whole transition region, is undoubtedly one of the most important characterization methods.

The tetrazole compounds of the general formula $[\text{Fe}(\text{R-tz})_6]\text{X}_2$ (R-tz =1-alkyl-tetrazole, $\text{X}=\text{BF}_4$, ClO_4) discussed in the present article have shown strong interdependences between crystal structure, spin transition features and thermal spin transition temperature. The three representative examples of this class of SCO compounds have different structure types with space groups $R\bar{3}$, $P2_1/n$ and $P\bar{1}$ for the ptz, mtz and etz derivatives, serially. There are several features which these compounds have in common: the molecular crystals contain centrosymmetric $[\text{Fe}(\text{Rtz})_6]^{2+}$ complexes with a nearly ideal octahedral FeN_6 core and twice as many anions BF_4^- or ClO_4^- , the cations and anions are arranged in electrically neutral layers with (more or less) trigonal symmetry, linked together by weak van der Waals forces. The cleavage planes of the crystals are parallel to these layers.

X-Ray structural studies of complexes in the light-induced HS state are vital to an understanding of the structural features of that state. So far structural determinations after LIESST have been performed on only three SCO compounds: $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ after LIESST($\text{LS} \rightarrow \text{HS}$)_A and after LIESST

(HS $\rightarrow$ LS)_B [29], [Fe(ptz)₆](BF₄)₂ during LIESST at 91 K [25] and after LIESST at 10 K [37] and [Fe(phen)₂(NCS)₂] after LIESST at 30 K [38].

The compound [Fe(ptz)₆](BF₄)₂ has turned out to be a fascinating SCO system, not only from the photophysical point of view (see Chap. 17 by Hauser), but also regarding the five different structural phases which can be identified in part from their involvement in photophysical phenomena such as LIESST and reverse LIESST:

1. The phase above T_{1/2}=130 K: stable HS molecules in the high temperature structure with space group R $\bar{3}$
2. The phase below 130 K after slow cooling: stable LS molecules in diffuse or disordered structure
3. The LS quenched phase after rapid cooling to below 100 K: stable LS molecules in the structure with space group R $\bar{3}$
4. The phase below 50 K after rapid cooling and LIESST: metastable HS molecules in the structure with R $\bar{3}$
5. Photo-induced metastable phase above 50 K: photo-excited HS molecules in metastable domains developing above a critical light intensity

Thermal spin transition in solid iron(II) complexes shows cooperative behaviour [3, 19, 39, 40]. The mechanism of the interaction between molecules in the HS and the LS states is still one of the primary aspects of present spin crossover research. Two proposed mechanisms are based on the observation of the increase of the metal-ligand bond lengths by ca. 0.2 Å on going from the LS to the HS state [9, 41]. An increase in the fraction γ_{HS} of molecules in the HS state is accompanied by an increase of the volume V(T) and a change of shape of the unit-cell. The relationship between the deformation of the crystal and the HS fraction has been used to determine the interaction energy between the spin changing molecules with calculations based on elastic continuum theory [10]. The first such theoretical models [9, 41] considered the molecules in the two spin states as rigid, so that the differences in volume and shape of the LS and HS molecules are taken to be independent of temperature. For [Fe(ptz)₆](BF₄)₂ the structural measurements have provided quantitative confirmation of this: the differences under consideration change by less than 1% from the spin transition over a temperature range of ca 30 K.

For [Fe(mtz)₆](BF₄)₂ the absence of a volume change of the lattice after LIESST (HS $\rightarrow$ LS)_B with red light at 10 K was very surprising, because the metal-donor atom distances at site B showed a similar decrease, on average by 0.170 Å, on going from the HS to the LS state, as compared to 0.187 Å for the corresponding bond length changes at site A after LIESST(LS $\rightarrow$ HS)_A with green light. The volume change after LIESST at sites A is 32 Å³. This example demonstrates that the elastic energy involved in the spin transition at sites B cannot be accounted for by considering the volume change alone.

Due to anisotropic lattice deformation all elements of the deformation tensor are important.

For many spin crossover compounds both a crystallographic and a spin crossover transition are observed together. The question then arises whether the spin state change is the cause or the result of a crystallographic phase transition. This question could be answered at least for $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$: the thermal spin transition with the concomitant changes of lattice parameters is an entropy driven process independent of a crystallographic phase change; it is in fact the cause of the observed crystallographic phase change. It is even safe to state that the structural changes (hysteresis) observed on slow cooling are consequences of the changes of the lattice parameters which follow spontaneously from the spin transition. Thus the “chicken and egg” question has been answered at least for this SCO system. At the present stage of spin crossover research it is not possible to generalize this conclusion due to the lack of detailed data for other similar examples.

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References

1. König E, Watson KJ (1970) *Chem Phys Lett* 6:457
2. Leipoldt JG, Coppens P (1973) *Inorg Chem* 12:2269
3. König E (1987) *Progr Inorg Chem* 35:527
4. Köppen H, Müller EW, Köhler CP, Spiering H, Meissner E, Gütlich P (1982) *Chem Phys Lett* 91:348
5. Wiehl L, Kiel G, Köhler CP, Spiering H, Gütlich P (1986) *Inorg Chem* 25:1565
6. Gallois B, Real JA, Hauw C, Zarembowitch (1990) *Inorg Chem* 29:1152
7. Müller EW, Spiering H, Gütlich P (1982) *Chem Phys Lett* 93:567
8. Kambara T (1979) *J Chem Phys* 7:4199; Kambara T (1980) *J Phys Soc Jpn* 49:1806
9. Spiering H, Meissner E, Köppen H, Müller EW, Gütlich P (1982) *Chem Phys* 68:65
10. Sanner I, Meissner E, Köppen H, Spiering H, Gütlich P (1984) *Chem Phys* 86:227; Willenbacher N, Spiering H (1988) *J Phys C Solid State Phys* 21:1423; Spiering H, Willenbacher N (1989) *J Phys Condens Matter* 1:10089
11. Kusz J, Böhm H (2002) *J Appl Cryst* 35:8
12. Decurtins S, Gütlich P, Köhler CP, Spiering H, Hauser A (1984) *Chem Phys Lett* 105:1; Decurtins S, Gütlich P, Hasselbach KM, Hauser A, Spiering H (1985) *Inorg Chem* 24:2174
13. Franke PL (1982) Thesis, Rijks University, Leiden
14. Franke PL, Haasnoot JG, Zuur AP (1982) *Inorg Chim Acta* 59:5
15. Wiehl L (1993) *Acta Cryst B* 49:289
16. Yamaura J, Kato R, Nagai Y, Saito H, Hyodo T (1998) *Phys Rev B* 58:14098
17. Nagai Y, Saito H, Hyodo T, Vertes A, Süvegh K (1998) *Phys Rev B* 57:14119

18. Ozarowski A, McGarvey BR (1989) *Inorg Chem* 28:2262
19. Gütlich P, Hauser A, Spiering H (1994) *Angew Chem Int Ed* 33:2024
20. Wiehl L, Spiering H, Gütlich P, Knorr K (1990) *J Appl Cryst* 23:151
21. Kusz J, Spiering H, Hinek R, Gütlich P (1996) *Workshop on Aperiodic Structures, Kraków*, p 185
22. Jung J, Schmitt G, Wiehl L, Hauser A, Knorr K, Spiering H, Gütlich P (1996) *Z Physik B* 100:523
23. Kusz J, Spiering H, Gütlich P (2000) *J Appl Cryst* 33:201
24. Moritomo Y, Kato K, Nakamoto A, Kojima N, Nishibori E, Takata M, Sakata M (2002) *J Phys Soc Jpn* 71:1015
25. Moritomo Y, Kato K, Nakamoto A, Kojima N, Nishibori E, Takata M, Sakata M (2002) *J Phys Soc Jpn* 71:2009
26. Kusz J, Böhm H, Gütlich P (2001) In: Morawiec H, Stróz D (eds) *Proceedings of XVIII Conference on Applied Crystallography*, World Scientific, p 104
27. Poganiuch P, Gütlich P (1988) *Hyperfine Interact* 40:331
28. Poganiuch P, Decurtins S, Gütlich P (1990) *J Am Chem Soc* 112:3270
29. Kusz J, Spiering H, Gütlich P (2001) *J Appl Cryst* 34:229
30. Wijnands PEM (1989) Thesis, Univ. Leiden, The Netherlands
31. Hinek R, Spiering H, Schollmeyer D, Gütlich P, Hauser A (1996) *Chem Eur J* 2:1427
32. Hinek R, Spiering H, Gütlich P, Hauser A (1996) *Chem Eur J* 2:1435
33. Hinek R (1995) Thesis, Universität Mainz
34. Hauser A (1986) *Chem Phys Lett* 124:543
35. Gütlich P, Jung J (1995) *J Mol Struct* 347:21
36. Juhasz G, Hayami S, Sato O, Maeda Y (2002) *Chem Phys Lett* 364:164
37. Kusz J, Gütlich P, Spiering H (2004) (to be published)
38. Marchivie M, Guionneau P, Howard JAK, Goeta AE, Chastanet G, Létard JF, Chasseau D (2002) *J Am Chem Soc* 124:194
39. Goodwin HA (1976) *Coord Chem Rev* 18:293
40. Gütlich P (1981) *Struct Bond (Berlin)* 44:83
41. Ohnishi S, Sugano S (1981) *J Phys C Solid State Phys* 14:39

Light-Induced Spin Crossover and the High-Spin→Low-Spin Relaxation

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Abstract The discovery of a light-induced spin transition at cryogenic temperatures in a series of iron(II) spin-crossover compounds in 1984 has had an enormous impact on spin-crossover research. Apart from being an interesting photophysical phenomenon in its own right, it provided the means of studying the dynamics of the intersystem crossing process between the high-spin and the low-spin state in a series of compounds and over a large temperature range. It could thus be firmly established that intersystem crossing in spin-crossover compounds is a tunnelling process, with a limiting low-temperature lifetime below 50 K and a thermally activated region above 100 K. This review begins with an elucidation of the mechanism of the light-induced spin transition, followed by an in depth discussion of the chemical and physical factors, including cooperative effects, governing the lifetimes of the light-induced metastable states.

Keywords Thermal and light-induced spin crossover · High-spin→low-spin relaxation · Intersystem crossing · External pressure · Chemical pressure · Cooperative effects · Iron(II) complexes

1 Introduction

The preceding contributions in this series of volumes of Topics in Current Chemistry dedicated to the phenomenon of spin crossover in transition metal complexes basically deal with the so-called thermal spin transition, that is, the transition from the low-spin state populated at low temperatures to an almost quantitative, entropy driven population of the high-spin state at elevated temperatures. The phenomenon as such goes back a long way. Therefore it is not surprising that already in the late 1970s and early 1980s the different manifestations of spin crossover, ranging from complexes of transition metal ions in solution to crystalline solids, were quite well understood, if not in detail then at least in principle [1].

Before the mid-1980s, the dynamics of the comparatively simple intersystem crossing process between the high-spin and the low-spin state were much less well studied. Almost exclusively, corresponding experiments had been performed in solution, using a variety of techniques, such as Raman temperature jump and ultrasonic relaxation as external perturbation of the spin equilibrium, and the results were generally discussed on the basis of classical Arrhenius type activation or absolute rate theory [2]. Two events in the early 1980s gave new impetus to spin-crossover research in general and to the question of the dynamics of the intersystem crossing process in particular. First of all, McGarvey et al. [3] discovered that for a number of iron(II) as well as iron(III) spin-crossover complexes in solution, the high-spin state could be populated efficiently at the expense of the low-spin state by pulsed laser excitation. At around ambient temperatures these light-induced high-spin states are transient states with lifetimes typically of the order of submicroseconds to microseconds. The discovery of McGarvey et al. was followed by the observation of Decurtins et al. [4] that at cryogenic temperatures, the high-spin→low-spin relaxation slows down to such an extent that by the way of irradiation in the visible region of the electromagnetic spectrum, iron(II) spin-crossover systems can be quantitatively trapped in the high-spin state. Subsequently, the term “light-induced excited state spin trapping (LIESST)” was coined to describe this effect. The discovery of LIESST triggered several years of intense research not only with regard to the mechanism for the trapping of the system in the high-spin state as such [5], but also with regard to the chemical and physical parameters governing the lifetimes of the low-temperature metastable high-spin states [6]. The fact that LIESST can be observed in crystalline solids opened a dynamic approach to the study of cooperative effects [7].

This review begins with the historical experiment as first described by Decurtins et al. [4] in the year of Orwell 1984 on the spin crossover compound $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$, ptz=1-propyltetrazole, which has since been the subject of intense study. This is followed by a discussion on the mechanism

and quantum efficiencies of the various steps involved. The second part of the review is dedicated to the dynamics of the high-spin→low-spin relaxation, including the influence of external pressure and cooperative effects. This review should serve as a common base for the more specialised aspects of light-induced spin crossover as discussed in subsequent contributions to this series.

2

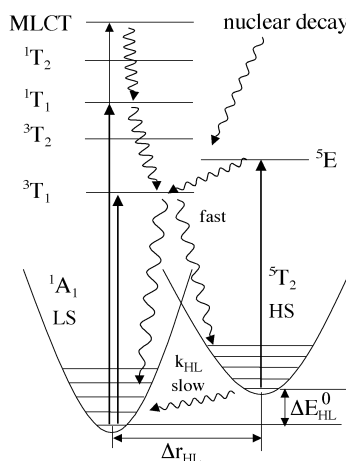
Light-Induced Excited Spin State Trapping (LIESST)

The discovery of LIESST firmly established iron(II) spin-crossover compounds as being interesting and even unique with regard to their photo-physical properties. The section on this phenomenon begins with a short summary of the relevant excited electronic states and their spectroscopic manifestation, at the same time introducing the different classes of compounds to be subsequently discussed in more detail. The section after next deals with the elucidation of the mechanism for LIESST, and in the section following that, the quantum efficiencies are discussed quantitatively.

2.1

Optical Properties of Spin-Crossover Compounds

The electronic structure of iron(II) coordination compounds has been addressed in previous chapters of this book [8]. In Scheme 1, the essential



Scheme 1 The electronic structure of iron(II) spin-crossover complexes. The mechanisms of LIESST and reverse-LIESST are indicated by curly arrows. At low temperatures the barrier effectively traps the complex in the high-spin state (adapted from [5])

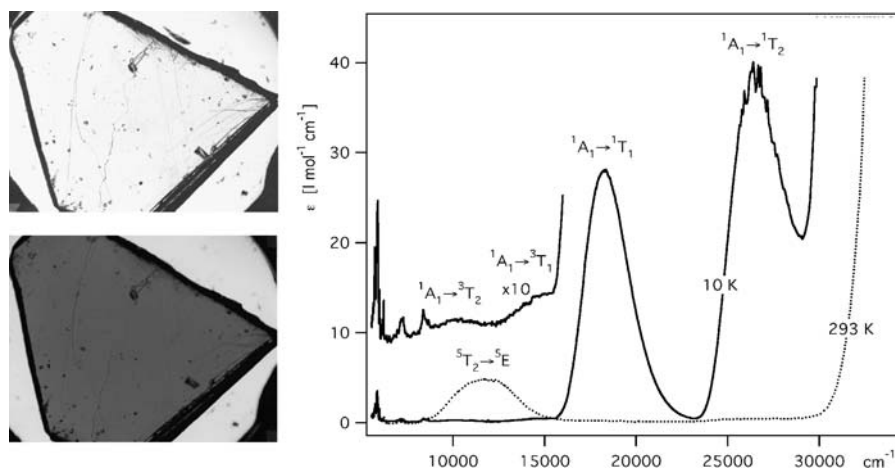


Fig. 1 Pictures of a single crystal of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ at 293 K (*top*) and at 10 K (*bottom*), and the corresponding single crystal optical absorption spectra (adapted from [5])

electronic states are shown, including the $^1\text{A}_1(\text{t}_{2\text{g}}^6)$ low-spin ground state, the thermally accessible $^5\text{T}_2(\text{t}_{2\text{g}}^4\text{e}_\text{g}^2)$ high-spin state as well as the higher excited singlet, triplet and quintet ligand-field states. In addition, the possibility of a comparatively low-lying metal-ligand charge transfer (MLCT) state for ligands with extended π -systems is indicated [9].

As depicted in Fig. 1, the most striking aspect of the thermal spin transition in $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ is the dramatic change in colour from basically colourless at 293 K to deep purple at 20 K. Based on Scheme 1, the bands in the corresponding single crystal optical absorption spectra [5] can easily be assigned: The one comparatively weak band in the near infrared of the 293 K spectrum, where the compound is essentially in the high-spin state, corresponds to the spin-allowed ligand-field transition of the high-spin species $^5\text{T}_2 \rightarrow ^5\text{E}$. At 20 K, where the compound is in the low-spin state, this band is gone. Instead there are two bands in the visible, which can be assigned to the spin-allowed ligand-field transitions of the low-spin species $^1\text{A}_1 \rightarrow ^1\text{T}_1$ and $^1\text{A}_1 \rightarrow ^1\text{T}_2$. Two additional very weak bands in the near infrared can be assigned to the spin-forbidden ligand-field transitions $^1\text{A}_1 \rightarrow ^3\text{T}_1$ and $^1\text{A}_1 \rightarrow ^3\text{T}_2$. In contrast to the so-called spin-flip transitions of chromium(III) compounds [10], these spin-forbidden transitions involve the promotion of an electron from the $\text{t}_{2\text{g}}$ orbitals to the e_g orbitals, and therefore the bands have a width comparable to that of the spin-allowed transitions.

Figure 2 shows the thermal spin transition curve, that is the high-spin fraction, γ_{HS} , vs temperature, for $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ and for the mixed crystal system $[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6](\text{BF}_4)_2$, $x=0.1$, as derived from the relative intensity as a function of temperature of the $^1\text{A}_1 \rightarrow ^1\text{T}_1$ absorption band [7]. They are in good agreement with curves obtained by magnetic susceptibility mea-

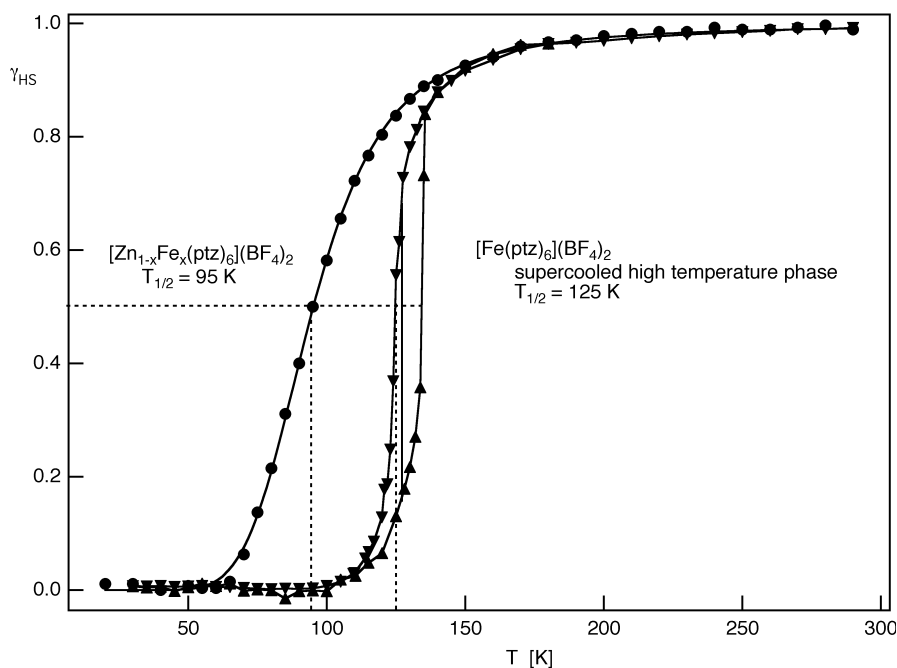


Fig. 2 Thermal spin transition curves for: $[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6](\text{BF}_4)_2$, $x=0.1$, (filled circles) experimental, (continuous line) calculated with $\Delta H_{\text{HL}}^0=568 \text{ cm}^{-1}$, $\Delta S_{\text{HL}}^0=5.9 \text{ cm}^{-1} \text{ K}^{-1}$, $T_{1/2}=95 \text{ K}$; $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ in the super cooled high temperature phase, (filled upside down triangles) experimental, (continuous line) calc. with $\Gamma=170 \text{ cm}^{-1}$, $T_{1/2}=125 \text{ K}$, as well as in the low temperature phase, (filled triangles) experimental. Crystallographic phase transition: $T_{\text{L}}^{\text{c}}=128 \text{ K}$, $T_{\text{H}}^{\text{c}}=135 \text{ K}$ (adapted from [7])

surements and Mössbauer spectroscopy [11]. As expected for a simple Boltzmann distribution between the two vibronic manifolds, the curve for the dilute system is gradual, with a transition temperature $T_{1/2}$ of 95 K. The one for the neat compound is abrupt, with a thermal hysteresis of 7 K. Abrupt spin transitions are the signature of cooperative effects of elastic origin [12], which may result in thermal hysteresis. In the case of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$, however, the hysteresis is due to a crystallographic phase transition [13] which is triggered by the spin transition [14]. This is borne out by the fact that the crystallographic phase transition can be suppressed by rapid cooling, in which case the spin transition is still abrupt but fully reversible with a transition temperature $T_{1/2}$ of 125 K.

In addition to the ligand-field bands, spin-crossover complexes with pyridyl type ligands have comparatively low-lying MLCT states [9], which may give rise to intense absorption bands in the visible. If such is the case, the ligand-field bands in particular of the low-spin species are usually submerged in these MLCT bands. This is exemplified in the absorption spectra

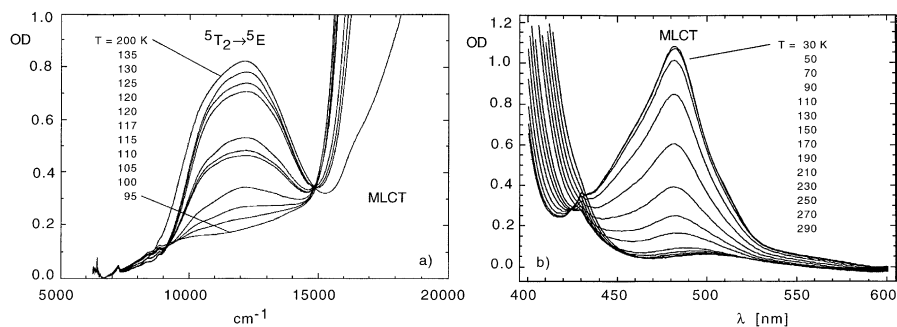


Fig. 3a,b Variable temperature single crystal absorption spectra of: **a** neat $[\text{Fe}(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$, ϵ_{max} of the $5T_2 \rightarrow 5E$ band is $22 \text{ l mol}^{-1} \text{ cm}^{-1}$ (adapted from [15]); **b** dilute $[\text{Zn}_{1-x}\text{Fe}_x(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$, $x \approx 0.0005$, ϵ_{max} of the MLCT band is of the order of $10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ (adapted from [16])

of another famous spin-crossover compound, namely $[\text{Fe}(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ ($\text{pic} = 2\text{-picolylamine}$) shown in Fig. 3a [15]. At room temperature the characteristic high-spin band is clearly observable at $12,000 \text{ cm}^{-1}$ (830 nm), but at 20 K the spectrum is dominated by the MLCT band in the visible, which is several orders of magnitude more intense than is typical for ligand-field transitions. In order to observe this band not just as an absorption edge at $15,000 \text{ cm}^{-1}$ (625 nm), the spin-crossover complex has to be diluted in an appropriate host lattice. In Fig. 3b the absorption spectrum of $[\text{Zn}_{1-x}\text{Fe}_x(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$, with $x \approx 0.0005$, is shown as a function of temperature [16]. At this concentration the high-spin ligand-field band is too weak to be observable, the MLCT band on the other hand increases in intensity as the temperature is lowered. This is due to the smaller metal-ligand bond length in the low-spin state which results in a better overlap between metal-centred and ligand-centred orbitals as compared to the high-spin state.

Figure 4 shows the thermal transition curves for $[\text{Zn}_{1-x}\text{Fe}_x(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$, $x \approx 0.0005$ and for neat $[\text{Fe}(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$. Again the one for the diluted system is gradual with $T_{1/2}$ of 97 K, whereas the one for the neat system is abrupt but without hysteresis. Despite the fact that all complexes are crystallographically equivalent, there is a plateau of $\sim 6 \text{ K}$ in the transition curve at the transition temperature of 118 K [17]. This is thought to be due to specific nearest neighbour interactions leading to the build-up of non-random distributions within the temperature interval of the plateau [18].

The two examples basically cover the various aspects with regard to the optical properties of spin-crossover compounds. The first one is characteristic for the whole class of compounds based on tetrazole [19], triazole, oxazole and pyrazolyl-borate ligands [20], the second one for all compounds with pyridyl type ligands having extended π electron systems.

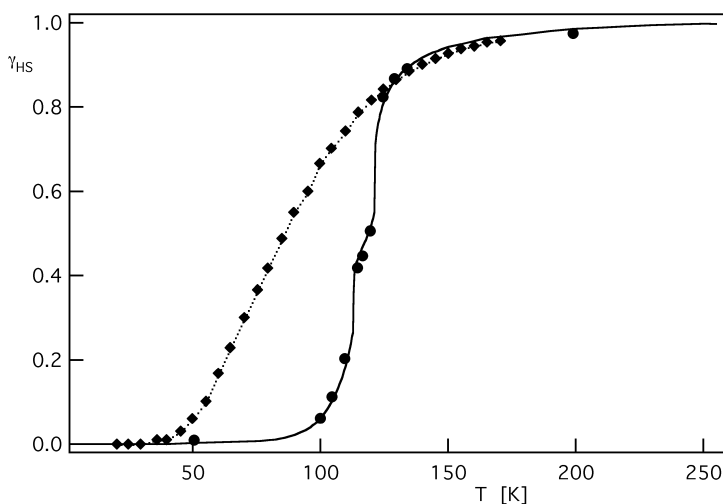


Fig. 4 Thermal transition curves for neat $[\text{Fe}(\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$ (filled circles) from optical spectroscopy [15], (continuous line) from magnetic susceptibility [17], and for dilute $[\text{Zn}_{1-x}\text{Fe}_x(\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$, $x\approx 0.0005$, (filled diamonds) from optical spectroscopy [16]

2.2

LIESST and Reverse-LIESST

As mentioned in the introduction, irradiation into the characteristic absorption bands of the low-spin species results in a light-induced population of the high-spin state at the expense of the population of the low-spin state. At cryogenic temperatures, the high-spin→low-spin relaxation slows down to such an extent that it is actually possible to trap some spin-crossover compounds quantitatively in the high-spin state. Indeed, irradiating a crystal of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ at 10 K into the $^1\text{A}_1\rightarrow^1\text{T}_1$ ligand-field band completely bleaches the red colour within a comparatively short time. Figure 5 shows the corresponding absorption spectra recorded before and after irradiation at 514.5 nm [4, 5]. The spectrum after irradiation is identical to the room temperature spectrum, with absolutely no trace of the low-spin bands left over. This conclusively proves that at 10 K the system is trapped in the metastable high-spin state. The mechanism for this “light-induced excited spin state trapping” (LIESST) is sketched in Scheme 1: a fast and highly non-adiabatic [21] double intersystem crossing step takes the complex from the initially excited state to the high-spin state, where, as result of the energy barrier between the high-spin and the low-spin state due to the large difference in metal-ligand bond length, Δr_{HL} , and the small value of the zero-point energy difference, ΔE_{HL}^0 , it stays trapped at sufficiently low temperatures.

Scheme 1 indicates the possibility of pumping the system back to the low-spin state by selectively irradiating into the high-spin ligand-field band

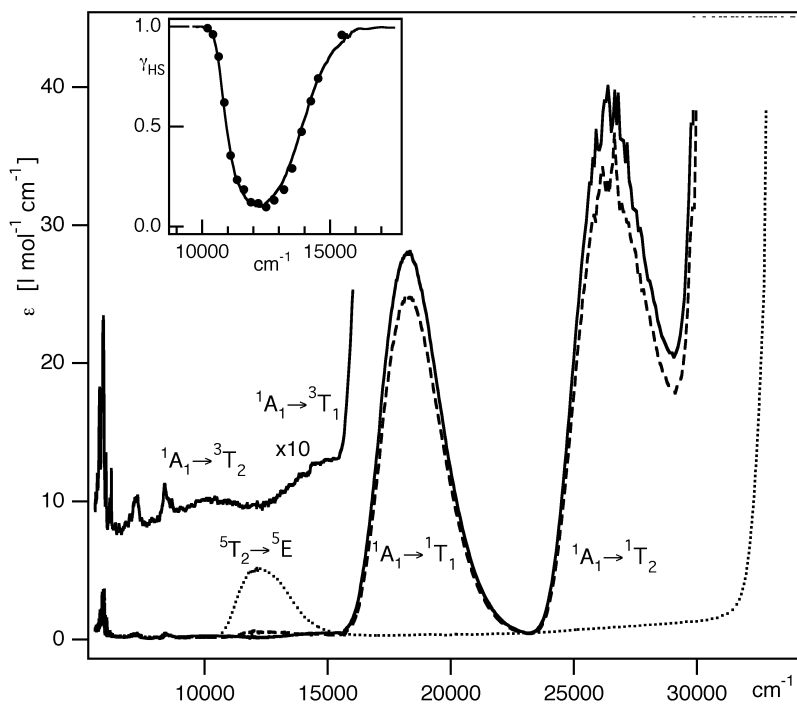


Fig. 5 Single crystal absorption spectra of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ at 10 K: (*continuous line*) before irradiation, (*dotted line*) and after irradiation at 514.5 or 980 nm, (*dashed line*) after irradiation at 830 nm. *Insert*: steady state high-spin fraction as a function of irradiation wavelength (adapted from [5])

in the near infrared. That this is indeed possible is demonstrated by the absorption spectrum of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ at 10 K recorded following irradiation at 830 nm, that is into the maximum of the ${}^5\text{T}_2 \rightarrow {}^5\text{E}$ band of the trapped high-spin compound [5]. However, the light-induced return to the low-spin state (reverse-LIESST) is not fully quantitative. Even after prolonged irradiation a low-spin fraction of only $\sim 85\%$ is obtained. This is due to the spectral overlap between the ${}^5\text{T}_2 \rightarrow {}^5\text{E}$ band of the high-spin species and the spin-forbidden ${}^1\text{A}_1 \rightarrow {}^3\text{T}_1$ and ${}^1\text{A}_1 \rightarrow {}^3\text{T}_2$ bands of the low-spin species, which leads to a steady state type situation. Variation of the excitation wavelength across the region of this spectral overlap results in different values for the steady state high-spin fraction, as depicted in the insert of Fig. 5. For irradiation outside the ${}^5\text{T}_2 \rightarrow {}^5\text{E}$ band, in particular also for irradiation exclusively into the ${}^1\text{A}_1 \rightarrow {}^3\text{T}_1$ band at 980 nm, LIESST is again quantitative.

LIESST and reverse LIESST are basically properties of an individual complex. They can also be observed for diluted mixed crystals such as the above-mentioned $[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6](\text{BF}_4)_2$. However, for some systems, partic-

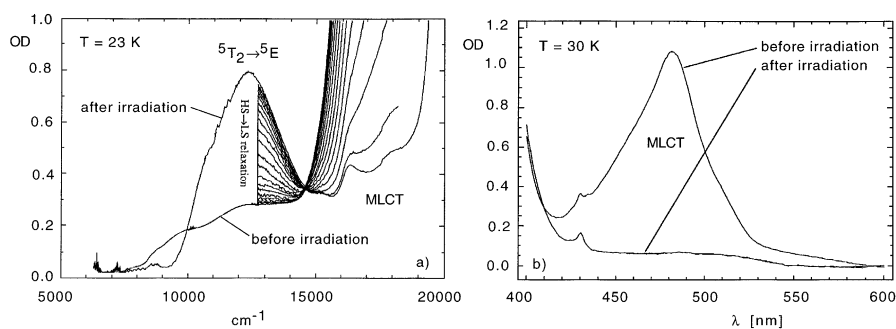


Fig. 6 **a** Single crystal absorption spectra at of $[\text{Fe}(\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$ at 23 K before and after irradiation at 647 nm. At this temperature the relaxation is not negligible and can conveniently be followed by optical spectroscopy (adapted from [15]). **b** Single crystal absorption spectra of $[\text{Zn}_{1-x}\text{Fe}_x(\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$ at 30 K before and after irradiation at 488 nm (adapted from [16])

ularly for those with intense charge transfer bands in the visible, certain precautions have to be taken. With extinction coefficients of the order of $10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$, the penetration depth of the light is less than a micrometer. Thus LIESST is more effective at the surface and creates concentration gradients which may lead to a destruction of the crystal. If at the same time the extinction coefficient of the high-spin species is not strictly zero at the maximum of the MLCT band of the low-spin species and if the high-spin→low-spin relaxation is not extremely slow, then LIESST in the sense of lifetimes of the metastable high-spin state of hours to days, is rather difficult to achieve experimentally.

Figure 6 shows the absorption spectrum of $[\text{Fe}(\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$ at 23 K with the edge to the intense MLCT band of the low-spin species [15]. Irradiation at 514.5 nm ($19,436 \text{ cm}^{-1}$) transforms a single crystal of this compound into a fine powder. Irradiation at 647 nm ($15,456 \text{ cm}^{-1}$), that is, into the tail of the MLCT band, results in a rapid conversion to the metastable high-spin state as demonstrated by the spectrum after irradiation included in Fig. 6a. For the dilute $[\text{Zn}_{1-x}\text{Fe}_x(\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$, $x \approx 0.0005$, irradiation at 488 nm, that is into the MLCT band, poses no problem, and as shown in Fig. 6b, it is very efficient in converting the complexes to the metastable high-spin state [16].

Since the discovery of LIESST a large number of spin-crossover complexes exhibiting the phenomenon have been investigated, not only in neat [22] or dilute crystalline form [5–7, 23], but also for complexes in Langmuir-Blodgett films [24] and embedded in polymer matrices [25]. The latter is exemplified in Fig. 7 for the spin-crossover complex $[\text{Fe}(\text{2-mephen})_3]^{2+}$ (2-mephen=2-methyl-phenantroline) embedded in PVA, for which the characteristic MLCT band, growing in intensity as the temperature is lowered, can be bleached efficiently at 12 K with irradiation at 514.5 nm.

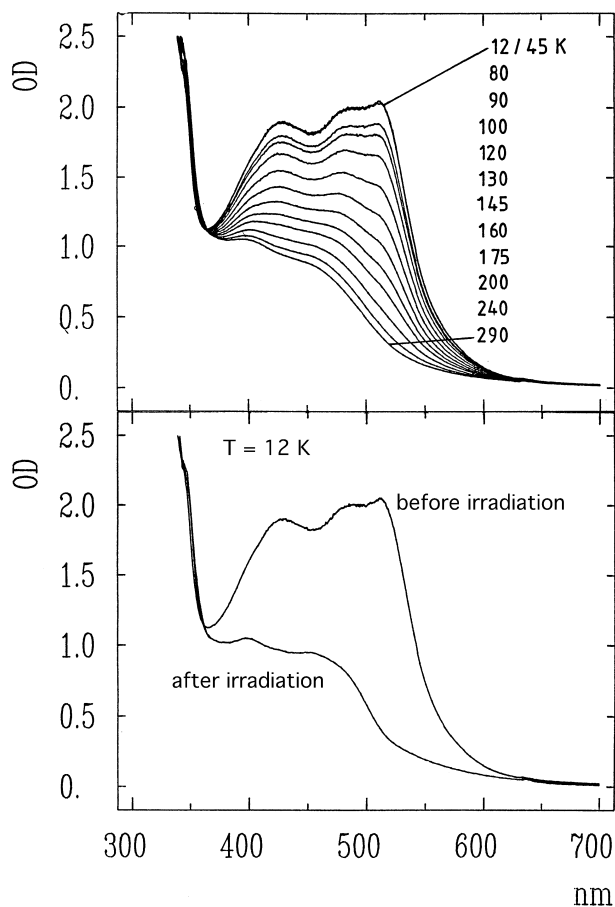


Fig. 7 Absorption spectra of $[\text{Fe}(\text{2-mephen})_3]^{2+}$ embedded in PVA as a function of T (*top*), and at 12 K before and after irradiation at 514.5 nm (*bottom*)

From a less anthropocentric point of view, LIESST is not restricted to spin-crossover compounds. The same mechanism for the population of the high-spin state also holds for low-spin compounds. However, due to the larger driving force (see below), the observed lifetimes are substantially shorter, and need pulsed laser excitation and fast detection equipment to determine them. This is borne out by the single crystal absorption spectrum and the transient absorption following pulsed laser excitation of the famous low-spin complex $[\text{Fe}(\text{bpy})_3]^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine) doped into the inert host lattice $[\text{Zn}(\text{bpy})_3](\text{PF}_6)_2$ shown in Fig. 8 [26]. The pulsed laser excitation bleaches the MLCT band efficiently. The insert shows that at 13 K the ground state is recovered within $1.5 \mu\text{s}$. That the transient state is indeed the high-spin state can be shown by direct comparison with results from time-

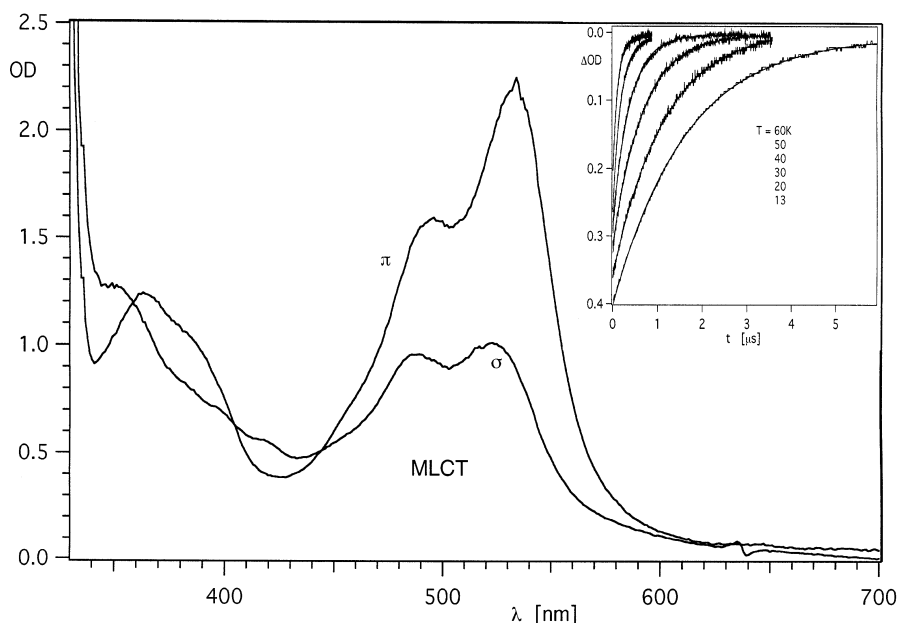


Fig. 8 Polarised single crystal absorption spectra of $[\text{Zn}_{1-x}\text{Fe}_x(\text{bpy})_3](\text{PF}_6)_2$ at 293 K. *Insert:* transient absorption showing the ground state recovery monitored at 510 nm following pulsed excitation at 532 nm (adapted from [25a])

resolved Mössbauer emission spectroscopy [27]. Indeed, previous low-temperature optical experiments on $[\text{Fe}(\text{phen})_3]^{2+}$ (1,10-phenanthroline) in an EtOH/MeOH glass [28] and the anomalous high-spin states observed in time-integral Mössbauer emission spectra of $[\text{Co}(\text{phen})_3]^{2+}$ doped into various matrices [29], later termed nuclear decay induced excited spin state trapping, NIESST (see below), already suggested this interpretation.

LIESST is thus a very general phenomenon, and provided the experimental conditions are right with regard to irradiation wave length, irradiation intensity and speed of detection, it can be observed for any iron(II) spin-crossover complex and even for low-spin complexes.

2.3

Quantum Efficiencies

Qualitatively, the light-induced population of the high-spin state is quite efficient. A quantitative determination of its quantum efficiency, that is, the number of iron(II) low-spin centres converted to the high-spin state per absorbed photon, is rather demanding. Several experimental parameters have to be controlled with sufficient precision in order to obtain a meaningful result, as follows. a) The absorption cross section of the low-spin state at the

irradiation wavelength has to be known precisely, and there should be minimal absorption of the high-spin state at this wavelength. b) The crystal must be thin enough for the optical density at the irradiation wavelength to be below 0.1. If such is the case, intensity gradients leading to concentration gradients inside the crystal during the irradiation can be neglected. Otherwise, the build-up of gradients has to be taken into account when evaluating the experimental data. c) The high-spin fraction has to be monitored background free. Because of variations in diffuse scattering from the sample during the excitation period, it is not sufficient to just follow the transmitted light intensity as function of irradiation time at a fixed wavelength. Full absorption spectra have to be recorded at given time intervals in order to correct for baseline shifts. To date, corresponding experiments have been performed for two systems only, namely $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ [5] and $[\text{Fe}(\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$ [30].

For an infinitely thin crystal, and assuming that at the irradiation wavelength the absorption of the high-spin species is negligible, the bleaching of the low-spin state is given by the first order differential equation

$$\frac{d\gamma_{\text{LS}}}{dt} = -k_{\text{ex}} \eta \gamma_{\text{LS}} = -k_{\text{obs}} \gamma_{\text{LS}} \quad (1)$$

where η is the quantum efficiency of the double intersystem crossing step, $k_{\text{ex}} = \sigma_{\text{LS}} \cdot \Phi$ is the excitation rate constant, which is proportional to the absorption cross section of the low-spin species, σ_{LS} [cm^2], and the photon flux, Φ [$\text{s}^{-1}\text{cm}^{-2}$], at the irradiation wavelength. $k_{\text{obs}} = \eta k_{\text{ex}}$ is the experimentally observed rate constant. The absorption cross section is related to the extinction coefficient ϵ [$\text{in l mol}^{-1} \text{cm}^{-1}$] according to $\sigma = 3.82 \times 10^{-21} \epsilon$ [31], and the photon flux is given by the irradiation intensity I according to $\Phi = I/h\nu_{\text{ex}}$. Thus the excitation rate constant can be expressed as $k_{\text{ex}} = \text{const} \cdot \epsilon_{\text{LS}} I$. Using the above units for the various quantities involved, and giving the intensity in I in [W cm^{-2}], *const* takes on a value of 10^{-2} at $\lambda_{\text{ex}} = 514.5 \text{ nm}$. The solution of the above differential equation gives a single exponential decay of the low-spin fraction upon irradiation according to

$$\gamma_{\text{LS}} = \gamma_{\text{LS}}^0 \cdot e^{-\eta k_{\text{ex}} \cdot t} = \gamma_{\text{LS}}^0 \cdot e^{-\eta \sigma \Phi \cdot t} = \gamma_{\text{LS}}^0 \cdot e^{-\text{const} \cdot \eta \epsilon I \cdot t} \quad (2)$$

where γ_{LS}^0 is the initial low-spin fraction before irradiation, and takes on a value of one for a complete thermal spin transition.

Figure 9 shows bleaching curves, plotted as the low-spin fraction vs the product of light intensity and irradiation time, $I \cdot t$, for neat $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ at 10 K, with $\lambda_{\text{ex}} = 514.5 \text{ nm}$ and $I = 0.35 \text{ mW mm}^{-2}$. The two curves correspond to curves obtained on a thick and on a thin crystal, respectively [5]. The thin crystal had an optical density at 514.5 nm of ~ 0.1 , and the bleaching of the low-spin state follows the single exponential behaviour predicted by the first order differential equation. With an extinction coefficient ϵ_{LS} of

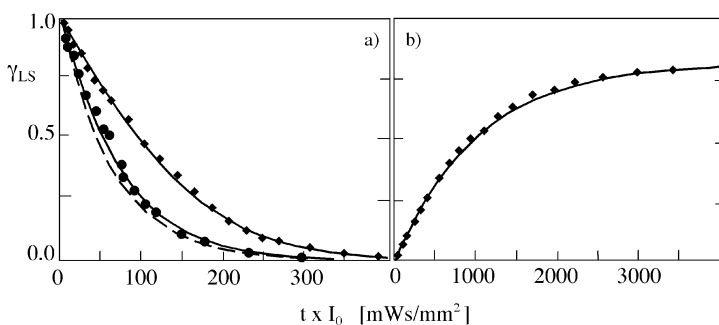


Fig. 9 **a** Bleaching of the low-spin state for $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ at 10 K, irradiation at 514.5 nm (LIESST): (filled circles) thin crystal, (filled diamonds) thick crystal, (solid line) calc, (dashed line) single exponential fit. **b** Build-up of the low-spin state at 10 K with subsequent irradiation at 752 nm: (filled diamonds) experimental, (solid line) single exponential fit (adapted from [5])

$19 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 514.5 nm and the above irradiation intensity, $k_{\text{ex}} = 6.6 \times 10^{-3} \text{ s}^{-1}$. The observed rate constant as obtained from a single exponential fit to the experimental curve $k_{\text{obs}} = 5.4 \times 10^{-3} \text{ s}^{-1}$. From these values, a quantum efficiency for LIESST of ~ 0.8 follows.

For the thick crystal, the non-negligible absorption results in the build-up of a concentration gradient across the sample during photo-excitation. This can be accounted for by including a time and x dependence of both the intensity and the concentration in the differential equations according to

$$\frac{d\gamma_{\text{LS}}(x, t)}{dt} = -k_{\text{ex}}(x, t)\eta\gamma_{\text{LS}}(x, t) \quad \text{with} \quad k_{\text{ex}}(x, t) = \text{const} \cdot \varepsilon_{\text{LS}}I(x, t) \quad (3a)$$

$$\frac{dI(x, t)}{dx} = -\varepsilon_{\text{LS}}c_0\gamma_{\text{LS}}(x, t)I(x, t) \quad (3b)$$

where c_0 is the molar concentration of spin-crossover complexes. For given values of the intensity of the incoming beam, extinction coefficient of the low-spin species, and quantum efficiency, the above set of coupled differential equations can be solved numerically for both $I(x, t)$ and $\gamma_{\text{LS}}(x, t)$ [5a]. This is shown in Fig. 10 for $\gamma_{\text{LS}}(x, t)$, with x and t in reduced units.

The experimentally determined quantity is the mean low-spin concentration within the irradiated volume. Indeed, the bleaching curve for the thick crystal of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$, included in Fig. 9, is faithfully reproduced using the quantum efficiency obtained from the excitation curve of the thin crystal and by taking into account the concentration gradients following the above procedure.

The quantum efficiency for reverse LIESST can be determined in the same way. Figure 9 includes the excitation curve of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ for irradiation

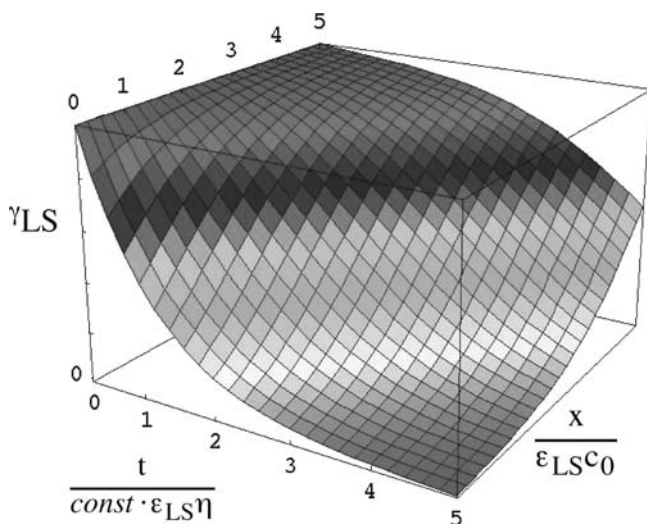


Fig. 10 Numerical solution of differential Eq. (3a) showing the build-up of gradients during the excitation process. t and x are given in reduced units

at 752 nm. The quantum efficiency in this case is 0.1. This is lower than the quantum efficiency for LIESST itself. The actual branching ratio at the $^3T_1$ state is estimated to be 4:1 in favour of LIESST.

Although the quantum efficiency for LIESST may vary to some extent from compound to compound and also as a function of temperature and even as a function of γ_{HS} , the value of ~ 0.8 may be regarded as typical. For instance, for $[\text{Fe}(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ [27] and even for $[\text{Fe}(\text{bpy})_3]^{2+}$ [25a] values on the same order have been determined. For reverse LIESST the situation is different. Even though the actual quantum efficiency might not be negligible, the light-induced high-spin $\rightarrow$ low-spin conversion is not or only very partially observed for compounds for which the intense MLCT band lies in the visible with a long tail extending towards the near infrared. Thus, for $[\text{Fe}(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$, reverse LIESST results in a steady state population of the low-spin state of at most 15% [15].

For $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ the lifetime of the light-induced high-spin state at 10 K is longer than 10^6 s (ten days) [14]. For other compounds such as $[\text{Fe}(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$, this lifetime is considerably shorter, and therefore relaxation has to be taken into account as competing process when evaluating photo excitation curves:

$$\frac{d\gamma_{LS}}{dt} = -k_{ex}\eta\gamma_{LS} + k_{HL}\gamma_{HS} \quad (4)$$

where k_{HL} is the high-spin $\rightarrow$ low-spin relaxation rate constant. Figure 11 shows a series of low-spin $\rightarrow$ high-spin conversion curves obtained on

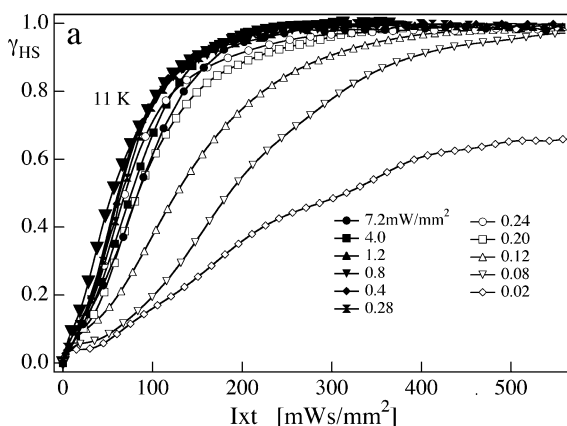


Fig. 11 Excitation curves for $[\text{Fe}(\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$ at 11 K with irradiation at 647 nm plotted vs the product of intensity and irradiation time. For light intensities below 0.2 mW/mm^2 , the high-spin→low-spin relaxation competes with the excitation (adapted from [30])

$[\text{Fe}(\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$ at different excitation intensities for irradiation at 647 nm [30]. In order to facilitate comparison, the curves are plotted as the product of intensity and irradiation time. For intensities above 0.2 mW mm^{-2} , the excitation becomes faster than the relaxation. For these intensities all curves are superimposable. The slightly sigmoidal shape of the curves is due to a small dependence of the quantum efficiency on the high-spin fraction. For intensities below the value of 0.2 mW mm^{-2} , relaxation does compete with excitation and the build-up of the metastable high-spin state is slowed down. The strongly sigmoidal shape of the corresponding excitation curves and the incubation period at the beginning are the signature of cooperative effects, and form the basis for the phenomenon of light-induced hysteresis [32].

3

The High-Spin→Low-Spin Relaxation

Up to the discovery of LIESST, investigations of the high-spin→low-spin relaxation were basically performed on spin-crossover complexes in solution at around ambient temperatures [2]. Various techniques were used, all depending on a transient perturbation of the spin equilibrium. Thus, investigations were restricted to spin-crossover complexes having transition temperatures $T_{1/2}$ at around ambient temperature. Not surprisingly, the range of experimentally determined high-spin→low-spin relaxation rate constants, k_{HL} , was fairly narrow, that is, between 10^6 and 10^8 s^{-1} . Experimental results were

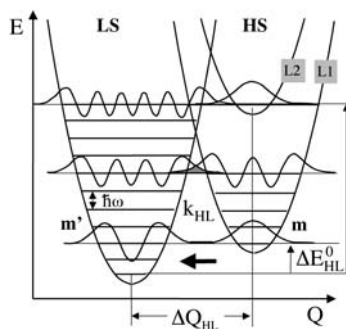
generally interpreted on the basis of absolute rate theory. However, in a theoretical paper, Buhks et al. [33] predicted that at low temperatures the high-spin $\rightarrow$ low-spin relaxation should proceed via a tunnelling process, and subsequently Xie and Hendrickson [34] showed this to be the case for a spin-crossover complex embedded in a polymer matrix. With the discovery of LIESST, relaxation measurements in the solid state and down to cryogenic temperatures became feasible, and the influence of cooperative effects on the spin-crossover dynamics could be investigated [7]. In the next section the basics of the theory of Buhks et al., including a brief comparison with the classical behaviour, will be presented. In the section after that it will be shown how the parameters governing the lifetime of the metastable state can be controlled both chemically and physically.

3.1

The Non-Adiabatic Multiphonon Relaxation

The potential wells of the high-spin and the low-spin state of a typical spin-crossover compound are shown in Scheme 2. The reaction coordinate Q is best described by a single normal mode, namely the totally symmetric breathing mode. Expressed in metal-ligand bond length difference, the horizontal displacement of the two potential wells relative to each other $\Delta Q_{HL} = \sqrt{6}\Delta r_{HL}$. With the average value for $\Delta r_{HL} \approx 0.2 \text{ \AA}$ [35], $\Delta Q_{HL} \approx 0.5 \text{ \AA}$.

Classically, complexes trapped in the high-spin state would have to acquire enough thermal energy to pass over the top of the energy barrier between the two wells. Quantum mechanically, the tunnelling probability for a spontaneous, non-radiative process from a given vibrational level m of the



Scheme 2 Potential wells of the high-spin and the low-spin state along the totally symmetric normal coordinate. For mathematical simplicity, equal vibrational frequencies are assumed for the two states. At low temperatures tunnelling occurs exclusively from the lowest vibrational state of the high-spin state. At elevated temperatures, tunnelling occurs as an activated process from thermally populated vibrational levels of the high-spin state. The zero-point energy difference ΔE^0_{HL} can be tuned chemically and physically

high-spin state to a vibrational level m' of the low-spin state is given by Fermi's Golden Rule [36]:

$$w_{mm'} = \frac{2\pi}{\hbar^2 \omega} \beta_{HL}^2 |\langle \chi_{m'} | \chi_m \rangle|^2 \delta(E_{m'}, E_m) \quad (5)$$

The electronic coupling matrix element $\beta_{HL} = \langle \Phi_{LS} | H_{SO} | \Phi_{HS} \rangle$ is given by second order spin-orbit coupling, $\hbar\omega$ is the vibrational energy of the active vibration, the delta function ensures energy conservation, and $|\langle \chi_{m'} | \chi_m \rangle|^2$ is the Franck-Condon factor of the overlap of the vibrational functions of the low-spin and the high-spin state at the corresponding energy. If, for mathematical simplicity, harmonic potentials with equal force constants and vibrational frequencies are assumed for the two states, energy conservation requires that $m' = m + n$, where $n = \Delta E_{HL}^0 / \hbar\omega$ corresponds to the zero-point energy difference expressed in units of vibrational quanta. This quantity, commonly referred to as the reduced energy gap, is a dimensionless measure of the vertical displacement of the potential wells relative to each other. The high-spin→low-spin relaxation rate constant can then be expressed as a thermal average over all vibrational levels of the high-spin state [36]:

$$k_{HL}(T) = \frac{2\pi}{\hbar^2 \omega} \beta_{HL}^2 F_n(T) \quad (6)$$

where the thermally averaged Franck-Condon factor is given by

$$F_n(T) = \frac{\sum_m |\langle \chi_{m+n} | \chi_m \rangle|^2 e^{-m\hbar\omega/k_B T}}{\sum_m e^{-m\hbar\omega/k_B T}} \quad (7)$$

At low temperatures, where only the vibrational ground state of the high-spin state is populated, the relaxation rate constant is given by

$$k_{HL}(T \rightarrow 0) = \frac{2\pi}{\hbar^2 \omega} \beta_{HL}^2 |\langle \chi_n | \chi_0 \rangle|^2 \quad (8)$$

In the case of the harmonic approximation with equal force constants the Franck-Condon factor from the lowest vibrational level of the high-spin state is given by [37]

$$|\langle \chi_n | \chi_0 \rangle|^2 = \frac{S^n e^{-S}}{n!} \quad (9)$$

where

$$S = \frac{\frac{1}{2} \Delta Q_{HL}^2}{\hbar\omega} \quad (10)$$

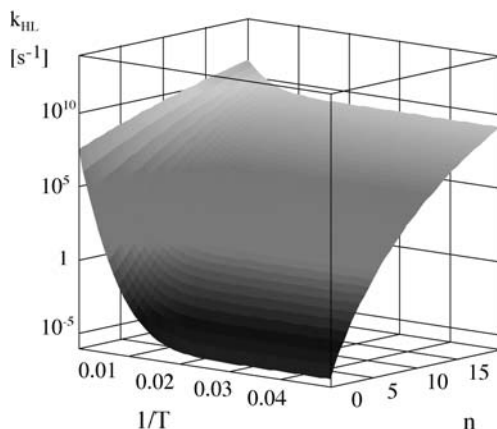


Fig. 12 Calculated relaxation rate constant k_{HL} plotted on a logarithmic scale as a function of T^{-1} and the reduced energy gap n . $S=45$, $\hbar\omega=250\text{ cm}^{-1}$ and $\beta_{HL}=150\text{ cm}^{-1}$

The quantity S , the so-called Huang-Rhys factor [37], is a dimensionless measure of the horizontal displacement of the potential wells relative to each other.

For iron(II) coordination compounds in the vicinity of the spin-crossover region the electronic matrix element β_{HL} takes on a value of $\sim 150\text{ cm}^{-1}$ [33]. As mentioned above, for iron(II) spin-crossover compounds, $\Delta Q_{HL} \approx 0.5\text{ \AA}$. With typical vibrational frequencies of the order of 250 cm^{-1} , and a corresponding average force constant of the order of $2 \times 10^5\text{ dyn/cm}$, the Huang-Rhys factor S takes on a value of ~ 45 . Both β_{HL} and S are not expected to vary to any great extent within the class of iron(II) compounds having $[\text{FeN}_6]$ coordination. ΔE_{HL}^0 and therefore n , however, vary quite substantially from compound to compound, manifesting itself by the range of values of the spin transition temperature $T_{1/2}$. Likewise, external pressure can be used to tune ΔE_{HL}^0 .

Figure 12 shows the high-spin $\rightarrow$ low-spin relaxation rate constant, k_{HL} , on a logarithmic scale vs $1/T$ (Arrhenius plot) calculated according to Eq. (6) using the above standard set of values for S , β_{HL} and $\hbar\omega$, and with the reduced energy gap n as variable parameter. At temperatures below $\sim 50\text{ K}$, the theory predicts a temperature independent process corresponding to pure tunnelling in which the electronic energy of the high-spin state is spontaneously transformed into vibrational energy in the low-spin state, followed by rapid and irreversible dispersion of this energy into the surrounding medium. For small values of n , the low-temperature tunnelling rate constant increases exponentially with n . At somewhat larger values of n , the increase becomes less dramatic, following the bell shaped curve of Marcus theory with, in principle, a maximum value as n approaches S [38].

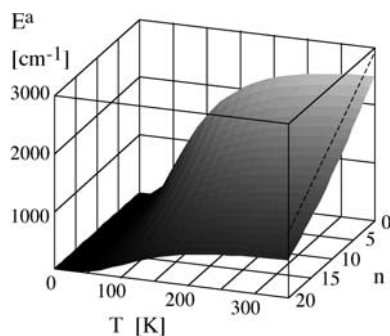


Fig. 13 The effective activation energy as a function of temperature with the reduced energy gap as parameter. (Dashed line) classical high-temperature limit according to Eq. (11)

At elevated temperature, the high-spin→low-spin relaxation becomes thermally activated. The classical energy barrier is given by [38]

$$E_{\text{clas}}^a = \frac{1}{4} \hbar \omega S \left(1 - \frac{n}{S}\right)^2 \quad (11)$$

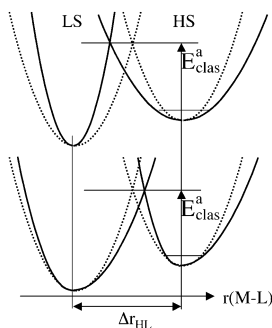
However, at finite temperatures corresponding effective activation energies are always smaller than the classical barrier. Thus in the thermally activated region, the high-spin→low-spin relaxation is to be regarded as tunnelling from thermally populated levels of the high-spin state having much larger Franck-Condon factors with the corresponding vibrational levels of the low-spin state. As shown in Fig. 13, the effective activation energy defined as

$$E_{\text{eff}}^a = - \frac{d(\ln k_{\text{HL}})}{d(1/k_{\text{B}}T)} \quad (12)$$

is, in fact, temperature dependent [39]. In particular between the low-temperature tunnelling region and the high-temperature region, that is between 50 and 150 K it increases from essentially zero to up to 2000 cm^{-1} for a given compound. Thus, when discussing and comparing experimental activation energies for different compounds, this must be done over a large and identical temperature range.

In line with the classical expression, the effective activation energy decreases with increasing zero-point energy difference. In the limit of $n \ll S$, both the effective and the classical energy barrier follow a linear free energy relationship, which for the classical barrier as high-temperature limit is given by [38]

$$E_{\text{clas}}^a = \frac{1}{4} \hbar \omega S - \frac{1}{2} \hbar \omega n \quad (13)$$



Scheme 3 The influence of frequency shift (*top*) and anharmonicity (*bottom*) on the high-spin→low-spin relaxation are comparatively small, because the height and width of the energy barrier between the two states remains constant

For the extremely large value of S of iron(II) spin-crossover compounds and the known differences in vibrational frequencies of the order of 50% between the high-spin and the low-spin state [40], anharmonicity and frequency shifts are potentially non-negligible. However, even quantitatively their influence on the high-spin→low-spin relaxation is surprisingly small. This is best explained with reference to Scheme 3. Taking the effective frequencies of the two states instead of the average frequency, does not significantly change the height and the width of the energy barrier. The same holds for the effect of anharmonicity.

3.2

Experimental Results

3.2.1

Variation of the Energy Gap by Chemical Substitution

Figure 14 shows the Arrhenius plots of the high-spin→low-spin relaxation rate constants, k_{HL} , for a series of iron(II) spin-crossover and low-spin complexes. In order to minimise complications due to cooperative effects at this stage, these rate constants were all determined from perfectly single exponential decay curves as obtained on dilute single crystals, with the active iron(II) complex doped into an inert host lattice. As predicted, there is low-temperature tunnelling below ~ 50 K with almost temperature independent rate constants, and a thermally activated region above ~ 100 K. Table 1 summarizes the low-temperature tunnelling rate constants, activation energies E_{HL}^a and frequency factors A_{HL} as well as $T_{1/2}$ for these and other iron(II) spin-crossover and low-spin complexes. In particular, the large range of rate constants from $<10^{-6} \text{ s}^{-1}$ to $>10^8 \text{ s}^{-1}$ for one and the same process within a class of chemically very similar compounds, namely iron(II) complexes having an $[\text{FeN}_6]$ core, is unique. Even the low-temperature tunnelling rate con-

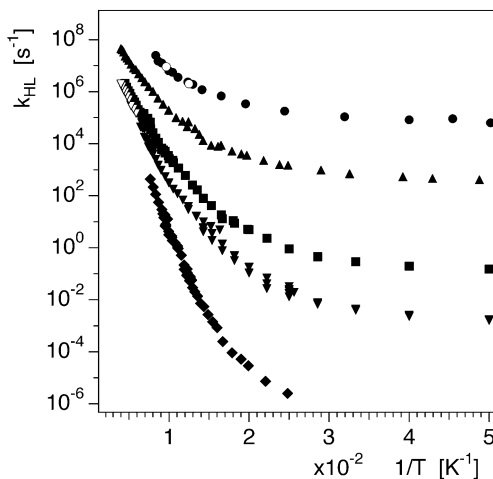


Fig. 14 k_{HL} on a log scale plotted against $1/T$ for a series of iron(II) spin-crossover and low-spin complexes diluted in inert host lattices: $[Zn:Fe(ptz)_6](BF_4)_2$ (filled diamonds), $[Mn:Fe(pic)_3]Cl_2EtOH$ (filled upside down triangle) from laser pulse excitation, (open upside down triangle) $[Fe(pic)_3]Cl_2EtOH$ from Mössbauer lineshape analysis [41], $[Zn:Fe(mepy)_3tren](PF_6)_2$ (filled squares), $[Zn:Fe(py)_3tren](PF_6)_2$ (filled triangles), $[Mn:Fe(bpy)_3tren](PF_6)_2$ (filled circles) from laser pulse excitation, (open circles) from time-differential Mössbauer emission [26]

stants vary over many orders of magnitude. But this is precisely as predicted by Eq. (8) for a value of $S \approx 45$ and a variation of the reduced energy gap n .

A qualitative measure for the zero-point energy difference, and thus n , is provided by the thermal transition temperature $T_{1/2}$. Accordingly, Fig. 15 shows $k_{HL}(T \rightarrow 0)$ vs $T_{1/2}$ for a large number of iron(II) spin-crossover systems (see also table 1). The exponential increase of $k_{HL}(T \rightarrow 0)$ with $T_{1/2}$ is obvious. Unfortunately, it is not straightforward to extract n from the thermodynamic parameters, ΔH_{HL}^0 and ΔS_{HL}^0 as obtained from thermal transition curves of diluted systems, because these parameters show a substantial dependence on temperature. Thus, the values given in the literature have to be interpreted as being the values at the transition temperature $T_{1/2}$, according to

$$T_{1/2} = \frac{\Delta H_{HL}^0}{\Delta S_{HL}^0} \quad (14)$$

where ΔE_{HL}^0 is a quantum mechanical energy difference, and, in principle, corresponds to $\Delta H_{HL}^0(T \rightarrow 0)$. However, if for the sake of simplicity, the T -dependence of ΔH_{HL}^0 is neglected,

$$n = \frac{\Delta E_{HL}^0}{\hbar\omega} \approx \frac{\Delta H_{HL}^0}{\hbar\omega} = \frac{T_{1/2}\Delta S_{HL}^0}{\hbar\omega} \quad (15)$$

Table 1 Transition temperatures $T_{1/2}$, activation energies E_{HL}^{a} and frequency factors A_{HL} for the high temperature region, and low temperature tunnelling rate constants $k_{\text{HL}}(T \rightarrow 0)$ for some Fe(II) coordination compounds in the solid state and embedded in polymer matrices. For comparison, values of k_{HL} extrapolated to room temperature are included

	$T_{1/2}$ [K]	E_{HL}^{a} [cm ⁻¹]	A_{HL} [s ⁻¹]	$k_{\text{HL}}(T \rightarrow 0)$ [s ⁻¹]	$k_{\text{HL}}(295 \text{ K})$ [s ⁻¹]
[Zn _{1-x} Fe _x (ptz) ₆](BF ₄) ₂	95	1100	5×10 ⁷	5×10 ⁻⁷	~5×10 ⁵
[Fe(ptz) ₆](BF ₄) ₂ ^a	125			5×10 ⁻⁶	
[Fe(ptz) ₆](BF ₄) ₂ ^b	138			3×10 ⁻⁵	
[Mn _{1-x} Fe _x (pic) ₃]Cl ₂ ·EtOH	76			6×10 ⁻⁶	
[Zn _{1-x} Fe _x (pic) ₃]Cl ₂ ·EtOH	95			2.5×10 ⁻⁵	
[Mn _{1-x} Fe _x (pic) ₃]Cl ₂ ·MeOH	118	1120	2×10 ⁸	2.5×10 ⁻³	~4×10 ⁶
[Zn _{1-x} Fe _x (pic) ₃]Cl ₂ ·MeOH	140			9×10 ⁻³	
[Fe(pic) ₃]Cl ₂ ·EtOH ^c	118			5×10 ⁻⁴	
[Zn _{1-x} Fe _x (mepy) ₃ tren](PF ₆) ₂	210	837	5×10 ⁸	1.4×10 ⁻¹	~8×10 ⁶
[Fe(mepy) ₂ (py)tren] ²⁺ in PMMA	270			~5×10 ¹	
[Fe(mepy)(py) ₂ tren](PF ₆) ₂	370			~2×10 ²	
[Zn _{1-x} Fe _x (py) ₃ tren](PF ₆) ₂	>400	640	1×10 ⁹	4×10 ²	~5×10 ⁷
[Mn _{1-x} Fe _x (bipy) ₃](PF ₆) ₂	Low-spin			6×10 ⁴	
[Zn _{1-x} Fe _x (bipy) ₃](PF ₆) ₂	Low-spin	364	2×10 ⁹	6×10 ⁵	~1×10 ⁹
[Fe(phen) ₃] ²⁺ in Nafion	Low-spin			~5×10 ⁶	

All values from [6], except for those listed below

^a [Fe(ptz)₆](BF₄)₂ high-temperature phase, from [14]

^b [Fe(ptz)₆](BF₄)₂ low-temperature phase, from [14]

^c [Fe(pic)₃]Cl₂·EtOH, from [15]

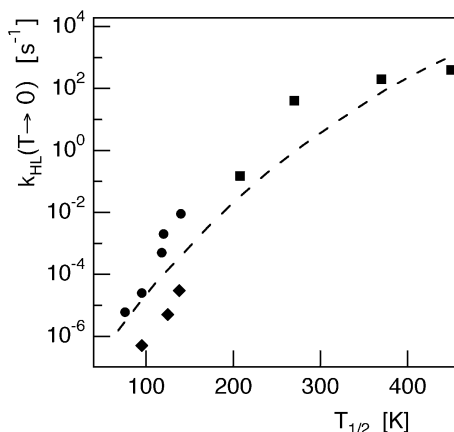


Fig. 15 The low-temperature tunnelling rate constant on a log scale as a function of chemical variation of the zero-point energy difference between the HS and the LS state as expressed by the transition temperatures of a series of spin-crossover complexes, (filled circles) picolylamine, (filled diamonds) tetrazoles, (filled squares) (mepy)_{3-x}(py)_x series, (dashed line) theoretical (adapted from [6])

Whereas ΔH_{HL}^0 varies substantially from compound to compound, ΔS_{HL}^0 takes on values within the comparatively small interval between 3 and 7 cm^{-1} (40–80 $\text{JK}^{-1} \text{mol}^{-1}$). With an average value of $\sim 5 \text{ cm}^{-1}$ (60 $\text{JK}^{-1} \text{mol}^{-1}$), and using the standard value of 250 cm^{-1} for $\hbar\omega$,

$$n \approx 0.02 \cdot T_{1/2} \quad (16)$$

The drawn line in Fig. 15 is calculated using the standard values for all parameters, Eq. (16) for the relation between n and $T_{1/2}$, and Eq. (9) for the low-temperature tunnelling rate constant, $k_{\text{HL}}(T \rightarrow 0)$, as a function of n . It describes to perfection the observed increase of $k_{\text{HL}}(T \rightarrow 0)$ from less than 10^{-6} s^{-1} ($\tau > 10$ days) for $[\text{Fe}(\text{ptz})_6]^{2+}$ with $T_{1/2} = 95 \text{ K}$ when doped into the inert Zn-host to more than 10^4 s^{-1} ($\tau < 1 \text{ ms}$) for $[\text{Fe}(\text{py})_3\text{tren}]^{2+}$ with $T_{1/2} > 400 \text{ K}$ also doped into the inert Zn-host. Indeed, it allows an estimate of the energy gap for low-spin systems based on $k_{\text{HL}}(T \rightarrow 0)$. For $[\text{Fe}(\text{bpy})_3]^{2+}$ doped into $[\text{Zn}(\text{bpy})_3](\text{PF}_6)_2$, $k_{\text{HL}}(T \rightarrow 0) = 5.2 \times 10^5 \text{ s}^{-1}$ ($\tau = 1.8 \text{ }\mu\text{s}$), from which $T_{1/2} \approx 700 \text{ K}$ and, subsequently, $\Delta E_{\text{HL}}^0 \approx 3500 \text{ cm}^{-1}$ can be estimated. This value is not accessible in any other way. With reference to Fig. 5 of the chapter on ligand-field theoretical considerations, the corresponding ligand field strength $10Dq^{\text{LS}} \approx 23,000 \text{ cm}^{-1}$. This value is not accessible through direct observation either, due to the low-lying MLCT band obscuring the ligand-field transitions, but it confirms the tentative assignment of a shoulder on the low-energy side of the MLCT band to the $^1A_1 \rightarrow ^1T_1$ transition [42].

The observed curves of the Arrhenius plots bend over more gradually from the low- T tunnelling region into the thermally activated region than predicted by the single frequency model. This is due to anharmonicity and frequency shifts, as well as to the fact that there is usually more than one active frequency. However, as mentioned above, in the strong coupling limit these effects are of secondary importance.

3.2.2

Variation of the Energy Gap by External Pressure

The effect of external pressure on the thermal spin transition has been widely investigated [43] and is discussed in detail in another chapter of this book. The key feature is that external pressure adds a work term of the form $p\Delta V_{\text{HL}}$ to the free energy, with $\Delta V_{\text{HL}} = V_{\text{HS}} - V_{\text{LS}}$ being the difference in unit cell volume per complex between the system in the high-spin and in the low-spin state. With values of ΔV_{HL} typically between 15 and 30 $\text{\AA}^3$ (9–18 $\text{cm}^3 \text{mol}^{-1}$), the low-spin state is stabilised such that $T_{1/2}$ shifts to higher temperatures by ~ 10 –30 K/kbar. Of course, in cases in which the external pressure triggers or shifts the temperature of a crystallographic phase transition, the resulting temperature shifts may be much larger and discontinuous [44].

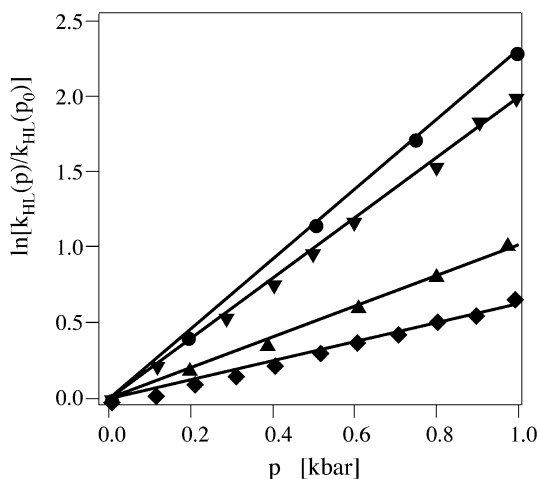


Fig. 16 Low-T tunnelling rate constants plotted as $\ln[k_{\text{HL}}(p)/k_{\text{HL}}(p=0)]$ as a function of pressure up to $p=1$ kbar: (filled circles) $[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6](\text{BF}_4)_2$ [45] (filled upside down triangles) $[\text{Zn}_{1-x}\text{Fe}_x(\text{mepy})_3\text{tren}](\text{PF}_6)_2$, (filled triangles) $[\text{Zn}_{1-x}\text{Fe}_x(\text{py})_3\text{tren}](\text{PF}_6)_2$ [46], (filled diamonds) $[\text{Zn}_{1-x}\text{Fe}_x(\text{bpy})_3](\text{PF}_6)_2$ [26b]

At the molecular level, the external pressure increases the zero-point energy difference by the work term according to

$$\Delta E_{\text{HL}}^0(p) = \Delta E_{\text{HL}}^0(p=0) + p\Delta V_{\text{HL}} \quad (17)$$

and for the reduced energy gap

$$n(p) = \frac{\Delta E_{\text{HL}}^0(p)}{\hbar\omega} = n_0 + \frac{\Delta V_{\text{HL}}}{\hbar\omega} p \quad (18)$$

with n_0 the reduced energy gap at zero external pressure. Qualitatively, the external pressure increases the driving force for the high-spin $\rightarrow$ low-spin relaxation and is thus expected to accelerate the relaxation process. As exemplified by the low-temperature tunnelling rate constants of four different complexes shown in Fig. 16 as function of an applied pressure of up to 1 kbar, this is indeed the case. For the four complexes, again diluted in inert host lattices, the increase follows an exponential law according to

$$k_{\text{HL}}(T \rightarrow 0, p) \sim e^{\beta p} \quad (19)$$

For $[\text{Fe}(\text{ptz})_6]^{2+}$, the value of the acceleration factor β as determined from the slope of the corresponding curve in Fig. 16, is 2.3 kbar^{-1} , that is, the high-spin $\rightarrow$ low-spin relaxation is accelerated by a factor of ~ 10 per kbar [45]. At the other extreme, the acceleration factor of only 0.7 kbar^{-1} for the low-spin complex $[\text{Fe}(\text{bpy})_3]^{2+}$ is considerably smaller [25b].

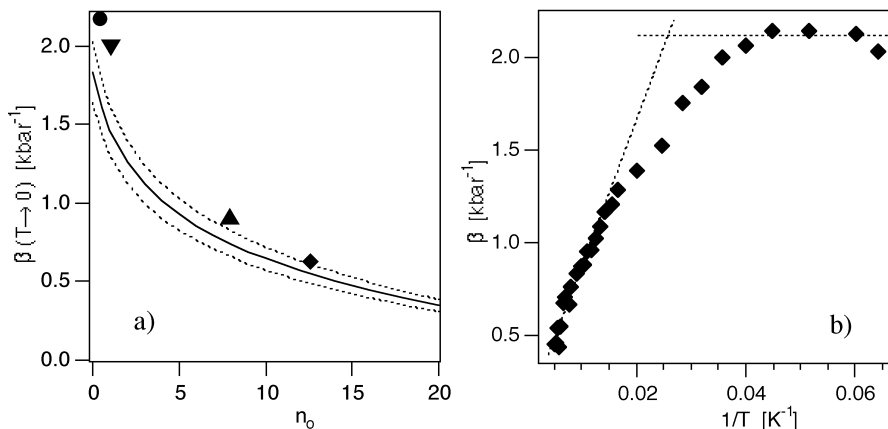


Fig. 17 **a** Pressure acceleration factor β as function of the reduced energy gap n . The experimental points correspond to the slopes from Fig. 16. **b** Pressure acceleration factor β of $[\text{Zn}_{1-x}\text{Fe}_x(\text{mepy})_3\text{tren}](\text{PF}_6)_2$ as a function of temperature (adapted from [46])

This behaviour can be rationalised on the basis of the model of non-adiabatic multiphonon relaxation. The low-temperature relaxation rate constant can be expressed quantitatively by using Eq. (9) with n as a function of external pressure:

$$k_{\text{HL}}(T \rightarrow 0, p) \sim \frac{e^{-S} S^{n(p)}}{n(p)!} \quad (20)$$

In the limit of small external pressure, that is $p \leq 1$ kbar, Eq. (20) can be shown to be well described by Eq. (19), with the acceleration factor β depending upon the value of n_0 , the reduced energy gap at zero external pressure. β can be evaluated numerically as shown in Fig. 17a using the standard set of parameters $S=45$, $\hbar\omega=250 \text{ cm}^{-1}$ and $\Delta V_{\text{HL}}=25 \text{ \AA}^3$. Analytically β can be approximated as

$$\beta = \frac{\Delta V_{\text{HL}}}{\hbar\omega} \ln\left(\frac{S}{n_0}\right) \quad \text{for } n_0 > 1 \quad (21a)$$

$$\beta = \frac{\Delta V_{\text{HL}}}{\hbar\omega} \ln(S) \quad \text{for } n_0 \leq 1 \quad (21b)$$

In Fig. 17a, the values of β for the four compounds using n_0 as derived in the previous section are included. They verify the above theoretical approach. The largest value to be expected for $n_0 < 1$ and the above set of model parameters is $\beta \approx 2.3$, close to the value found for $[\text{Fe}(\text{ptz})_6]^{2+}$, that is, the complex with the lowest transition temperature of the series.

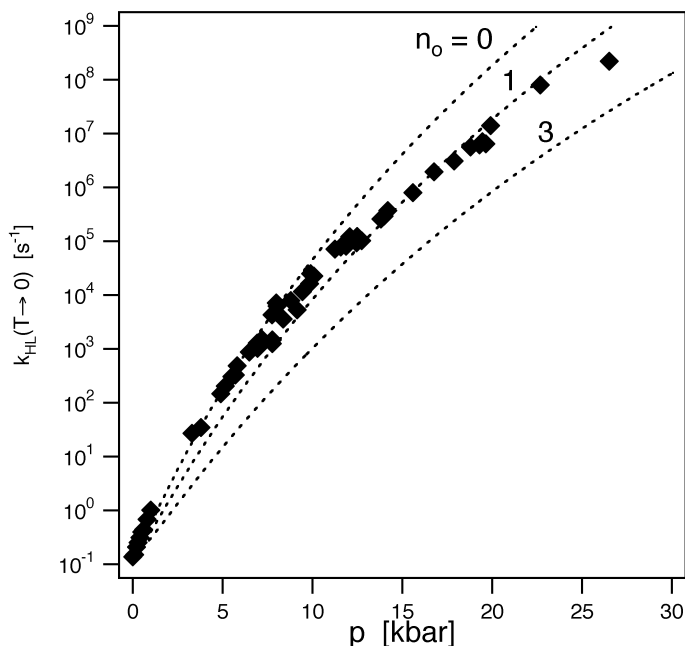


Fig. 18 Low-temperature tunnelling rate constant for $[\text{Zn}_{1-x}\text{Fe}_x(\text{mepy})_3\text{tren}](\text{PF}_6)_2$ as a function of pressure, (filled diamonds) experimental, (dashed line) calculated for various values of n_0 (adapted from [46])

The acceleration factor β is a decreasing function of temperature, as shown in Fig. 17b for the dilute system $[\text{Zn}_{1-x}\text{Fe}_x(\text{mepy})_3\text{tren}](\text{PF}_6)_2$. In the low-temperature region it is given by the limiting value of Eq. (21), at higher temperatures it can be calculated using Eq. (6). In the classical limit it can be identified with the activation volume according to

$$\beta(T) = -\frac{\Delta V_{\text{HL}}^a}{k_B T} \quad (22)$$

From the slope of the plot of $\beta(T)$ vs $1/T$ at elevated temperature, a value of the activation volume of $-11 \text{ \AA}^3$ ($7 \text{ cm}^3 \text{ mol}^{-1}$) can be derived for the above spin-crossover complex. Classically and as expected, this value indicates that the transition state is approximately half way between the high-spin and the low-spin state. It may be considered as a typical value for the high-spin $\rightarrow$ low-spin relaxation in spin-crossover as well as in low-spin compounds.

The approximation of Eq. (20) by the simple exponential law of Eq. (19) is only valid for comparatively small external pressures, that is $p \leq 1$ kbar. At more elevated pressure, deviations from a strictly exponential increase of $k_{\text{HL}}(T \rightarrow 0)$ with increasing pressure are to be expected. This is exemplified for $[\text{Zn}_{1-x}\text{Fe}_x(\text{mepy})_3\text{tren}](\text{PF}_6)_2$ in Fig. 18. At ambient pressure

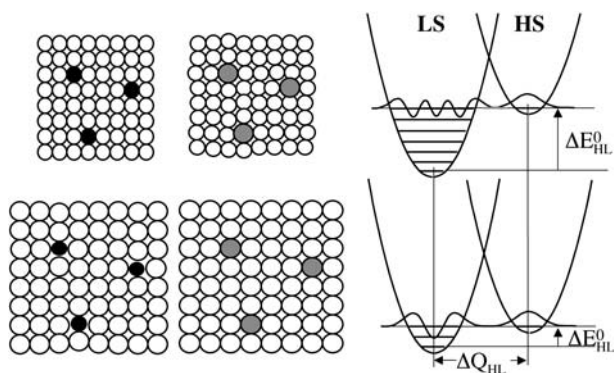
$k_{\text{HL}}(T \rightarrow 0) \approx 10^{-1} \text{ s}^{-1}$ ($\tau \approx 10 \text{ s}$). At 28 kbar, $k_{\text{HL}}(T \rightarrow 0) \approx 10^8 \text{ s}^{-1}$ ($\tau \approx 10 \text{ ns}$). The relaxation rate constant increases by an astonishing nine orders of magnitude. However, after the initial acceleration of almost a factor of 10 per kbar, the acceleration slows down considerably at elevated pressures. Indeed, the experimental curve follows the bell shaped curve predicted by Eq. (20) shown as drawn line in Fig. 18.

3.2.3

Matrix Effects

The zero-point energy difference is not only a function of the ligands of a given spin-crossover complex, it can be fine tuned by the second coordination sphere. For the much studied $[\text{Fe}(\text{pic})_3]^{2+}$ complex, the transition temperature increases from 74 K when doped into $[\text{Mn}(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ to 97 K when doped into $[\text{Zn}(\text{pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ [16]. $T_{1/2}$ of the neat iron compound is 117 K [17]. In the former cases, the transition is gradual, in the latter cases it is much more abrupt due to cooperative effects (see below). To some extent, the effect of the different host lattices can be thought of as a variation in internal pressure, which, like an external pressure, influences the zero-point energy difference of the spin-crossover guest complex, by providing cavities of different size. This is shown schematically in Scheme 4.

For instance Zn(II) has a smaller ionic radius, typically similar to the one of iron(II) in the high-spin state, than Mn(II). Therefore, the value of ΔE_{HL}^0 of the iron(II) guest in the Zn-host is expected to be larger than in the Mn-host. This is in accordance with the observation that $T_{1/2}$ for the Mn-host is lower than $T_{1/2}$ for the Zn-host. With respect to the high-spin→low-spin relaxation this translates into a slower relaxation for the Mn-host than for the Zn-host. Substitution of EtOH by MeOH creates a still denser lattice, and consequently the $T_{1/2}$ values for the methanolates are higher still and



Scheme 4 Potential wells for a spin-crossover complex doped into different host lattices, demonstrating the effect of different lattice pressures

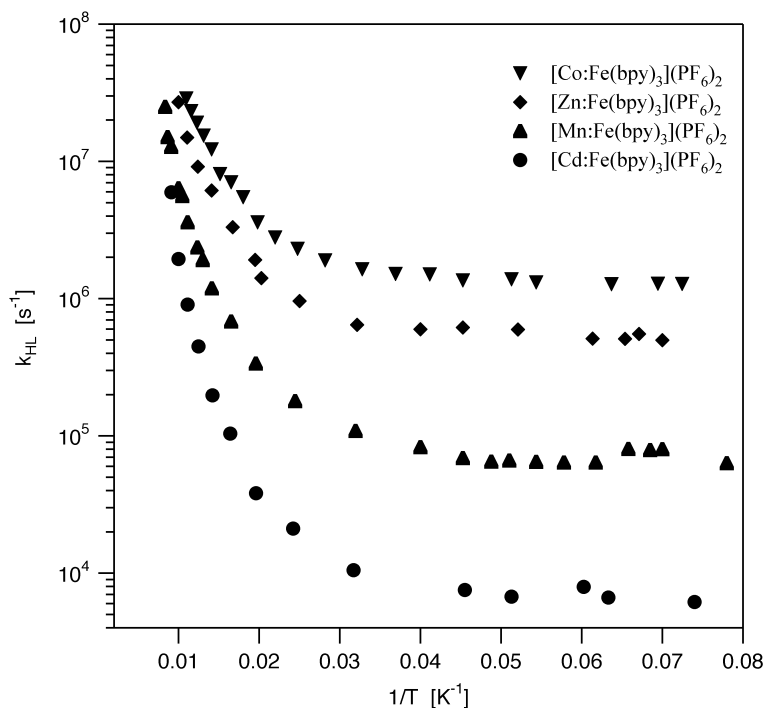
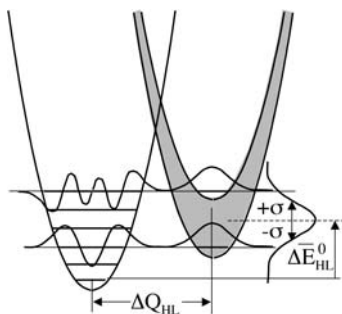


Fig. 19 Matrix influence on the HS→LS relaxation rate constant for $[\text{Fe}(\text{bpy})_3]^{2+}$ doped into the series of isostructural host lattices $[\text{M}(\text{bpy})_3](\text{PF}_6)_2$, $\text{M}=\text{Co}, \text{Zn}, \text{Mn}, \text{Cd}$

the lifetimes of the light-induced high-spin states shorter than for the ethanولات. The corresponding data are included in Table 1. Even more striking is the sequence of isostructural host lattices $[\text{M}(\text{bpy})_3](\text{PF}_6)_2$, $\text{M}=\text{Cd}, \text{Mn}, \text{Zn}, \text{Co}$, doped with $[\text{Fe}(\text{bpy})_3]^{2+}$ shown in Fig. 19. The comparatively small decrease in unit cell volume of $\sim 2\%$ across the series is sufficient to result in an increase of the low-temperature tunnelling rate constant by a factor of 250 [47].

This is in line with observations from Mössbauer emission experiments making use of the NIESST effect: At a given temperature, the intensity of the emission lines from the nucleogenic $^{57}\text{Fe}(\text{II})$ high-spin species following the nuclear decay in the host lattices $[\text{M}^{\text{II}}(\text{phen})_3](\text{ClO}_4)_2$ decreases in the series $\text{Zn}(\text{II}) > \text{Co}(\text{II}) > \text{Ni}(\text{II}) > \text{Fe}(\text{II})$ -LS, that is, in the order of decreasing ionic radius of M^{2+} . This indicates that with decreasing ionic radius of the metal of the host lattice, the internal pressure increases, as a result of which the lifetime of the nucleogenic high-spin state decreases [48].

The influence of the surrounding medium can be even more subtle. In dilute single crystals or even in liquid solutions each spin-crossover complex sees exactly the same environment, and therefore ΔE_{HL}^0 has the same value



Scheme 5 Potential wells with inhomogeneous distribution of the zero-point energy difference around a mean value ΔE_{HL}^0 . Complexes at the top of the distribution relax considerably faster than those at the bottom

for each and every complex, and relaxation curves following the light-induced population of the high-spin state are invariably single exponential. Frozen solutions, polymer matrices and poorly crystallised solids on the other hand are far from homogeneous. As a result, ΔE_{HL}^0 is distributed around a mean value as schematically shown in Scheme 5. The influence of such an inhomogeneous distribution on the thermal spin transition is not necessarily very dramatic. In most cases it just makes the transition slightly more gradual. In particular cases it could be the reason for residual high-spin fractions at low temperatures. Without a reference, such an inhomogeneous distribution is very difficult to quantify, as a fit to a simple model with ΔH_{HL}^0 and ΔS_{HL}^0 as free parameters does not have the potential to “see” such an inhomogeneous distribution. Basically it just results in a slightly reduced value for ΔS_{HL}^0 . The influence on the high-spin→low-spin relaxation, however, is dramatic. As shown in Fig. 19 for the spin-crossover complex $[\text{Fe}(\text{mephen})_3]^{2+}$ embedded in PMMA, the relaxation curve at 50.6 K is far from single exponential [25b]. The initial relaxation is quite fast. It comes from the complexes with ΔE_{HL}^0 at the top edge of the distribution. The complexes at the bottom edge, on the other hand, result in a long slow tail to the relaxation curve. The relaxation curve in Fig. 20 can be modelled based on the assumption of a Gaussian distribution of ΔE_{HL}^0 around some mean value. The best fit to the experimental data in the present case is obtained with $\sigma = 170 \text{ cm}^{-1}$. Although this value seems large at first sight, it is only large in comparison to ΔE_{HL}^0 itself. In absolute terms, this value is not exceedingly large.

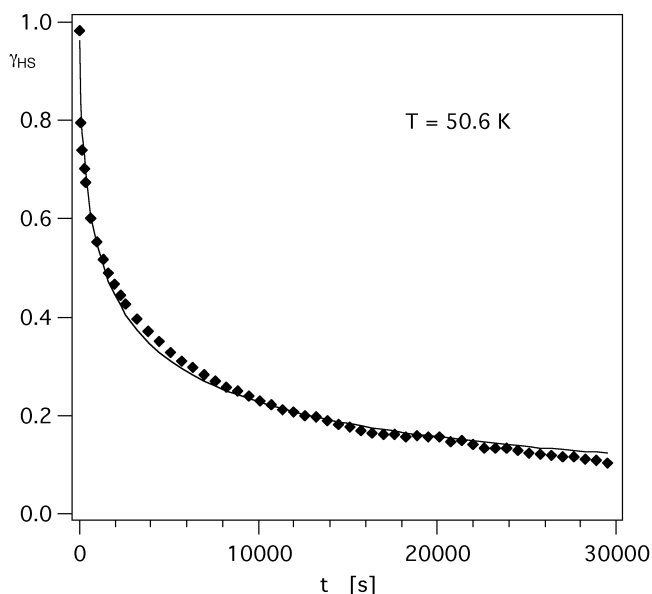


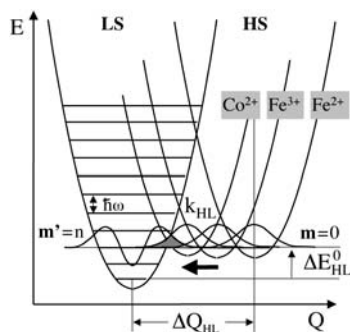
Fig. 20 Relaxation curve for $[\text{Fe}(\text{mephen})_3]^{2+}$ embedded in PMMA at 50.6 K, (filled diamonds) exp., (continuous line) calc., with $\sigma=170 \text{ cm}^{-1}$ (adapted from [25b])

3.2.4

Variation of the Bond Length Difference

Within the class of iron(II) spin crossover compounds the actual bond length differences lie in a comparatively small interval around the model value of $0.2 \text{ \AA}$. Thus the value of the Huang-Rhys factor S lies within the range of 40 to 50. In order to arrive at appreciably different values of S , spin-crossover compounds with different d-electron configurations have to be considered: for instance, those of iron(III) with a ${}^2\text{T}_2 \rightleftharpoons {}^6\text{A}_1$ spin transition, or those of cobalt(II) with a ${}^2\text{E} \rightleftharpoons {}^4\text{T}_1$ spin transition. For the former, the bond length difference between the low-spin and the high-spin state is typically $0.13\text{--}0.16 \text{ \AA}$ [49], for the latter $0.09\text{--}0.12 \text{ \AA}$ [50]. As becomes apparent from Scheme 6, such a variation influences the low-temperature tunnelling rate constant considerably, as the Franck-Condon factor increases exponentially with decreasing bond length difference.

With the above range of bond length differences for iron(III) and cobalt(II) spin-crossover compounds, the Huang-Rhys factors S are between 25 and 30 for the former and between 15 to 20 for the latter, as compared to 40 to 50 for iron(II) spin-crossover compounds. In Fig. 21, the corresponding ranges are indicated. Using Eq. (9) and assuming all other factors to have a minor influence on the relaxation rate constant, the low-temperature lifetime of the high-spin state for cobalt(II) spin-crossover compounds is ex-



Scheme 6 Potential well of the high-spin state relative to the potential well of the low-spin state for different metal-ligand bond lengths. Because the Franck-Condon factor (*shaded area*) increases exponentially with decreasing bond length difference, the high-spin→low-spin relaxation becomes considerably faster for shorter bond-length differences. This is exemplified by the series Fe^{2+} , Fe^{3+} , Co^{2+}

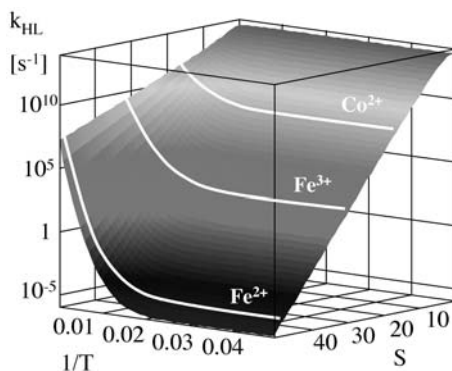


Fig. 21 Calculated relaxation rate constant k_{HL} plotted on a logarithmic scale as a function of T^{-1} and the Huang-Rhys factor S . The reduced energy gap $n=1$, $\hbar\omega=250\text{ cm}^{-1}$, and $\beta_{\text{HL}}=150\text{ cm}^{-1}$

pected to be of the order of microseconds, the one for iron(III) spin-crossover compounds of the order of milliseconds, as compared to seconds to days for iron(II) spin-crossover compounds.

Figure 22 shows the experimentally determined high-spin→low-spin relaxation rate constants following pulsed laser excitation for the iron(III) spin-crossover compound $[\text{Fe}(\text{acpa})_2]\text{PF}_6$ dispersed in KBr [51]. For comparison, Fig. 22 includes the relaxation rate constants of the iron(II) system $[\text{Mn}_{1-x}\text{Fe}_x(\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$ having approximately the same thermal transition temperature of 150 K and thus a similar value of the zero-point energy difference as the iron(III) compound. As predicted, the high-spin→low-relaxation of the iron(III) system is a factor of 10^4 faster. A preliminary determi-

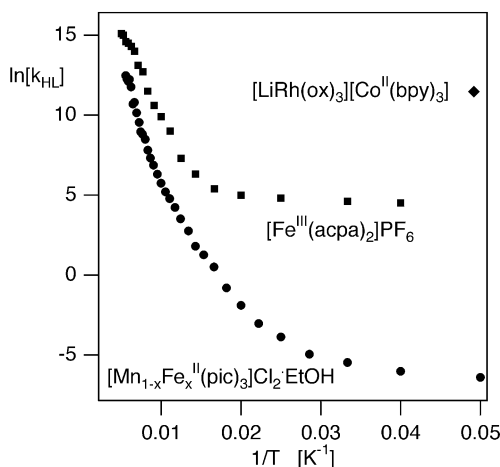


Fig. 22 High-spin→low-spin relaxation rate constants plotted as $\ln[k_{\text{HL}}]$ (k_{HL} in s^{-1}) vs $1/T$ of $[\text{Fe}^{\text{III}}(\text{acpa})_2]\text{PF}_6$ dispersed in KBr (*filled squares*), and for direct comparison of $[\text{Mn}_{1-x}\text{Fe}_x^{\text{II}}(\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$ (*filled circles*) as well as the low-temperature value for $[\text{LiRh}(\text{ox})_3][\text{Co}^{\text{II}}(\text{bpy})_3]$ (*filled diamonds*) (adapted from [51])

nation of the low-temperature relaxation rate constant in the cobalt(II) spin-crossover system $[\text{LiRh}(\text{ox})_3][\text{Co}^{\text{II}}(\text{bpy})_3]$ [52] confirms the expected order of magnitude in the microsecond region of the low-temperature lifetime of the high-spin state for cobalt(II) compounds.

4 Cooperative Effects

4.1 The Mean-Field Approximation

Cooperative effects of elastic origin are a recurring topic in this series of articles. The basics with regard to the thermal spin transition are covered in the contribution by Spiering et al. and others [12]. Very soon after the discovery of LIESST it was realised that cooperative effects also play an important role in the high-spin→low-spin relaxation, in so far as in concentrated compounds relaxation curves following the light-induced population of the high-spin state deviate substantially from first order kinetics [7]. This is exemplified by the relaxation curves for neat $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ in the crystallographic high-temperature phase shown in Fig. 23 [53]. Whereas for the previously discussed dilute systems relaxation curves are strictly single exponential, the ones in the concentrated compound show the sigmoidal behaviour of a self-accelerated process.

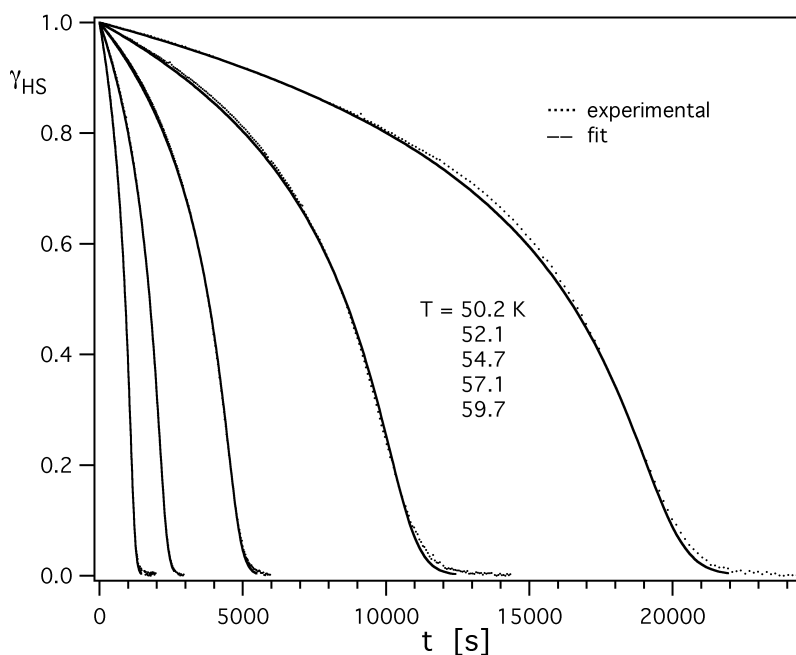


Fig. 23 High-spin→low-spin relaxation curves for neat $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ in the temperature interval 50–60 K, (dotted line) experimental, (continuous line) least squares fit to the phenomenological equation (adapted from [53])

Phenomenologically, the sigmoidal relaxation curves can be described by a relaxation rate constant which depends upon the low-spin fraction according to

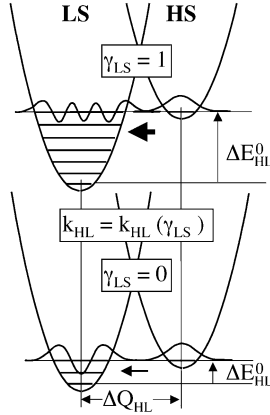
$$k_{\text{HL}}(T, \gamma_{\text{LS}}) = k_{\text{HL}}(T, \gamma_{\text{LS}} = 0) \cdot e^{\alpha(T)\gamma_{\text{LS}}} \quad (23)$$

and the standard differential equation

$$\frac{d\gamma_{\text{HS}}}{dt} = -k_{\text{HL}}(T, \gamma_{\text{LS}})\gamma_{\text{HS}} \quad (24)$$

with $\gamma_{\text{HS}} + \gamma_{\text{LS}} = 1$. This differential equation does **not** have an analytical solution, but it is straightforward to extract both $k_{\text{HL}}(T, \gamma_{\text{LS}} = 0)$ and the acceleration factor $\alpha(T)$ from least squares numerical fits to the experimental data.

Within the framework of mean-field theory and based on similar arguments as used in the discussion of the matrix influence, this behaviour is straightforward to understand. In the beginning of the relaxation, high-spin complexes sitting in a predominantly high-spin lattice relax to the low-spin state. With the majority of the complexes in the high-spin state, the internal pressure is low and ΔE_{HL}^0 at $\gamma_{\text{HS}} \approx 1$ is comparatively small. As the low-spin



Scheme 7 Potential wells taking into account cooperative effects: in mean-field approximation $\Delta E_{HL}^0(\gamma_{LS}) = \Delta E_{HL}^0(\gamma_{LS}=0) + 2\Gamma\gamma_{LS}$

concentration increases, the lattice gets more dense, the internal pressure increases, as a consequence ΔE_{HL}^0 increases and the relaxation is accelerated. In mean-field approximation the zero-point energy difference as a function of the low-spin fraction can be expressed as

$$\Delta E_{HL}^0(\gamma_{LS}) = \Delta E_{HL}^0(\gamma_{LS}=0) + 2\Gamma\gamma_{LS} \quad (25)$$

where Γ is the so-called interaction constant [12, 44] (see Scheme 7). The reduced energy gap as a function of the high-spin fraction is therefore given by

$$n(\gamma_{LS}) = n_0 + \frac{2\Gamma}{\hbar\omega}\gamma_{LS} \quad (26)$$

with n_0 being the reduced energy gap at $\gamma_{LS}=0$. Equation (26) is reminiscent of Eq. (19) with γ_{LS} in the role of internal pressure. Thus, using the same approximations as for the case of small external pressures, the exponential increase of k_{HL} with increasing low-spin fraction of Eq. (23) can be rationalised on the basis of a mean-field description of the cooperative effects. In the low-temperature tunnelling region, the acceleration factor is given by

$$\alpha = \frac{2\Gamma}{\hbar\omega} \ln(S) \quad \text{for } n_0 \leq 1 \quad (27a)$$

$$\alpha = \frac{2\Gamma}{\hbar\omega} \ln\left(\frac{S}{n_0}\right) \quad \text{for } n_0 > 1 \quad (27b)$$

At elevated temperatures, α becomes a function of T . In principle this can be calculated using Eq. (6), and the corresponding curves with the limiting

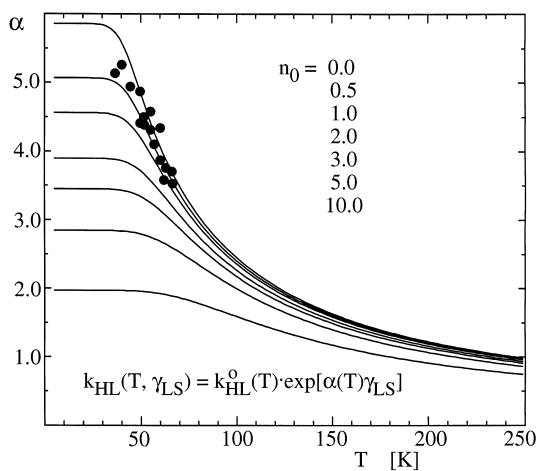


Fig. 24 The acceleration factor α as a function of temperature, (*continuous line*) calculated for $\Gamma=170 \text{ cm}^{-1}$ and for various values of the initial reduced energy gap n_0 at $\gamma_{LS}=0$, and (*large dots*) experimental values for $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ (adapted from [7b])

low-temperature value depending on n_0 , are shown in Fig. 24. The classical expression for the acceleration factor in the thermally activated region for small values of n_0 is given by [7, 41]

$$\alpha(T) = \frac{\Gamma}{k_B T} \quad (28)$$

In the thermally activated region, the self-acceleration can be expressed classically by an effective activation energy which depends on the low-spin fraction according to [7, 41]

$$E^a(\gamma_{LS}) = E^a(\gamma_{LS} = 0) - \Gamma \gamma_{LS}$$

In Fig. 24, experimental values α for $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ are included. Although the experimental data are still rather close to the low-temperature tunnelling region, it verifies Eq. (28) with a value of $\Gamma=165 \text{ cm}^{-1}$ [7a]. This value is in perfect agreement with the value of 170 cm^{-1} as derived for this compound from the thermal spin transition in the crystallographic high-temperature phase.

How can the relaxation data on neat spin-crossover compounds be implemented in the plot of the low-temperature tunnelling rate constant vs $T_{1/2}$ of Fig. 14? Well, in order to be consistent, k_{HL} has to be taken at $\gamma_{HS}=0.5$, that is

$$k_{HL}(\gamma_{HS} = 0.5) = k_{HL}(\gamma_{HS} = 0) e^{\alpha/2} \quad (29)$$

Because values of α can be as large and even larger than 5, the exponential factor may accelerate the decay rate by more than one order of magnitude by the time it reaches a value of $\gamma_{\text{HS}}=0.5$. Accordingly, Fig. 15 also includes points for neat compounds, derived using Eq. (29).

4.2

Beyond the Mean-Field Approximation

Sigmoidal, self-accelerating high-spin $\rightarrow$ low-spin relaxation curves are abundant in concentrated spin-crossover systems and for many of them the mean-field approximation gives an adequate quantitative description. However, in some cases there are characteristic deviations from mean-field behaviour as for instance for $[\text{Fe}(\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$. Figure 25 shows the relaxation curve for this compound at 23.2 K following quantitative light-induced conversion to the high-spin state. The curve follows mean-field behaviour with a value of α in accordance with the value of the interaction constant $\Gamma=175\text{ cm}^{-1}$ about halfway along the relaxation. For values of $\gamma_{\text{HS}}<0.5$ the relaxation slows down considerably with respect to the prediction of mean-field theory. Such long tails are characteristic for the build-up of correlations during the relaxation process due to specific nearest neighbour interactions [15, 54]. In case of $[\text{Fe}(\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$, these interactions are thought to be

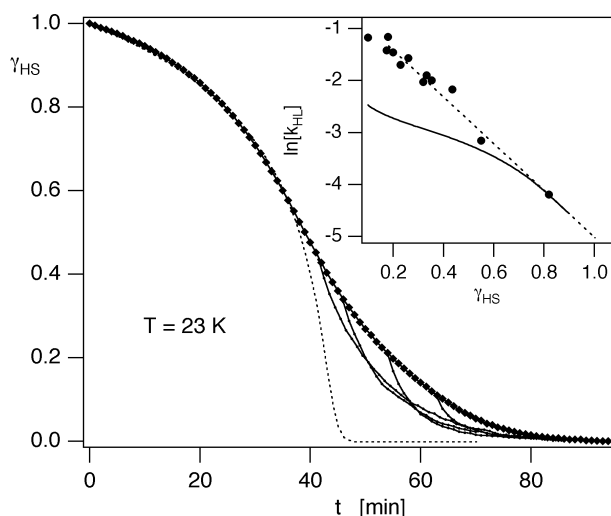


Fig. 25 The high-spin $\rightarrow$ low-spin relaxation in $[\text{Fe}(\text{pic})_3]\text{Cl}_2\cdot\text{EtOH}$ at 23 K: full relaxation curve following a quantitative light-induced conversion to the high-spin state, (*filled diamonds*) experimental, (*dashed line*) mean-field prediction, (*dots*) relaxation curves following partial conversion. *Insert:* $\ln[k_{\text{HL}}]$ (k_{HL} in min^{-1}) plotted as a function of the low-spin fraction: (*continuous line*) from the full relaxation curve, (*dashed line*) mean field prediction, (*filled circles*) from the initial rate constants following partial conversion

of an “antiferromagnetic” type [18], that is, favouring patterns of alternating high-spin and low-spin molecules. This effectively slows down the process. Much in the same way these interactions lead to the step in the thermal transition. In addition to the usually dominant long-range part of the elastic interactions, the nearest neighbour interactions can be taken into account explicitly using Monte Carlo methods [15, 54]. In the insert of Fig. 25, the relaxation rate constant as a function of γ_{HS} is shown. As expected from the relaxation curve, it does not follow the straight line of the mean-field behaviour. If, however, the initial rate constant following a partial light-induced low-spin→high-spin conversion of the crystal is plotted against the initial high-spin fraction, mean-field behaviour is recovered! This is due to the fact that the partial conversion creates a random distribution of high-spin and low-spin complexes at a given high-spin fraction, whereas at the same high-spin fraction resulting from a full light-induced conversion and subsequent relaxation, the correlations have had time to build up.

4.3

Light-Induced Bistability

For values of $\Delta E_{\text{HL}}^0 < 0$, the high-spin state is the thermodynamically stable state at all temperatures, with only at best a low-spin fraction of a few percent for values of ΔE_{HL}^0 close to zero. However, even if such is the case, in some systems the low-spin state can be populated at low temperatures by irradiation in the red, as first observed by Poganiuch et al. [55] on $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ (mtz=1-methyltetrazole). In Fig. 26 this is illustrated by the absorption spectra of the tetrazole system $[\text{Fe}(\text{etz})_6](\text{BF}_4)_2$ (etz=1-ethyltetrazole) [56]. In accordance with crystallographic data, the temperature dependent spectra indicate that the iron complexes occupy more than one crystallographically non-equivalent site with a population ratio of 2:1. As shown in Fig. 27, for site A complexes there is a fairly abrupt thermal spin transition at 105 K, whereas site B complexes stay in the high-spin state down to 10 K.

As expected, irradiation at 515.5 nm and at 20 K quantitatively converts the complexes on site A to the high-spin state, and as shown in Fig. 28, at around 70 K they return non-exponentially back to the low-spin state. Irradiation at 830 nm and 20 K, on the other hand, converts a large fraction of the complexes on site B to the low-spin state, as evidenced by the increase in the intensities of the characteristic low-spin bands in the visible. Surprisingly, as at 70 K relaxation sets in, the complexes on site B do not return to the high-spin state, rather the remaining high-spin complexes decide to join their colleagues in the low-spin state, resulting in an overall low-spin fraction of 100%! At 70 K, the lifetime of the system in this state is infinite. Only at 80 K does it return to the high-spin fraction of the thermal spin transition. How can this behaviour be understood? Obviously, with all complexes on site A in the low-spin state and all complexes on site B in the high-spin state, the

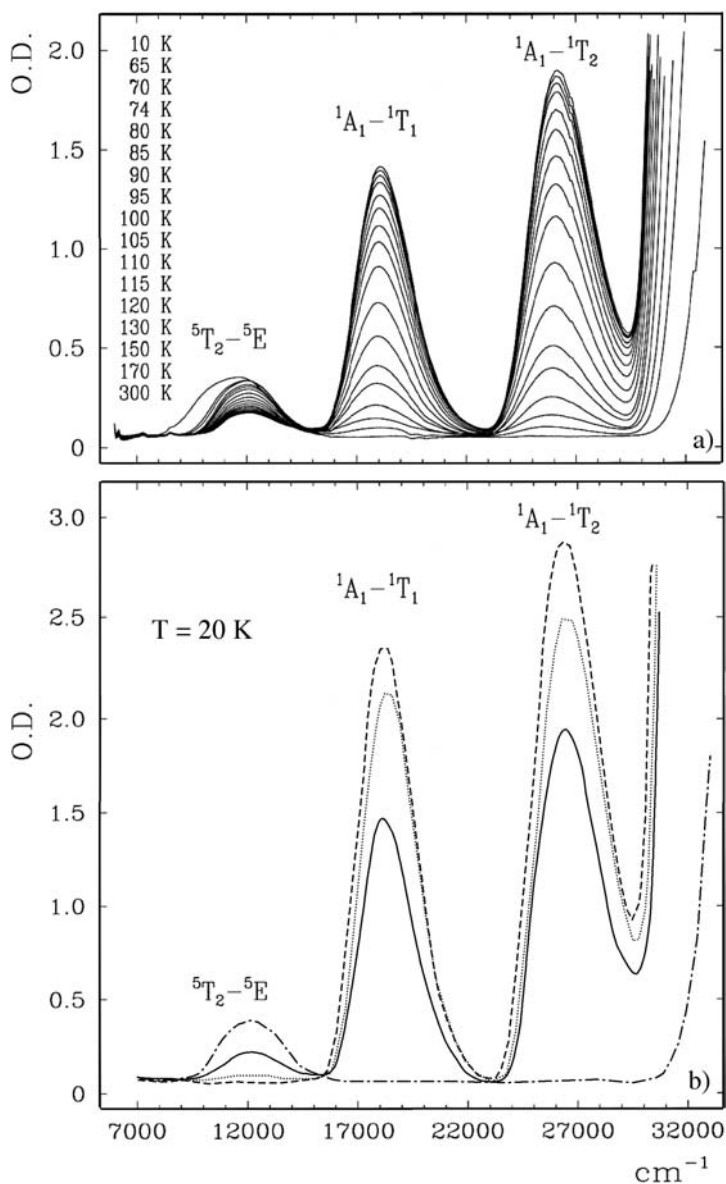


Fig. 26a,b Single crystal absorption spectra of $[\text{Fe}(\text{etz})_6](\text{BF}_4)_2$: **a** as a function of temperature; **b** at 20 K before irradiation (*continuous line*), after irradiation at 514.5 nm (*dash dot line*), after irradiation at 830 nm (*dotted line*), and subsequent relaxation at 70 °K (*dashed line*)

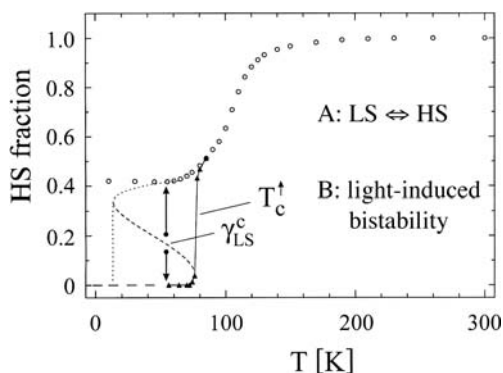


Fig. 27 Thermal spin transition curve for $[\text{Fe}(\text{etz})_6](\text{BF}_4)_2$ (open circles), and the light-induced bistability on site B (filled triangles) (adapted from [56])

high-spin state is the electronic ground state of the complexes on site B. As the overall low-spin fraction increases due to the irradiation at 830 nm, the internal pressure increases and destabilises the high-spin state sufficiently for the low-spin state to become the electronic ground state. This implies a critical overall low-spin fraction below which the system will return to the thermal transition curve, and above which it will proceed to the state with a total low-spin fraction of 100%. This is indeed the case, as is shown by the relaxation curves following partial excitation in Fig. 27. The initial comparatively fast process corresponds to the return of complexes on site A to the low-spin state, the slow process to the relaxation of site B complexes. The critical overall low-spin fraction $\gamma_{\text{LS}}^{\text{crit}} \approx 0.7$. This is a true light-induced bistability, that is, in whichever overall state the system is prepared, below 80 K it will remain in this state for ever without any further irradiation, because there is a macroscopic energy barrier between the two states of the system.

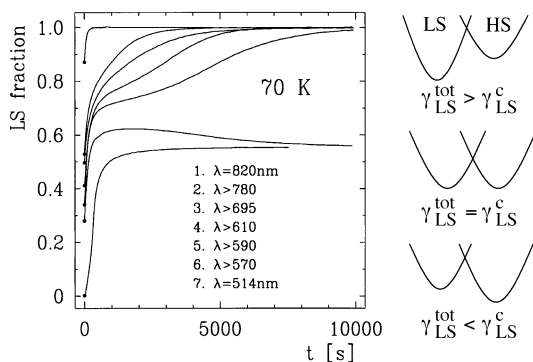


Fig. 28 Relaxation curves for $[\text{Fe}(\text{etz})_6](\text{BF}_4)_2$ at 70 K with different initial low-spin fractions and potential wells of site B as a function of the total low-spin fraction

5 Concluding Remarks and Outlook

LIESST is a general phenomenon of iron(II) spin crossover systems, and it has the basic properties required for an all-optical data storage and processing device. However, for all systems discussed above, the rapid increase of the high-spin→low-spin relaxation rate constant above approximately 50 K prohibits its potential applications in such devices. A straightforward strategy to achieve substantially higher temperatures would be to search for compounds with a still larger value of the bond length difference between the two states. Unfortunately, chemistry sets a limit to this strategy. Wu et al. [57] report that with phosphine ligands bond length differences may be as high as 0.27 Å. As a consequence, the low-temperature tunnelling rate constant is estimated to be one order of magnitude smaller than for the complexes with nitrogen donors, and the temperature at which rapid relaxation sets in shifts to approximately 80 K. Another strategy could be based on the light-induced bistability described in the previous section, which shows that irradiation inside the hysteresis of a thermal spin transition may result in a switching between two macroscopic states of the crystal, each having infinite lifetime. To date, corresponding experiments on systems with a thermal hysteresis at elevated temperatures have not yet been fully successful. Indeed, at higher temperatures, the intrinsic relaxation rates are high, and the threshold value for the passage from one branch of the thermal hysteresis to the other would have to be achieved with one strong laser pulse. A more promising strategy is to make use of a secondary photochemical process triggered by the light-induced population of the high-spin state. Thus, the rate determining step in the high-spin→low-spin relaxation of a system with a potentially octadentate ligand is not the intersystem crossing process as such but an intramolecular ligand exchange [58], which is two orders of magnitude slower. By the same token, Renz et al. [59] obtained a long lived metastable high-spin state for the low-spin system $[\text{Fe}(\text{terpy})_2]^{2+}$ doped into an inert manganese host. Boillot et al. [60] successfully photoisomerised a stylobene type ligand in such a way that the ligand-field strength changed sufficiently to actually result in a spin state change on the metal ion. As this photoisomerisation is reversible, and as the lifetime of the ligand in either the *cis* or the *trans* state is long even at room temperature, this presents a truly bistable spin system at a molecular scale.

What about other systems exhibiting LIESST or LIESST like effects such as NIESST. In principle, for spin crossover systems of other d^n ions, the intersystem crossing processes are too fast even at low temperatures to allow for a metastable state with lifetimes of seconds to hours. Nevertheless, Hayami et al. [61] achieved a light-induced long-lived metastable state in an iron(III) spin-crossover compound exhibiting strong cooperative interactions.

I am aware of the fact that this chapter reviews basically the work on the photophysical properties of spin-crossover compounds I've been involved in personally over the past 15 years. Nevertheless, I do think it presents the cornerstones of the developments in this research field, and that it may serve as the basis for the discussion of the more special aspects on the subject covered in other contributions of this series, such as LIESST in the binuclear compounds with a competition between spin crossover and superexchange [62] or the polymeric systems with very strong cooperative interactions [63], and the light-induced hysteresis behaviour referred to above [32].

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References

1. a) Martin RL, White AH (1968) In: Carlin RL (ed) *Transition metal chemistry*, vol. 4. Marcel Dekker, p. 113; b) Goodwin HA (1976) *Coord Chem Rev* 18:293; c) Gütlich P (1981) *Struct Bond* 44:83; d) König E (1987) *Progr Inorg Chem* 35:527
2. a) Beattie JK (1988) *Adv Inorg Chem* 32:1; b) Bacci M (1988) *Coord Chem Rev* 86:245; c) König E (1991) *Struct Bond* 76:51; d) Toftlund H (1989) *Coord Chem Rev* 97:67
3. a) Lawthers I, McGarvey JJ (1984) *J Am Chem Soc* 106:4280; b) McGarvey JJ, Lawthers I (1982) *J Chem Soc Chem Comm* 1982:906
4. a) Decurtins S, Gütlich P, Köhler CP, Spiering H, Hauser A (1984) *Chem Phys Lett* 13:1; b) Decurtins S, Gütlich P, Hasselbach KM, Spiering H, Hauser A (1985) *Inorg Chem* 24:2174
5. a) Hauser A (1986) *Chem Phys Lett* 124:543; b) Hauser A (1991) *J Chem Phys* 94:2741
6. a) Hauser A, Vef A, Adler A (1991) *J Chem Phys* 95:8710; b) Hauser A (1991) *Coord Chem Rev* 111:275
7. a) Hauser A, Gütlich P, Spiering H (1986) *Inorg Chem* 25:4245; b) Hauser A, Jeftic J, Romstedt H, Hinek R, Spiering H (1999) *Coord Chem Rev* 190/192:471
8. Hauser A. This series (ligand field theoretical considerations)
9. a) Lever ABP, Dodsworth E (1999) In: Solomon EI, Lever ABP (eds) *Inorganic electronic structure and spectroscopy*, vol II. Wiley, New York, p 227; b) Endicott JF (2001) In: Balzani V (ed) *Electron transfer in chemistry*, vol 1. Wiley, New York, p 238
10. Sugano S, Tanabe Y, Kamimura H (1970) *Pure and applied physics*, vol 33. Academic Press, New York
11. a) Franke PL, Haasnot JG, Zuur AP (1982) *Inorg Chim Acta* 59:5; b) Müller EW, Ensling J, Spiering H, Gütlich P (1983) *Inorg Chem* 22:2074
12. Gütlich P, Hauser A, Spiering A (1994) *Angew Chem Int Ed Engl* 33:2024
13. a) Wiehl L (1993) *Acta Cryst B* 49:289; b) Kusz J, Spiering H, Gütlich P (2000) *J Appl Crystallography* 33:201

14. Jeftic J, Hauser A (1997) *J Phys Chem B* 101:10,262
15. Romstedt H, Hauser A, Spiering H (1998) *J Phys Chem Solids* 59:265
16. Vef A, Manthe U, Gütlich P, Hauser A (1994) *J Chem Phys* 101:9326
17. a) Köppen H, Müller EW, Köhler CP, Spiering H, Meissner E, Gütlich P (1982) *Chem Phys Lett* 91:348; b) Jakobi R, Spiering H, Gütlich P (1992) *J Phys Chem Solids* 53:267
18. a) Kohlhaas T, Spiering H, Gütlich P (1997) *Z Phys B* 102:455; b) Spiering H, Kohlhaas T, Romstedt H, Hauser A, Bruns-Yilmaz C, Kusz J, Gütlich P (1999) *Coord Chem Rev* 190/192:629
19. Haasnot JG. This series (tetrazole chemistry)
20. Long G. This series (pyrazoylborates)
21. a) McCusker JK, Walda KN, Dunn RC, Simon JD, Magde D, Hendrickson DN (1992) *J Am Chem Soc* 114:6919; b) McCusker JK, Walda JN, Dunn RC, Simon JD, Magde D, Hendrickson DN (1993) *J Am Chem Soc* 115:298
22. a) Decurtins S, Gütlich P, Köhler CP, Spiering H (1985) *J Chem Soc Chem Comm* 1985:430; b) Moliner N, Gaspar AB, Munoz MC, Niel V, Cano J, Real JA (2001) *Inorg Chem* 40:3986; c) Capes L, Letard JF, Kahn O (2000) *Chem Eur J* 6:2246; d) Hayami S, Gu Z, Einaga Y, Kobayashi Y, Ishikawa Y, Yamada Y, Fujishima A, Sato O (2001) *Inorg Chem* 40:3240; d) Herber RH (1987) *Inorg Chem* 26:173; e) Figg DC, Herber RH, Potenza JA (1992) *Inorg Chem* 31:2111; f) Moliner N, Salmon L, Capes L, Munoz MC, Letard JF, Bousseksou A, Tuchagues JP, McGarvey JJ, Dennis AC, Castro M, Burriel R, Real JA (2002) *J Phys Chem B* 106:4276; and many more
23. a) Buchen T, Poganiuch P, Gütlich P (1994) *J Chem Soc Dalton* 1994:2285; b) Enachescu C, Constant-Machado H, Codjovi E, Linares J, Boukheddaden K, Varret F (2001) *J Phys Chem Solids* 62:1409
24. Letard JF, Nguyen O, Soyer H, Mingotaud C, Delhaes P, Kahn O (1999) *Inorg Chem* 38:3020
25. a) Baldenius KU, Campen AK, Hönk HD, Rest AJ (1987) *J Mol Struct* 157:295; b) Hauser A, Adler J, Gütlich P (1988) *Chem Phys Lett* 152:468
26. a) Hauser A (1990) *Chem Phys Lett* 173:507; b) Schenker S, Hauser A, Wang W, Chan IY (1998) *Chem Phys Lett* 297:281
27. Deisenroth S, Hauser A, Spiering H, Gütlich P (1994) *Hyperfine Int* 93:1573
28. Bergkamp MA, Brunschwig BS, Gütlich P, Netzel TL, Sutin N (1981) *Chem Phys Lett* 81:147
29. a) Ensling J, Fitzsimmons BW, Gütlich P (1970) *Angew Chem* 9:637; b) Grimm R, Gütlich P, Kankeleit E, Link R (1977) *J Chem Phys* 67:5491
30. Enachescu C, Oetliker U, Hauser A (2002) *J Phys Chem B* 106:9540
31. Birks J (1970) *Photophysics of aromatic molecules*. Wiley, New York
32. a) Desaix A, Roubeau O, Jeftic J, Haasnoot JG, Boukheddaden K, Codjovi E, Linares J, Nogues M, Varret F (1998) *Eur Phys J B* 6:183; b) Letard JF, Guionneau P, Rabardel L, Howard JAK, Goeta AE, Chasseau D, Kahn O (1998) *Inorg Chem* 37:4432; c) Varret F. This series (optical bistability)
33. Buhks E, Navon G, Bixon M, Jortner J (1980) *J Am Chem Soc* 102:2918
34. a) Xie CL, Hendrickson DN (1987) *J Am Chem Soc* 109:6981; b) Conti A, Xie CL, Hendrickson DN (1989) *J Am Chem Soc* 111:1171
35. a) Hoselton MA, Wilson LJ, Drago RS (1975) *J Am Chem Soc* 97:1722; b) Katz BA, Strouse CE (1979) *J Am Chem Soc* 101:6214; c) Mikami M, Konno M, Saito Y (1982) *Acta Cryst B* 38:452; d) Binstead RA, Beattie JK (1986) *Inorg Chem* 25:1481; e) Konno M, Mikami-Kido M (1991) *Bull Chem Soc Japan* 64:339; f) Wiehl L, Kiel G, Köhler CP, Spiering H, Gütlich P (1986) *Inorg Chem* 25:1565; g) Letard JF, Guionneau P, Rabardel L, Howard JAK, Goeta AE, Chasseau D, Kahn O (1998) *Inorg Chem* 37:4432; h) van

- Koningsbruggen PJ, Garcia Y, Kahn O, Fournes L, Kooijman H, Spek AL, Haasnoot JG, Moscovici J, Provost K, Michalowicz A, Renz F, Gülich P (2000) *Inorg Chem* 39:1891
36. Donnelly CJ, Imbusch GF (1991) In: DiBartolo B (ed) NATO ASI B 245. Plenum Press, New York, p 175
37. a) Brunold TC, Güdel HU (1999) In: Solomon EI, Lever ABP (eds) *Inorganic electronic structure and spectroscopy*, vol I, Wiley, New York, p 259; b) Struck CW, Fonger WH (1991) *Understanding luminescence spectra and efficiencies using Wp and related functions*. Springer, Berlin Heidelberg New York
38. a) Suppan P (1992) *Top Curr Chem* 163:95; b) Barbara PF, Meyer TJ, Ratner MA (1996) *J Phys Chem* 100:13,148
39. Hauser A (1995) *Comments Inorg Chem* 17:17
40. a) Takemoto JH, Hutchinson B (1973) *Inorg Chem* 12:705; b) Paulsen H, Duelund L, Winkler H, Toftlund H, Trautwein AX (2001) *Inorg Chem* 40:2201
41. a) Adler P, Spiering H, Gülich P (1987) *Inorg Chem* 26:3840; b) Adler P, Hauser A, Vef A, Spiering H, Gülich P (1989) *Hyperfine Int* 47:343
42. Ferguson J, Herren F (1983) *Chem Phys* 76:45
43. a) Adams DM, Long GJ, Williams AD (1982) *Inorg Chem* 21:1049; b) Meissner E, Köppen H, Spiering H, Gülich P (1983) *Chem Phys Lett* 95:163; c) Pebler J (1983) *Inorg Chem* 22:4125; d) König E, Ritter G, Kulshreshtha SK, Waigel J, Goodwin HA (1984) *Inorg Chem* 23:1896; e) König E, Ritter G, Waigel J, Goodwin HA (1985) *J Chem Phys* 83:3055; f) Usha S, Srinivasan R, Rao CN (1985) *Chem Phys* 100:447; g) Long GJ, Hutchinson B (1987) *Inorg Chem* 26:608; h) McCusker JK, Zvagulis M, Drickamer HG, Hendrickson DN (1989) *Inorg Chem* 28:1380; i) Granier T, Gallois B, Gauthier J, Real JA, Zarembowitch J (1993) *Inorg Chem* 32:5305; j) König E, Ritter G, Grünstredel H, Dengler J, Nelson J (1994) *Inorg Chem* 33:837; k) Roux C, Zarembowitch J, Itie JP, Polian A, Verdaguer M (1996) *Inorg Chem* 35:574; l) Boillot ML, Zarembowitch J, Itie JP, Polian A, Bourdet E, Haasnoot JG (2002) *New J Chem* 26:313; m) Levchenko GG, Ksenofontov V, Stupakov AV, Spiering H, Garcia Y, Gülich P (2002) *Chem Phys* 277:125
44. a) Slichter CP, Drickamer HG (1972) *J Chem Phys* 56:2142; b) Drickamer HG, CW Frank (1973) *Electronic transitions and the high pressure chemistry and physics of solids*. Wiley, New York; c) Grey JK, Butler IS (2001) *Coord Chem Rev* 219:713
45. Jestic J, Hauser A (1996) *Chem Phys Lett* 248:458
46. Schenker S, Hauser A, Wang W, Chan IY (1998) *J Chem Phys* 109:9870
47. Hauser A, Amstutz N, Delahaye S, Schenker S, Sadki A, Sieber R, Zerara M (2003), *Structure and bonding*. To be published
48. Gülich P (1984) In: Matsuura T (ed) *Hot atom chemistry*. Kodansha Ltd, Tokyo, p 265
49. a) Maeda Y, Takashima Y (1988) *Comments Inorg Chem* 7:41; b) Milne AM, Maslen EN (1988) *Acta Cryst B* 44:254; c) Oshio H, Toriumi K, Maeda Y, Takashima Y (1991) *Inorg Chem* 30:4252
50. a) Figgis BN, Kucharski ES, White AH (1983) *Aust J Chem* 36:1537; b) Thuery P, Zarembowitch J, Michalowicz J, Kahn O (1987) *Inorg Chem* 26:851; c) Sieber R, Decurtins S, Stoeckli-Evans H, Wilson C, Yufit D, Howard JAK, Capelli SC, Hauser A (2000) *Chem Eur J* 6:361
51. Schenker S, Hauser A, Dyson RM (1996) *Inorg Chem* 35:4676
52. Zerara M (2003) PhD thesis, Geneva
53. Hauser A (1992) *Chem Phys Lett* 192:65

54. a) Enachescu C, Linares J, Varret F (2001) *J Phys Condens Matter* 13:2481; b) Boukheddaden K, Shteto I, Hoo B, Varret F (2000) *Phys Rev B* 62:14,796 and 14,806
55. Poganiuch P, Decurtins S, Gütlich P (1990) *J Am Chem Soc* 112:3270
56. a) Hinek R, Spiering H, Gütlich P, Hauser A (1996) *Chem Eur J* 2:1435; b) Hinek R, Spiering H, Schollmeyer D, Gütlich P, Hauser A (1996) *Chem Eur J* 2:1427
57. Wu CC, Jung J, Ganzel PK, Gütlich P, Hendrickson DN (1997) *Inorg Chem* 36:5339
58. Schenker S, Stein PC, Wolny JA, Brady C, McGarvey JJ, Toftlund H, Hauser A (2001) *Inorg Chem* 40:134
59. Renz F, Oshio H, Ksenofontov V, Waldeck W, Spiering H, Gütlich P. (2000) *Angew Chem Int Ed* 39:3699
60. a) Boillot ML, Sour A, Delhaes P, Mingotaud C, Soyer H (1999) *Coord Chem Rev* 190/192:47; b) Sour A, Boillot ML, Riviere E, Lesot P (1999) *Eur J Inorg Chem* 12:2117
61. Hayami S, Gu Z, Shiro M, Einaga Y, Fujishima A, Sato O (2000) *J Am Chem Soc* 122:7126
62. Letard JF, Real JA, Moliner N, Gaspar AB, Capes L, Cador O, Kahn O (1999) *J Am Chem Soc* 121:10,630
63. Niel V, Munoz MC, Gaspar AB, Galet A, Levchenko G, Real JA (2002) *Chem Eur J* 8:2446

On the Competition Between Relaxation and Photoexcitations in Spin Crossover Solids under Continuous Irradiation

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Abstract We report recent work on the competition between opposite kinetic processes: (i) photo-excitation (LIESST) and relaxation processes, and (ii) direct and reverse LIESST. The light-induced instability eventually occurring at the light-induced equilibrium temperature is attributed to a cooperative origin. The subsequent light-induced thermal hysteresis (LITH) and intensity threshold effect (LIOH) are adequately described through a mean-field macroscopic master equation assuming a linear photo-excitation term and a self-accelerated term for cooperative relaxation. Further analysis provides

evidence for non-linear character of the photo-excitation terms, capable of inducing bistability in the light-driven quasi-static regime when the direct and reverse LIESST regimes compete. The behaviour of correlations under permanent irradiation is also considered, both experimentally and theoretically, through a kinetic Ising-model including a photo-excitation term and accounting for both long- and short-range interactions. Paradoxical effects of light are reported, with various experimental features and theoretical model providing a qualitative explanation.

A novel instability effect is introduced, due to the non-linear competition between direct and reverse LIESST, for which the expected hysteresis with respect to wavelength is denoted Light Induced Spectral Hysteresis (LISH).

Keywords Light-induced instability · Cooperative relaxation · Photo-excitation · Dynamic Ising-like model · Correlations

List of Abbreviations and Symbols

SCO	Spin crossover
btr	4,4'-Bis(1,2,4-triazole)
LIESST	Light-induced excited spin state trapping
LIMH	Light-induced magnetic hysteresis
LIOH	Light-induced optical hysteresis
LIPH	Light-induced pressure hysteresis
LISH	Light-induced spectral hysteresis
LITH	Light-induced thermal hysteresis
LPTH	Light-perturbed thermal hysteresis
$T_{1/2}$	Spin transition temperature
$T_{1/2}^*$	Light-driven equilibrium temperature
α	Self-acceleration factor of the relaxation rate (Hauser factor)

1 Introduction

Recent interest was devoted to the competition between photo-excitation (LIESST) and relaxation of the metastable state in spin crossover (SCO) solids, due to the observation of a light-induced instability [1, 2] obviously associated with the non-linear character of cooperative relaxation [2]. Various hysteresis phenomena are associated with light-induced instability, denoted light induced thermal, optical, pressure hysteresis, (LITH [1], LIOH [2], LIPH [3, 4]) according to the external parameter which is swept during the experiment.

Rather good agreement was readily found with a simple macroscopic mean-field model [5], merely combining a previous analytical expression of the “cooperative” self-accelerated relaxation, due to Hauser [6–9] and a linear photo-excitation term, assuming the LIESST effect [6, 10–15] to be a molecular process with constant yield. The molecular character of the photo-process was inferred on the basis of similar qualitative features of photo-induced effects in solution [16] and in the solid state. The expected correla-

tion between interaction parameters deduced from the thermal hysteresis loop (J) and the self-acceleration parameter responsible for the LITH was indeed found in the diluted series $[\text{Fe}_x\text{Co}_{1-x}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ [17]. The main results concerning the light-induced instability due to self-accelerated relaxation will be reviewed here.

However, further experimental work [18–20] has led to questions concerning the linear character of the photo-excitation terms and will be examined here. Quite recently, a light-induced instability associated with the competition between direct and reverse LIESST was demonstrated [21].

Our recent theoretical work beyond the mean-field approximation [4, 22–26] has made it possible to investigate the behaviour of correlations due to short-range interactions, under permanent irradiation. The dynamic model will be briefly presented in Appendix. As previously suggested by A. Hauser, the onset of correlations is observed to be severely hindered by the effect of photo-excitation (a random process). The present calculations show that the photo-effect should even be able to speed up relaxation in some cases. We investigate here this paradoxical effect.

For practical applications, the search for photo-switching at higher temperatures, near the spontaneous thermal hysteresis loop, is presently very active, and obviously implies the competition between photo-excitation and very rapid relaxation. Under irradiation with a continuous laser beam, a sizable shift of the SCO thermal loop was reported, and denoted “light-perturbed thermal hysteresis” [27]. However, according to the available kinetic models [4, 22–26] the effect should be small with usual sources of light, and the actual mechanism for the LPTH effect remains to be found. Recent experiments on photo-switching in the SCO hysteresis loop [28] (or in the similar thermal hysteresis loop of photo-magnetic Prussian blue analogue [29]) using a pulsed laser, have demonstrated quantitative optical switching. For the latter case, the light-induced phase transition results from a nucleation and growth process, for which theoretical approach requires treatment beyond the mean-field approximation, and should be investigated in the near future.

2

Mean-field Master Equation, Light-driven Equilibrium and Instability

The competition between relaxation and photo-excitation induces transient states and light-driven equilibrium. In the simple case of a non-interacting single-molecule process, the Master Equation governing the evolution of the system under light may be written

$$d\gamma_{\text{HS}}/dt = I_0\sigma\gamma_{\text{LS}}(t) - k_{\text{HL}}(T)\gamma_{\text{HS}}(t) + k_{\text{LH}}(T)\gamma_{\text{LS}}(t), \quad (1)$$

where $I_0\sigma$ is the photo-excitation term accounting for light intensity and absorption cross section, and k_{HL} , k_{LH} are the spontaneous transition rates of the system. Since most experiments reported here correspond to a low temperature situation, such that the equilibrium probabilities $w_{HS} \ll w_{LS}$, then $k_{HS} \gg k_{LS}$ (detailed balance condition), and the spontaneous up-going term is usually dropped. For independent SCO units, the high-spin fraction $\gamma_{HS} = 1 - \gamma_{LS}$ can be considered as the probability, for any SCO unit, at time t , of being in the HS state, and thus gives Eq. 1 a microscopic meaning.

In the case of interacting SCO units, a set of coupled microscopic equations similar to Eq. 1 have to be considered. The photo-excitation and relaxation rates are functions of the state of the system. Approximations are needed to solve the problem: in the mean-field approximation, the state of the system is represented by the single variable γ_{HS} , so that the general form of the **mean-field macroscopic master equation** is

$$d\gamma_{HS}/dt = I_0\sigma(\gamma_{HS})\gamma_{LS}(t) - k_{HL}(T, \gamma_{HS})\gamma_{HS}(t) + k_{LH}(T, \gamma_{HS})\gamma_{LS}(t), \quad (2)$$

and, of course, more sophisticated descriptions of the “state of the system”, e.g. accounting for the average value of the first-neighbour correlation [22–24], will lead to sets of coupled differential equations, as shown in the theoretical section (Appendix).

A useful concept is the light-driven equilibrium temperature [4], $T_{1/2}^*$ such that $\gamma_{HS} = \gamma_{LS} = 1/2$ in the steady state. $T_{1/2}^*$ provides an easy comparison of the spontaneous and light-driven equilibrium. Just neglecting the spontaneous up-going term, the equilibrium steady state of non-interacting SCO units is given by

$$I_0\sigma = k_{HL}(T_{1/2}^*), \quad (3)$$

leading to, in the thermal activation regime

$$T_{1/2}^* = [E_A(\gamma_{HS} = 1/2)/k_B] / \ln(k_{HL}^\infty / I_0\sigma), \quad (4)$$

where E_A is the barrier energy and $I_0\sigma/k_{HL}^\infty$ is the frequency factor ($\sim$ metal-ligand stretching vibrations $\sim 10^{13} \text{ s}^{-1}$).

Most experiments under continuous irradiation tend to determine the quasi-static properties (*steady*, or *photo-stationary states*), i.e. the properties obtained at a vanishing sweep rate of the external parameter (temperature, intensity of light, pressure, magnetic field etc.). Kinetic aspects appear at non-zero sweep rate, as shown later. In the case of non-interacting SCO units, the quasi-static values obey the following equation (from Eq. 1):

$$\gamma_{HS}/\gamma_{LS} = I_0\sigma/k_{HL}(T), \quad (5)$$

obviously leading to an explicit expression of γ_{HS} .

The case of interacting SCO units has been carefully considered from the viewpoints of both photo-excitation and relaxation processes. Photo-excita-

tion at low temperature (the LIESST effect) is a molecular process with a quantum yield close to unity [20], which in a first approximation can be taken as a constant, contrary to the case of the relaxation process, which may exhibit a spectacular self-acceleration, due to the progressive lowering of the barrier energy associated with the depopulation of the HS state [7–9, 30]. Such a cooperative relaxation was observed both at moderate temperature (thermally activated tunnelling regime) and in the low-temperature tunnelling regime. At any temperature, it is conveniently represented by the so-called Hauser factor, as follows:

$$k_{\text{HL}}(T, \gamma_{\text{HS}}) = k_{\text{HL}}(T, 0) \exp(-\alpha \gamma_{\text{HS}}), \quad (6)$$

which becomes, for the thermal activation regime

$$k_{\text{HL}}(T, \gamma_{\text{HS}}) = k_{\text{HL}}^{\infty} \exp(-E_A/k_B T) \exp(-\alpha \gamma_{\text{HS}}), \quad (7)$$

where $\alpha(T)$ is expected to be proportional to the interaction parameter and also to the inverse temperature in the thermal activation regime. Microscopic models which clear up the assumptions of this macroscopic model can be found in [23]. The case of interacting molecules seems to require a self-consistent resolution of Eq. 5. However, as previously remarked in [23] for the spontaneous equilibrium, the explicit resolution of T as a function of γ_{HS} is possible, in the thermal activation regime (*where αT is a constant*), through

$$(E_A + \alpha k_B T \gamma_{\text{HS}})/k_B T = \ln(\gamma_{\text{HS}}/\gamma_{\text{LS}}) - \ln(I_0 \sigma/k_{\text{HL}}^{\infty}) \quad (8)$$

The effect of the self-acceleration parameter α mainly affects the vicinity of light-driven equilibrium temperature, so as to induce a light-driven instability above $\alpha=4$, the threshold value established from previous work [2, 5]. We show in Fig. 1 a set of curves computed according to Eq. 8.

The light-driven thermal hysteresis loop, previously denoted LITH by Olivier Kahn [1], is the archetype of all hysteresis effects which occur in the vicinity of the light driven equilibrium, under the variation of any parameter which may affect the relaxation rate: intensity of light, pressure, magnetic field. Therefore Optical (LIOH), Pressure (LIPH), Magnetic (LIMH) hysteresis, all having the same origin, can be expected. The LIOH effect, already observed, can be described as a threshold effect [5] of major importance for future applications of the optical switching of SCO solids. Preliminary evidence for the LIPH effect has been presented [3], but the recording of a complete loop has not so far been possible with the available pressure apparatus. In most cases the major experimental difficulties lie in the kinetic character of the experiment, and in the bulk absorption of light in the sample, as will be seen in a further section.

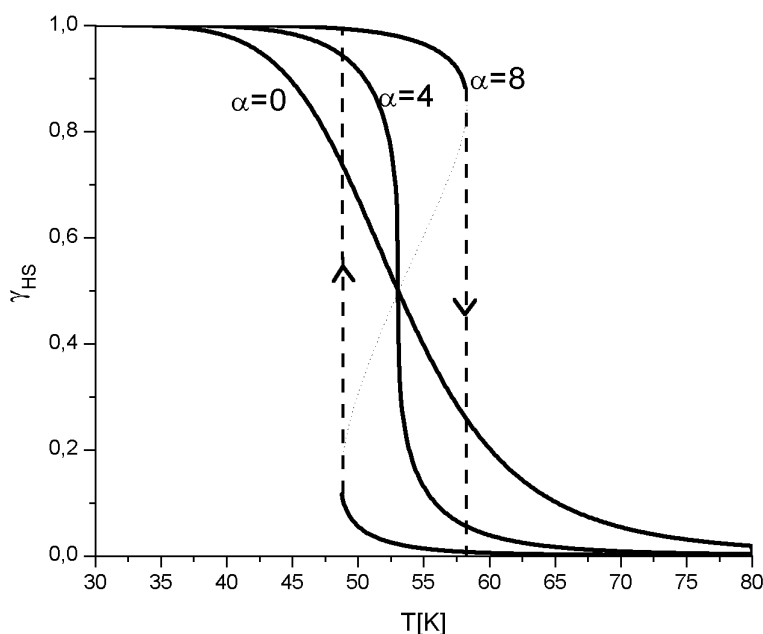


Fig. 1 Temperature dependence of the steady states under irradiation at constant intensity, computed using Eq. 8, for different values of the self-acceleration parameter at the light-induced equilibrium temperature: $\alpha(T_{\text{equil}}^*)=0$ (non-interacting SCO centres), 2, 4, 8, from centre to exterior. The thermal hysteresis loop (quasi static LITH) obtained in the latter case has been completed by arrows

3 Experimental LITH and LIOH loops

Most of the experimental results presented here concern the series of polymeric compounds $[\text{Fe}_x\text{Zn}_{1-x}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ provided by J. Haasnoot. The “pure” ($x=1$) complex exhibits a rather large thermal hysteresis ($T_{1/2}^{\text{up}}$ 150 K, $T_{1/2}^{\text{down}} \sim 120$ K), and dilution by the isomorphous Zn compound (SCO inactive) allowed us to tune the cooperativity strength, for the most convenient observation of the various light-induced hysteretic effects [31, 32]. On the other hand, several groups have made considerable efforts to obtain LITH loops free from kinetic effects on other compounds [33, 34]. A typical example is shown in Fig. 2.

The vertical lines in Fig. 2 report the data obtained at constant temperature, as a function of time, and by extrapolation to time infinity, the quasi static data are obtained (the dotted line). The square data points show the kinetic LITH loop recorded at finite temperature sweeping rate.

An alternative method for obtaining the quasi-static LITH data might consist in recording the thermal loops at various temperature sweeping

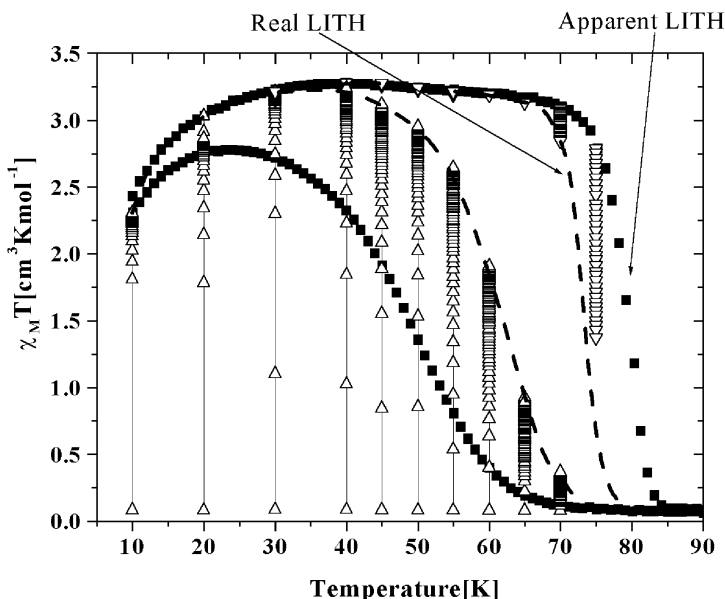


Fig. 2 Light induced thermal hysteresis (LITH), from magnetic data for $[\text{Fe}(\text{PM-BiA})_3(\text{NCS})_2]$: determination of the *quasi-static* loop: the χT product (proportional to γ_{HS}) is plotted vs temperature. The low-temperature decrease in χT is due to zero-field splitting (after [34])

rates, and then extrapolate the data at each temperature (and for each branch) to the temperature sweep rate of zero. A typical example is shown in Fig. 3.

A striking feature common to Figs. 2 and 3 is the distortion of the quasi-static loop with respect to the expected shape shown in Fig. 1. The finite slope of the edges of the loop can be attributed to the effect of bulk absorption of light in the sample, which spreads the value of the light-driven equilibrium temperature through the sample. Numerical simulations of this bulk absorption effect [35] indeed provided a distortion of the LITH loop in qualitative agreement with the experiments. The presence of bulk absorption of light in the systems under study can also be inferred from simultaneous magnetisation and reflectivity measurements [36, 37]; see Fig. 4.

The data of Fig. 4 are discussed in terms of surface and bulk probes [37, 38], the properties reported for reflectivity and magnetic techniques, respectively: (i) reflectivity and magnetic data superimpose quite well for the spontaneous thermal hysteresis; (ii) reflectivity data are basically independent of the thickness of the sample; (iii) bulk absorption of light is evidenced in the LITH loop of the thicker sample.

Reflectivity data for LITH are closer to the theoretical shape (vertical edges). Better results can be expected from thin layers of sufficient crystal-

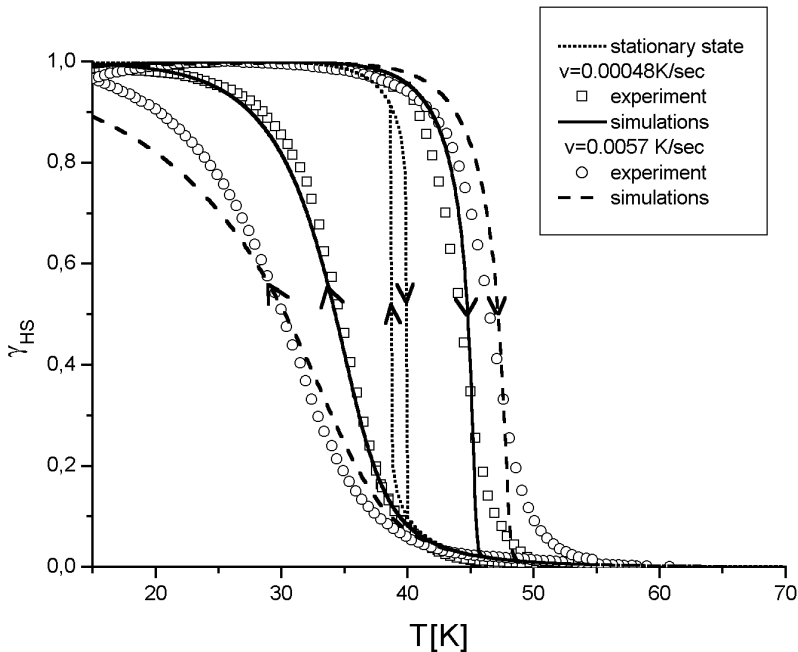


Fig. 3 LITH loops of $[\text{Fe}_{0.52}\text{Ni}_{0.48}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$, $\lambda=550$ nm, $P=6$ mW/cm², (from magnetic data). The temperature sweep rates are (from exterior to interior): 0.34 K/min, 0.03 K/min. *Full lines*=computed curves, according to the master equation Eq. (2), in the thermal activation regime. Parameter values (derived from relaxation data) are: $E_A=380$ K, $\alpha T=200$ K, $k_{\alpha}=100$ s⁻¹ (apparent values), $I_0\sigma=0.0005$ s⁻¹

line quality. It is, however, worth mentioning here that in some examples [39] reflectivity does not seem to scale properly with the high-spin fraction, according to the wavelength used. On the other hand the surface properties may differ from the bulk ones. To summarise, *the use of the reflectivity technique is well suited to follow qualitatively spin transitions, but it requires some care in interpretation.*

We have shown in Fig. 5 the spontaneous and LITH loops of a thin sample (1 mg) of a more cooperative compound, recorded in the same conditions as the less cooperative one, reported above. The degree of photo-excitation acquired during the LITH recording is much lower. This is a combined effect of bulk absorption and cooperative relaxation: the larger value of the self acceleration factor ($\alpha \sim 10$, according to Fig. 15 below), leads to a dramatic intensity threshold effect: indeed the relaxation rate varies by a factor $e^{\alpha} \sim 2 \times 10^4$ during the total variation of γ_{HS} . Consequently the initial photo-excitation rate has to be very high, and it is easily conceived that the required intensity is only present close to the top layers of the sample.

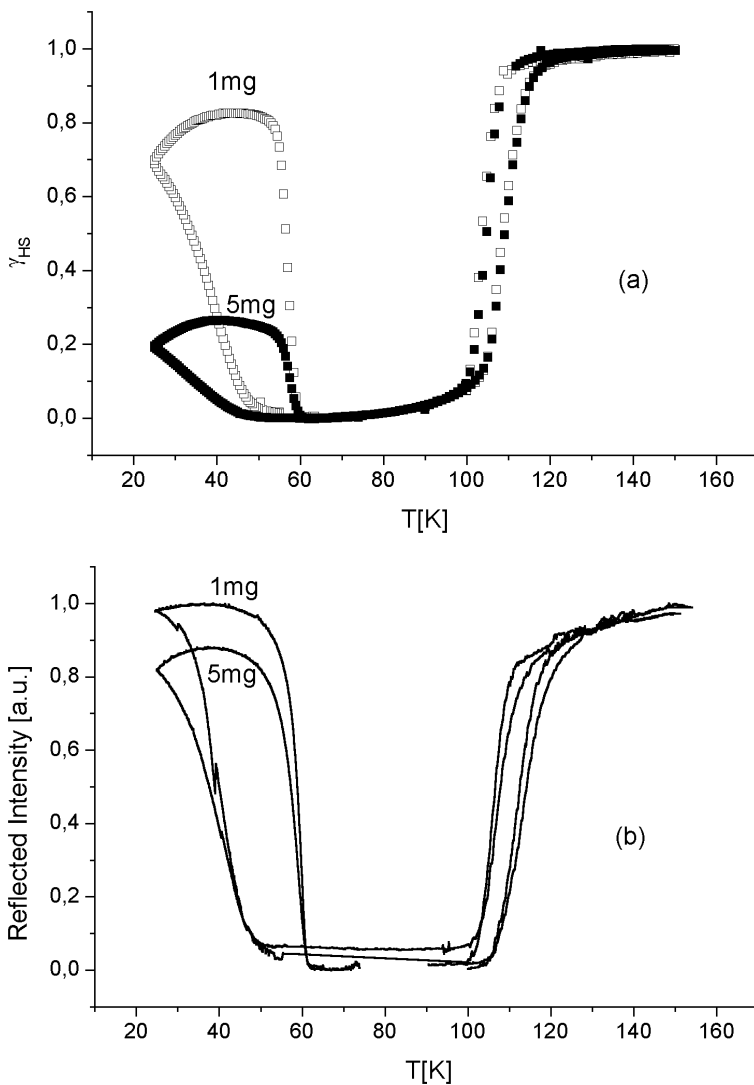


Fig. 4a,b Spontaneous and LITH loops of $[\text{Fe}_{0.5}\text{Zn}_{0.5}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$, $\lambda=550$ nm, $P=1.3$ mW/cm², from simultaneous: **a** magnetic data; **b** reflectivity data, obtained for sample masses 1 mg and 5.5 mg. The temperature sweep rates were 0.4, 0.1 K min⁻¹, for the spontaneous and LITH loops, respectively

Another consequence of the light-driven instability is the Light Induced Optical Hysteresis (LIOH), the first example of which was given in [2]. We performed a very time-consuming series of experiments, using the reflectivity device. At the spontaneous thermal hysteresis loop, experimental condi-

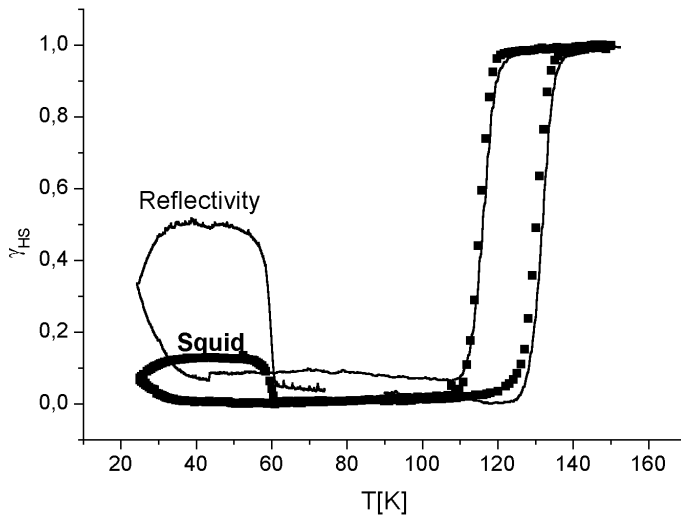


Fig. 5 Spontaneous and LITH loops of $[\text{Fe}_{0.8}\text{Zn}_{0.8}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$, $\lambda=550$ nm, $P=1.3$ mW/cm², sample mass: 1 mg from simultaneous magnetic and reflectivity data. The temperature sweep rates are the same as in Fig. 4

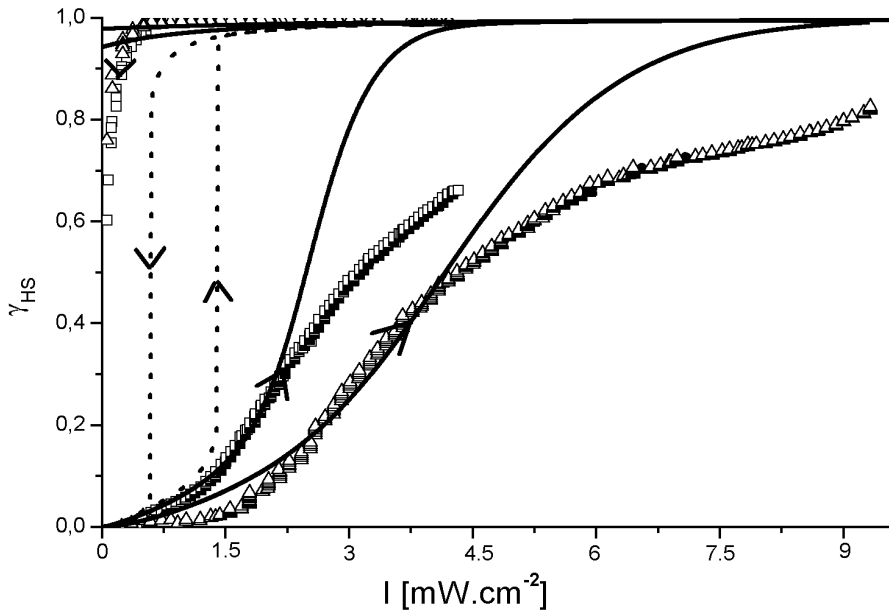


Fig. 6 The LIOH loop of $\text{Fe}_{0.52}\text{Ni}_{0.48}$ at 33 K under 550 nm irradiation at variable intensity: experimental (*symbols*), kinetic calculations (*continuous lines*) and their quasi-static limit (*dotted lines*). The intensity sweep rates were 1 and 0.02 mW/cm²/h. Parameter values, derived from relaxation curves were: $E_A=380$ K, $k_\alpha=100$ s⁻¹ (apparent values), $\alpha(33 \text{ K})=5$

tions were arranged such that the reflectivity response at the same wavelength was identical to the magnetic response. We also repeated the experiments, at different intensity sweep rates, so as to tend to the quasi-static loop. The best data obtained so far are reported in Fig. 6. The optical hysteresis here corresponds to a large intensity threshold effect. The width of the experimental LIOH loops results from the combination of 3 factors: (i) cooperative effect—however with $\alpha=5$ not much higher than the threshold instability value $\alpha=4$, the theoretical quasi-static loop is relatively narrow; (ii) bulk absorption of light, which reduces inhomogeneously the intensity value through the sample; (iii) the experimental kinetics, the effect of which is increased by the decrease in intensity. Therefore we expect better results from a sample in the shape of a thin layer, with good optical quality. However, the shape of the LIOH loop might be very sensitive also to the non-linearity of the photo-excitation term, which will be reviewed in a further section.

Such an experiment would be very difficult for the more cooperative system $[\text{Fe}_{0.8}\text{Zn}_{0.2}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ ($\alpha \sim 10$ in the 10–45 K temperature range): extremely small values of intensity, are sufficient to retain the HS-rich metastable state (see Fig. 11).

4 The Correlation Problem

As a matter of fact, we were amazed that the mean-field approach would reproduce so well (once the bulk absorption correction was included) the light-induced properties, while it was known for a long time that it often failed to reproduce well the relaxation curves of the metastable state after photo-excitation. The “relaxation tail” observed at long times for the most cooperative systems was analysed by H. Spiering as due to the onset of correlations associated with short-range interactions [40]. The presence of *negative* short range interactions was rather obvious in dinuclear compounds, and explained well the two-step shape of the spin transition curve [41, 42] (see also the contribution of Real et al.). The presence of *positive* short range interactions was later admitted, on the basis of relaxation tails, and also can explain the square shape of some (spontaneous) thermal hysteresis loops [43].

We shall address here the problem of the correlations in the light-driven properties. For clarity, we first present typical data for cooperative relaxation, recorded on the $[\text{Fe}_x\text{Zn}_{1-x}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ system ($x=0.50, 0.80$), see Fig. 7. The curve for $x=0.8$ has been re-scaled to the initial value $\gamma_{\text{HS}}=1$, considering a schematic inhomogeneous state of the sample, with a saturated top side (irradiated side), and a non-excited bottom side (due to the rapid relaxation of the non saturated state), as discussed in [38].

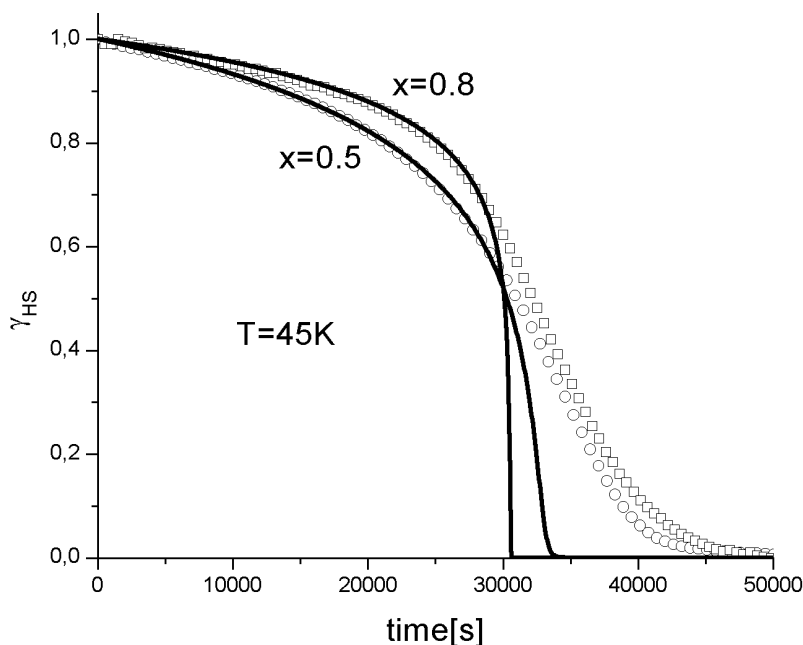


Fig. 7 Relaxation curves of $[\text{Fe}_x\text{Zn}_{1-x}(\text{btr})_2(\text{NCS})_2]\cdot\text{H}_2\text{O}$, in the dark, $T=45$ K. The *full line*=mean-field model, with fitted parameter values determined by the linear plot in the next figure

In order to best account for the tail effect, following [8], we plotted the derivative of the relaxation rate, on a logarithmic scale, as a function of the high-spin fraction. Indeed, according to Eq. 6, a linear plot is then expected:

$$\ln k_{\text{HL}}(T, \gamma_{\text{HS}}) = \ln k_{\text{HL}}(T, 0) - \alpha(T) \gamma_{\text{HS}}, \quad (9)$$

with the relaxation rate derived from Eq. 2 (in the dark):

$$k_{\text{HL}}(T, \gamma_{\text{HS}}) = -d \ln \gamma_{\text{HS}}(t) / dt \quad (10)$$

Such a treatment was applied to the present relaxation data; see Fig. 8: the self-acceleration law (straight line) is obeyed at short times, and the departure at long times (the tail effect) is easily identified. In agreement with the available models [22–25], it was generally observed that the correlation effects are enhanced at longer times and for the more cooperative samples (as shown here).

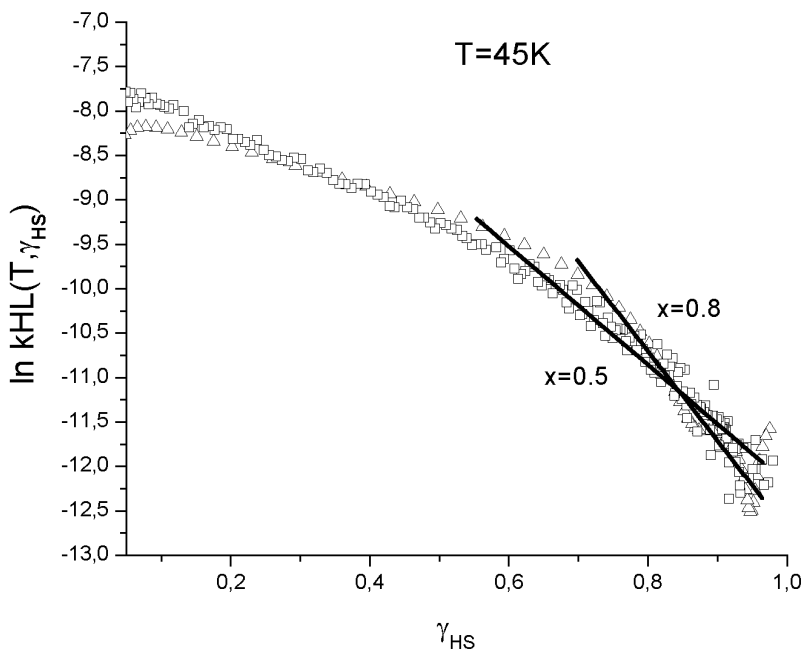


Fig. 8 Relaxation data of $[\text{Fe}_x\text{Zn}_{1-x}(\text{btr})_2(\text{NCS})_2]\cdot\text{H}_2\text{O}$ at 45 K (previous figure), plotted in a suitable scale, so as to determine the self-accelerated stage of the process. The parameter values deduced by linear regression are: $k_{HL}(\gamma_{HS}=0)=2.7\times 10^{-3}$, $3.9\times 10^{-2} \text{ s}^{-1}$, $\alpha=6.7$, 10.1 for $x=0.5$, 0.8 respectively

5 Correlations and Light

The onset of correlations was first simulated by Spiering, Hauser and co-workers [40], using the Ising-like Hamiltonian [41, 44, 45] resolved by the Montecarlo Metropolis technique. Unfortunately, so far there has not been any direct observation of these correlations. Indirect evidence for the presence of correlations was suggested in another photo-switchable solid, the photo-magnetic Prussian Blue analogue $\text{Rb}_{0.52}\text{Co}[\text{Fe}(\text{CN})_6]_{0.84}\cdot 2.3\text{H}_2\text{O}$ [46], by following the decrease of the Curie temperature during the spontaneous dilution of the photo-induced magnetic system, caused by relaxation [47, 48]: the observed Curie temperature remained high in the cooperative system (due to clustering), up to a rather high degree of dilution, while it decreased much more progressively in the non-cooperative system $\text{Cs}_{0.175}\text{Co}[\text{Fe}(\text{CN})_6]_{0.72}\cdot 4\text{H}_2\text{O}$. Further similar data in SCO solids would be extremely helpful for a quantitative analysis of the correlation problem, i.e. of the range of interactions in SCO solids. Alternative techniques might be neutron

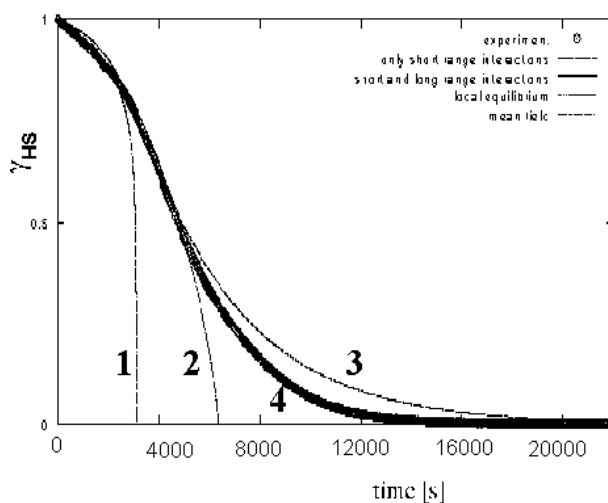


Fig. 9 The relaxation tail of $[\text{Fe}_{0.52}\text{Ni}_{0.48}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$, $T=40$ K, experimental data and computed curves: (1) mean-field, (2) local equilibrium approximation, (3) short-range interactions, (4) combined short and long range interactions=superimposed to the experimental data (after [22])

diffraction and Mössbauer nuclear forward scattering (in a synchrotron beam).

We recently proposed an analytical approach [22], based on a Bethe-type treatment of the dynamic Ising-like model, which affords an accurate fitting of the relaxation tail; see Fig. 9. Further developments [24] accounted for spatial inhomogeneities, which spontaneously appear during relaxation [5].

Such a fitting, once systematically applied to a series of compounds, will provide valuable data for understanding the origin of the short-range interaction. Preliminary results [49] on Co, Ni, Zn diluted $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ suggest the problem is quite complex, with specific roles of the diluting cations.

It was worth extending the available correlation model, to account for photo-excitation. A complete description of the model, developed by author Boukheddaden, is given in the Appendix. The principle for this extension is to give the SCO unit an additional probability (i.e. transition rate) for photo switching from the LS to the HS state. In a first approach, a constant photo-induced transition rate is written in the set of microscopic master equations; then, in the case of non interacting SCO units, this set reduces to Eq. 1.

The random character of the light-induced process tends to destroy the correlations which spontaneously build up during relaxation [50]. Therefore quantitative analyses of light-driven instability might be performed within the mean-field approximation. A predictable effect of light is to reduce the relaxation tail, i.e. to speed-up relaxation, but this *paradoxical* effect might

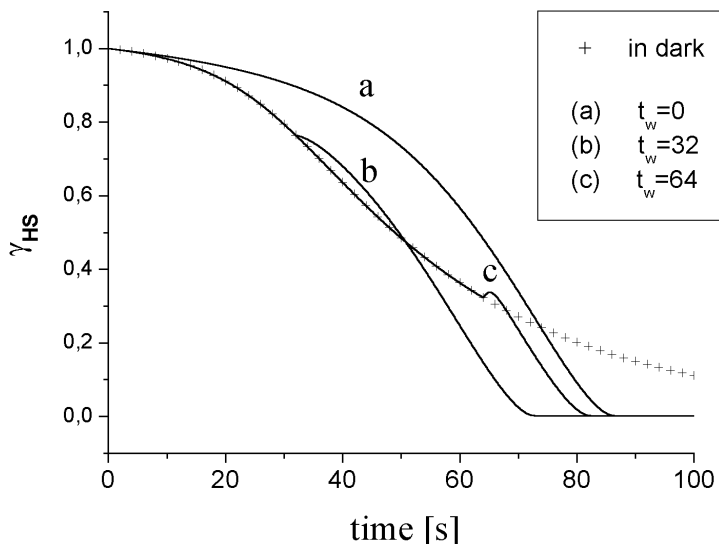


Fig. 10 Computed relaxation curves, accounting for short-range correlations, in the dark (dotted line) and under constant photo-excitation (full lines). Initial state was saturated ($\gamma_{\text{HS}}=1$). The light was introduced after variable waiting times, $t_w=0, 32, 64$ time units. Other parameter values: $J=50$ K (short-range positive interaction), $G=0$ (long-range interaction), energy gap $2\Delta=1000$ K, $g=150$ (degeneracy ratio). Time unit is $k(\gamma_{\text{HS}}=1/2)^{-1}$ at the considered temperature. Intensity value is such that $I\omega=0.05$ time unit $^{-1}$

be compensated by the photo-excitation process. We have performed numerical simulations in order to determine which was the predominant effect. As shown in Fig. 10, we have found that, for adequate parameter sets, in the final stage, i.e. in the conditions such that large spontaneous correlations would occur in the dark, the speeding up effect might clearly appear. We stress the paradoxical character of the photo-effect: *at the molecular scale light induces the LS→HS conversion, while in the solid state, under some conditions, it might speed up the HS→LS cooperative relaxation*. Further developments of this model are under consideration and will be reported elsewhere.

6

A First Experimental Search of the Paradoxical Effect of Light

We have performed a very first set of experiments in order to investigate this expected *paradoxical* effect of light. For all these experiments we have prepared the initial state by following an identical procedure: 550 nm, 10 K, 1.3 mW/cm², 9 h, then the sample was heated to 45 K, still under irradiation, and a reproducible value of the initial magnetic moment (under the same

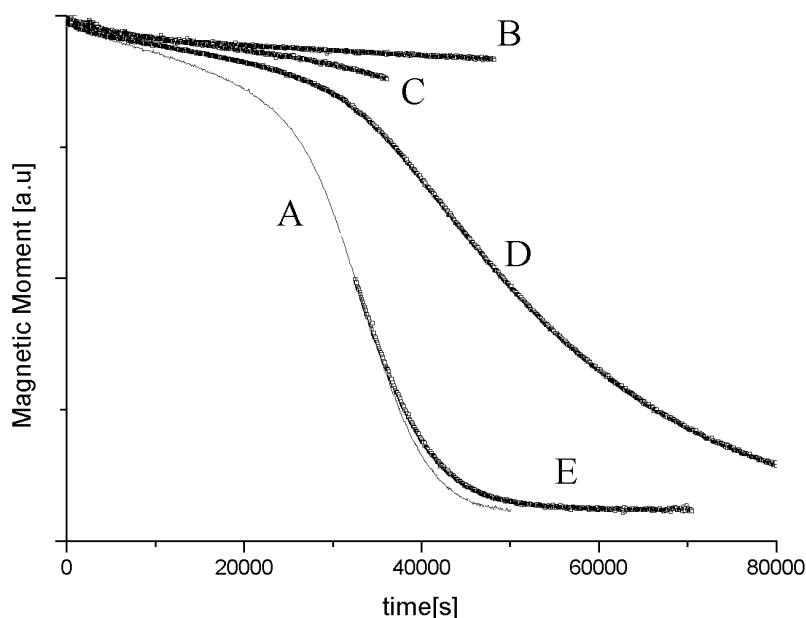


Fig. 11 Relaxation curves of $[\text{Fe}_{0.8}\text{Zn}_{0.2}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$, at 45 K: in the dark (*solid line*, A) and under weak illumination at 550 nm: 0.2, 0.05, 0.02, 0.02 mW/cm^2 , for curves B, C, D, E respectively

field 0.1 T) was obtained. Then we have observed the changes of the system, under different light intensities. We also applied light after some delay (9 h), as suggested in the theoretical approach. All these curves are reported in Fig. 11.

In agreement with the concept of a strong self acceleration effect, amazingly small intensities (with respect to those used for photo-excitation) have spectacular effects. For example, see curve D, the lowest intensity $\sim 1:60$ of the photo-excitation intensity, slows down the relaxation by a timescale factor of ~ 1.5 . However, when the same intensity of light is applied only after a sizeable relaxation in the dark, see curve E, it does not sizeably affect the end of the relaxation curve. A possible reason why the expected paradoxical effect did not occur here, might be the presence of long-range interactions in this compound. Indeed the paradoxical effect is not expected in mean-field approach.

7 Unexplained and Paradoxical Effects During Photo-excitation and Relaxation

We report here, see Fig. 12, several unexplained *paradoxical* features of relaxation exhibited by the same compound: (i) the relaxation tail at 46 K, in the dark, is shortened, and it is followed by an increase in HS population (Fig. 12, left and right); (ii) subsequent application of green light induces transiently a *paradoxical* decrease in HS population (Fig. 12, middle); (iii) in one instance, we could observe at 45 K, in the dark, after a higher intensity low-temperature photo-excitation, a *paradoxical* initial increase of the γ_{HS} fraction, lasting ~ 6 h, before the expected decay took place. We did not succeed in reproducing such an effect.

Extensive work is of course planned in order to try to attain quantitative agreement between such experiments and the present kinetic theory. Of course, the real solid state effects occurring in solid phase transitions, such as domain structure, internal stresses, nucleation processes may be of some importance and should be introduced. The effect of internal stresses might be related to irreversible pressure effects observed in the (pure) system

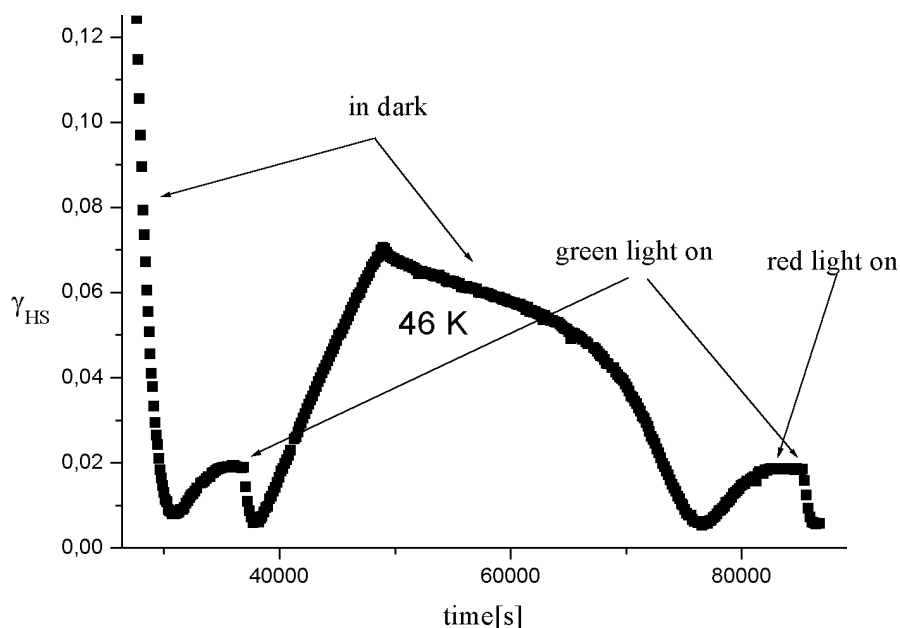


Fig. 12 Unexplained effects on $[\text{Fe}_{0.8}\text{Zn}_{0.2}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$, at 46 K: (i) the climb at the end of the relaxation curve in the dark, (ii) the initial decrease of γ_{HS} upon LS $\rightarrow$ HS photo-excitation, in contrast to HS $\rightarrow$ LS photo-excitation which reveals itself as being inefficient (after [52])

$[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ [3, 51, 52], which have led us to postulate the occurrence of a pressure-induced structural phase transition. Eventual coupling to subtle inhomogeneities of the structural properties is not the only issue here. We shall see in the following section that even the basic assumption of a linear photo-process is questionable, to some extent.

8

Quantitative Approach to the Photo-excitation Process

We review here recent efforts to investigate the linear (or non-linear?) character of the photo-excitation process. From the very first LIESST experiments the process was considered as a single-molecule one, but a few years ago LIESST experiments performed under a rather intense laser beam [18] have shown a clearly non-linear response of the material under the laser beam, and it was reported that the quantum yield was ~ 34 , the highest value which might be obtained, assuming all the incoming photon energy to be transformed into the needed increase in the internal energy ($34 \times$ the HS-LS energy gap). The idea behind this result was to develop analogies with the so-called Photo Induced Phase Transitions [53] which are induced in

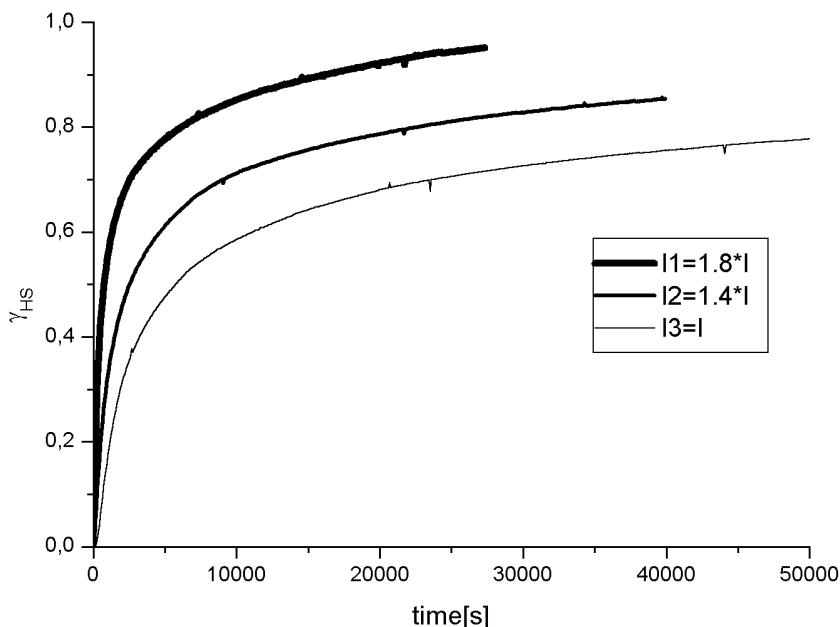


Fig. 13 $[\text{Fe}_{0.8}\text{Zn}_{0.2}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$, photo-excitation curves at 10 K, under permanent illumination at 600 nm, for intensity values 5.6, 8, 11 mW/cm^2 , from bottom to top. Data were derived from magnetic measurements with a 1 mg sample

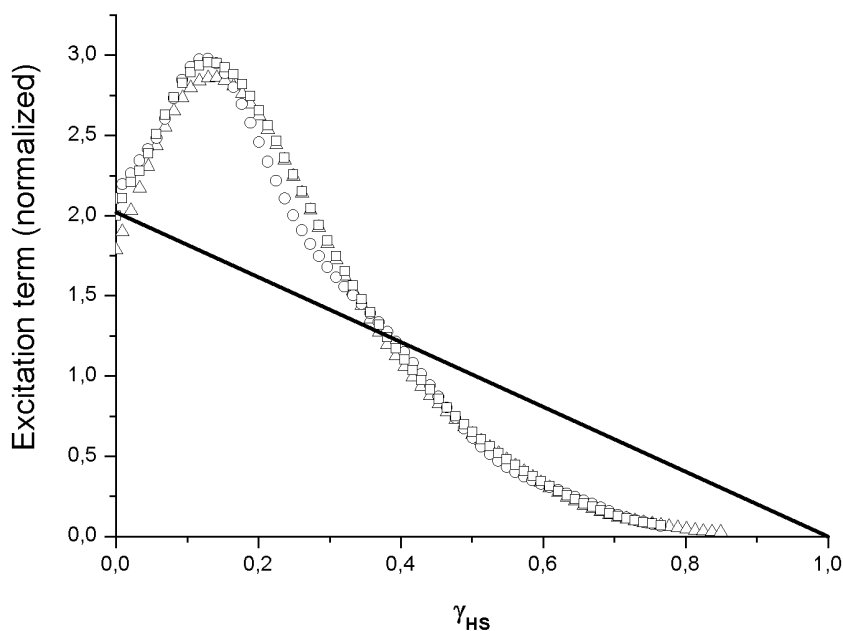


Fig. 14 $[\text{Fe}_{0.8}\text{Zn}_{0.2}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$, at 10 K: experimental determination of the photo-excitation term of Eq. 1, obtained by appropriate linear combinations of the photo-excitation curves in γ_{HS} scale (method developed in [19]). Three sets of data, derived from a comparison of the 3 curves in Fig. 13, are represented after normalisation. The *straight line* represents the expected variation for a linear photo-excitation process, i.e. with a constant yield

charge-transfer systems at the vicinity of an electronic phase transition. The involved “Domino effect” would apply, indeed, to a photo-excitation process performed in the thermal hysteresis loop, and of course should refer to nucleation and growth processes.

As reported in the introduction, a more recent, thorough re-investigation of these experiments [20] re-assessed the quantum yield value to $\sim$ unity. However a progressive increase of the yield value, during the experiment, was also observed.

We had independently addressed the non-linearity problem in an alternative manner, which consisted in disentangling the photo-excitation and relaxation terms by appropriate linear combinations of kinetic data recorded at various intensities of light [19]. In this mean-field approach, the experimental values of the derivatives $d\gamma_{\text{HS}}/dt$ are calculated and, according to Eq. 2, convenient linear combinations of the $d\gamma_{\text{HS}}/dt$ vs γ_{HS} curves provide the photo-excitation and the relaxation terms, expressed of course as functions of γ_{HS} (such as had previously been used by Romstedt et al. [54] for demonstrating the correlation effect, as a departure from a linear plot).

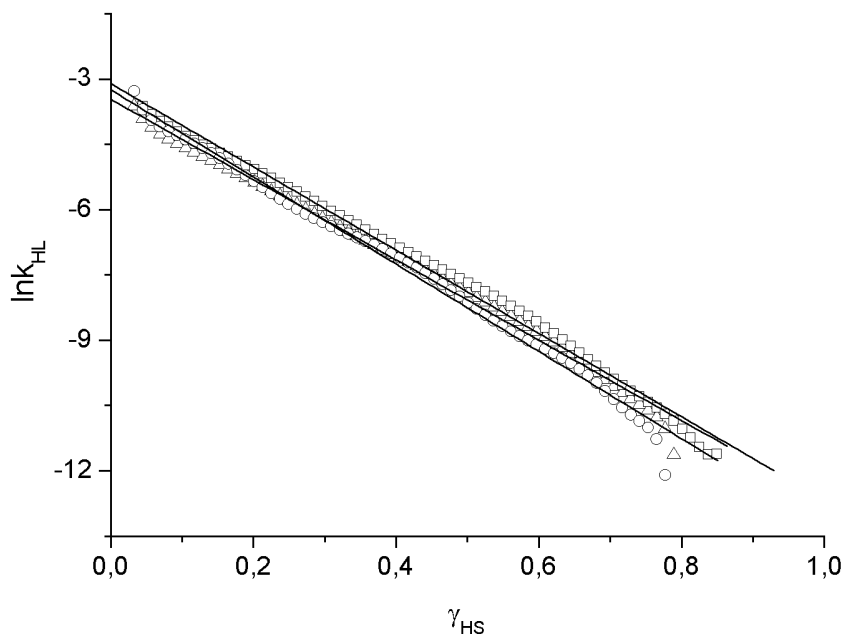


Fig. 15 $[\text{Fe}_{0.8}\text{Zn}_{0.2}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$, relaxation at 10 K as derived from suited linear combinations of the photo-excitation curve. The linear regression of the data yields the self-acceleration factor value $\alpha(10 \text{ K})=9.6 (0.3)$ and the final relaxation rate: $k_{\text{HL}}(\gamma_{\text{HS}}=0)=3.8 \times 10^{-2} \text{ s}^{-1}$

In this way, the self-acceleration character of the cooperative relaxation could be observed in the tunnelling regime, despite the very small values of the relaxation rates. Also, some departure of the photo-excitation term from the expected linear variation was observed, i.e. the photo-excitation rate exhibited a sizeable increase after the first stages of photo-excitation. This was in agreement with the independent observations reported in [18, 20], finally leading to the schematic picture of an incubation period before the photo-induced process takes place quantitatively. Whether this incubation effect is a matter of time, radiation intensity, concentration of photo-excited species, or has some other origin, remains to be established.

We show in Fig. 13 typical kinetic data for $[\text{Fe}_{0.8}\text{Zn}_{0.2}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$. In this compound, cooperativity is appreciably greater than in the example reported in [19], $[\text{Fe}_{0.5}\text{Zn}_{0.5}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$. Again, the initial part of the photo-excitation curve exhibits a sizeable non-linearity. This is of course confirmed by the analysis of the data, the results of which are shown in Figs. 14 and 15. The quantitative comparison of the data of both compounds illustrates the cooperative origin of the self-acceleration factor, approximately proportional to the concentration of SCO species. In the tunnelling regime (10 K) $\alpha=6.1 (0.3)$, $9.6 (0.3)$, for $x=0.5$, 0.8 respectively.

9 Competing Direct and Reverse LIESST

We briefly report on non-linear effects occurring when both direct and reverse LIESST compete against each other. This can be obtained by irradiation in the near IR, between the spin-allowed transition ($^5T_2 \rightarrow ^5E$, HS $\rightarrow$ LS, $\lambda \sim 750$ nm) and the spin forbidden transition ($^1A_1 \rightarrow ^3T_1$, LS $\rightarrow$ HS, $\lambda \sim 1000$ nm) [14]. A preliminary result [47] was shown in the case of $[\text{Fe}_{0.5}\text{Zn}_{0.5}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$, for which some departure from the expected linear form of the photo-excitation terms was detected by the reflectivity technique: the observed time dependence of $\gamma_{\text{HS}}(t)$ under constant irradiation did not closely follow first-order kinetics, and furthermore the intensity factors needed for fitting the curves according to the macroscopic master equation differed by a large ratio: $I_0\sigma(\text{up})/I_0\sigma(\text{down}) \sim 1.5$. We show here the preliminary results of the same investigation performed on $[\text{Fe}_{0.8}\text{Zn}_{0.2}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$; see Fig. 16. The data are derived from magnetic measurements, and re-scaled so as to correspond to an initial state $\gamma_{\text{HS}}=1$ after extended irradiation (2 h) at ~ 10 K by a solid-state laser (532 nm 100 mW/cm²). Bistability of the steady state (light driven equilibrium) is clearly observed at $\lambda=1000$ and 950 nm, and suspected to be present at $\lambda=700$, i.e. when both LS $\rightarrow$ HS and HS $\rightarrow$ LS photo-excitation processes are efficient.

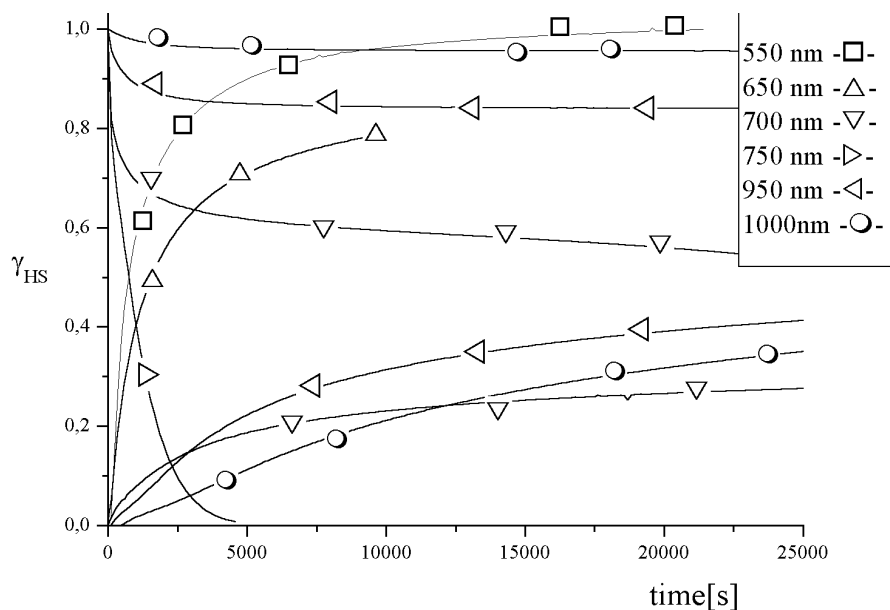


Fig. 16 $[\text{Fe}_{0.8}\text{Zn}_{0.2}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$, the photo-excitation curves at different wavelengths, from magnetic data

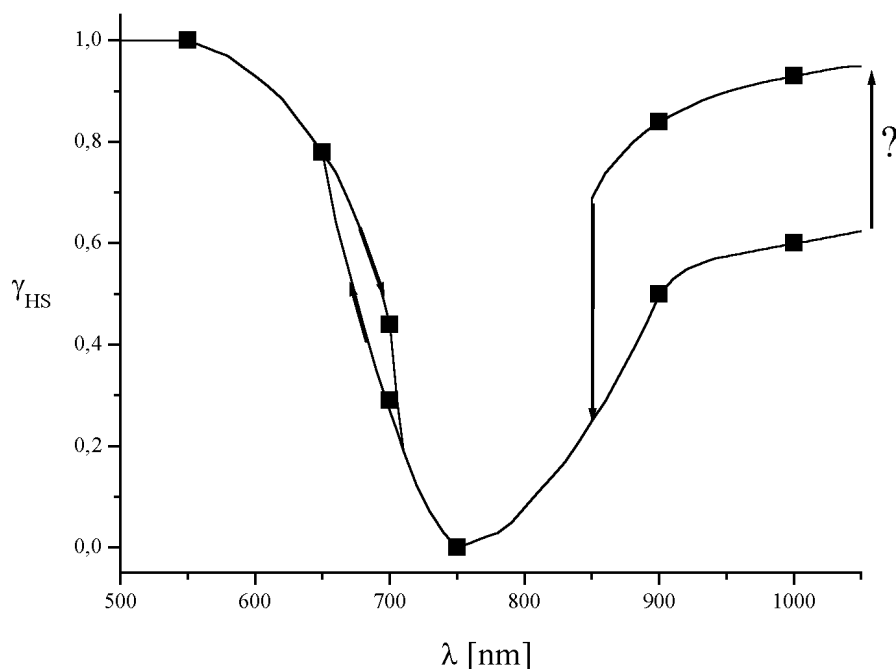


Fig. 17 $[\text{Fe}_{0.8}\text{Zn}_{0.2}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$, the Light Induced Spectral Hysteresis (LISH) loop, as suggested by the quasi-static data derived from the previous figure. The *full line* curve is a guide for the eye

The detailed origin of the non-linearity responsible for optical bistability is not clear, with several possibilities meriting consideration: differential bulk absorption effects, light-induced shift or broadening of the absorption bands, unexpectedly large relaxation rates, but in any case this optical bistability is in some way a consequence of cooperativity. Since the relevant parameter for the light-induced equilibrium is the wavelength, one may imagine slowly sweeping the wavelength in the visible-near IR range, thus allowing the stable and bistable situations to be successively induced. Hysteresis may be obtained, which we shall denote Light Induced Spectral Hysteresis (LISH). We have reported in Fig. 17 the available quasi-static data which suggest the shape of the LISH loop. It is noteworthy that a LISH loop may occur in each wavelength range limited by opposite photo-excitation effects: therefore we indicated the presence of two loops in the figure. Further work is in progress in order to quantify the roles of light intensity, bulk absorption and relaxation.

10

Conclusion and Future Trends

The investigation of SCO compounds under continuous irradiation has provided an additional opportunity for quantitative analyses of the basic properties of the system: photo-excitation (direct, reverse) and relaxation processes.

Some of their properties are well described qualitatively, e.g. the light-induced instability due to cooperative relaxation and its subsequent hystereses (LITH, LIOH, LIPH). The intensity threshold effect associated with cooperative materials can be important in hindering the LIESST effect, even at low temperatures in the example given here. A novel bistability effect has been presented: the Light Induced Spectral Hysteresis (LISH) associated with the competition between direct and reverse LIESST. We anticipate further access to the analysis of long range and short range interactions, through the “paradoxical” photo-induced effects, in addition to previous features such as relaxation tails, or the shape of the spontaneous thermal hysteresis loops, for which useful conclusions were derived from 1-D [43] and recently 2-D [55] models.

Quantitative experimental improvements are expected to result from the preparation of samples of good optical quality, as thin layers in order to minimise bulk absorption effects. The systematic investigation of further systems, different in nature (pure systems, other switchable compounds), or recourse to other physical techniques (neutron diffraction, nuclear forward scattering, time-resolved crystallography) would contribute to the understanding of the behaviour of correlations and the origin of the non-linear characters of the photo-excitation processes.

The main improvement might come from the theoretical side, by consideration of (i) non-linear photo-process, (ii) the possible coupling to a structural phase transition [56] and (iii) the transient inhomogeneity of the system at a macroscopic scale [5]. Indeed, segregation occurs in physical systems subjected to bistable conditions, leading to spin domain structures, which makes it possible to enter the light-induced hysteresis loops, by adequate variations of temperature [2], light [2] or pressure [3, 57, 58]. Then the domain structure of the sample should be accounted for according to the general concepts of phase transitions in the solid state. This indeed is a very challenging problem for theoreticians, and parallel efforts to observe directly the spacio-temporal patterns are called for on the part of experimentalists.

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1

Appendix. The dynamic Ising Model in the Presence of Photo-excitation

1.1

Introduction

The aim of this section is to present the Ising-like model which is very often used to describe the static and dynamic properties of the spin-crossover (SC) systems. We are interested here in these properties under photo-excitation. In particular we will study the photo-excitation effect on the relaxation curve of the HS fraction in order to analyze their effect on the developments of the correlations during the relaxation.

1.2

Ising-Like Model

The microscopic models developed for cooperative spin-crossover solids are based on the Ising-like hamiltonian, following the pioneering works of Wajnsflasz and Pick and Bousseksou et al. [41a, 41b]. Such a two-state model can be viewed as a simple Ising model under a temperature-dependant “effective” field which accounts for the different degeneracies of the levels [44].

In the Ising like model, the two states associated with the eigenstates of the *fictitious* spin ± 1 , have different degeneracies, denoted respectively, g_+ and g_- . In the spin crossover systems, the eigenvalues $+1$ and -1 of the fictitious spin correspond to the high-spin (HS) and low-spin (LS) molecular states respectively.

The Ising-like hamiltonian including long- and short-range interactions [59] writes:

$$H = -J \sum_{\{i,j\}} s_i s_j - \Delta_{eff} \sum_i s_i \quad (11)$$

where: $\Delta_{eff} = (1/2) k_B T \ln(g_+/g_-) - \Delta + G \langle s \rangle$ is the effective field, $\langle s \rangle = m$ is the net fictitious magnetization, J and G are the short- and long-range interactions associated with short- and long-range elastic effects [60] respectively. 2Δ is the energy difference $E(\text{HS}) - E(\text{LS})$ for isolated molecules. g_+/g_- is the degeneracy ratio between the HS and LS states and T the temperature. The ratio g_+/g_- may be quite large (up to a few thousands) because it involves both the spin degeneracies and the density of vibrational levels [61] in the two spin states.

The static properties of this model in the case $J > 0$ and $J < 0$ have been studied analytically in [59]: thermal hysteresis loops with simple and double transitions can occur, due to the competing effect of short-range “ferro-” or “anti-ferromagnetic” interaction and long-range “ferromagnetic” interac-

tions. The phase diagram of this model has been obtained in [59, 41a], where the conditions of the occurrence of the first order transitions of the Ising-like model have been analyzed.

1.3

Master Equation

Now, we are interested in the dynamical properties of such cooperative SC systems. So as to do it, we use the well known general stochastic formalism developed by Glauber [62]. In this stochastic approach, the spin-flips $s_i \rightarrow -s_i$ are induced by the thermal bath, with transition rates $W(s_i)$.

Following Glauber we consider $P(\{s\};t)$ the probability of observing the system in the configuration $(s_1, \dots, s_N) = \{s\}$ at time t . The time evolution $P(\{s\};t)$ is given by the master equation:

$$\frac{\partial P(\{s\};t)}{\partial t} = - \sum_{j=1}^N W_j(s_j) P(\{s\}_j, s_j; t) + \sum_{j=1}^N W_j(-s_j) P(\{s\}_j, -s_j; t) \quad (12)$$

In the last formula, $\{s\}_j$ denotes the configuration of all spins excepted spin s_j and the expectation value of the j -th spin is defined as: $\langle s_j \rangle = \sum_{\{s\}} s_j P(\{s\}; t)$, where the sum is taken over all spin configurations.

The detailed balance condition at equilibrium writes as:

$$\frac{W_i(s_i)}{W_i(-s_i)} = \frac{P_e(\{s\}_i, -s_i)}{P_e(\{s\}_i, s_i)} = \frac{e^{-g s_i \sum_a s_{i+a} - b s_i}}{e^{g s_i \sum_a s_{i+a} + b s_i}} \quad (13)$$

where $P_e(s_1, s_2, \dots, s_N) \sim \exp[-\beta E(s_1, \dots, s_{\dot{1}}, \dots, s_N)]$ is the equilibrium probability of finding the system with the energy $E(s_1, \dots, s_{\dot{1}}, \dots, s_N)$, i.e. in the spin configuration $(s_1, s_2, \dots, s_N)$.

1.4

The Dynamic Choice

Several dynamic choices leading to the same equilibrium states are possible according to Eq. 13 which only provides the ratio of the probabilities of opposite transition rates. We have established recently [4] that the choice suited to the spin-crossover systems (above the tunneling regime) was of the Arrhenius-type [63], because the dynamical process in these systems is thermally activated over an intra- and/or inter-molecular energy barrier (see Fig. 18), and this fact is strongly correlated to the sigmoidal character of the relaxation curves in these systems.

Let's assume that E_a^0 is the energy barrier corresponding to the saddle point energy of the double well configurational energy diagram of Fig. 18

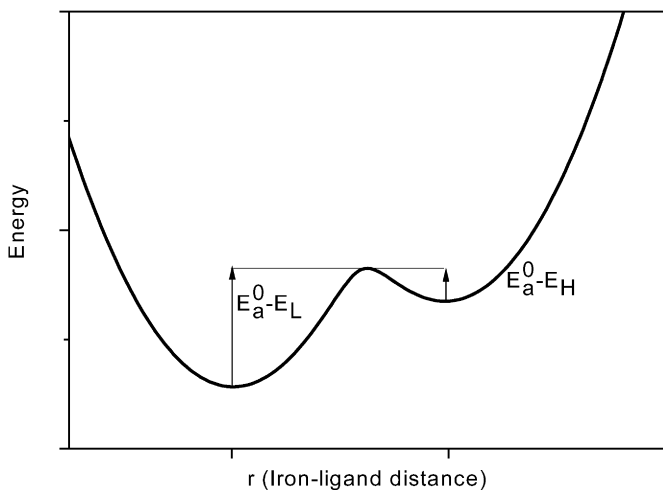


Fig 18 Schematic representation of the potential wells of the (HS) and (LS) states of a spin crossover system. E_H and E_L denote their respective energies, and E_a^0 is the intramolecular energy barrier due to the vibronic interaction

when the HS and the LS fractions are equal, i.e. at equilibrium temperature. Therefore, we can re-write the Eq. 13 under the following form, which obeys the detailed balance equation:

$$\frac{W_i^{\text{Therm}}(s_i)}{W_i^{\text{Therm}}(-s_i)} = \frac{e^{-\beta(E_a^0 - E(s_i))}}{e^{-\beta(E_a^0 - E(-s_i))}} \quad (14)$$

where $\beta E(s_i) = -g \sum_{\alpha=1,q} s_{i+\alpha} - b s_i$, with $g=\beta J$, $b=\beta \Delta_{\text{eff}}$, and α runs over the neighbours. We choose for the transition rate the general form $W^{\text{Therm}}(s_i) \sim \exp[-\beta (E_a^0 - E(s_i))]$, which can be re-written as:

$$W_i^{\text{Therm}}(s_i) = \frac{1}{2\tau} (x - x' s_i) \prod_{\alpha=1}^q (y - y' s_{i+\alpha}) \quad (15)$$

with the following notations: $x = \cosh b$, $y = \cosh g$, $x' = \sinh b$, $y' = \sinh g$.

Under photo-excitation, which is assumed to induce only the LS→HS transitions, we must introduce an additional optical transition rate W^{Opt} given by:

$$W_i^{\text{Opt}}(s_i) = I_0 \sigma (1 - s_i) \quad (16)$$

where I_0 is the intensity of the incident radiation and σ is the absorption cross-section, related to the quantum photo-process. σ is considered as independent of the lattice configuration $\{s\}$. Photo-excitation is considered here as a non-cooperative process, since it is written as a single site term.

The exact formulation of the dynamic equations leads to the following evolution equations for the fictitious magnetization and the equal-time correlation:

$$\frac{d\langle s_i \rangle}{dt} = \frac{dm_i}{dt} = -2\langle s_i [W_i^{\text{Therm}}(s_i) + W_i^{\text{Opt}}(s_i)] \rangle_t \quad (17)$$

and

$$\frac{d\langle s_i s_j \rangle}{dt} = \frac{dr_{ij}}{dt} = -4\langle s_i s_j [W_i^{\text{Therm}}(s_i, s_j) + W_i^{\text{Opt}}(s_i, s_j)] \rangle_t \quad (18)$$

The right-hand sides of Eqs. 17, 18 involve the average of clusters of spins. In the present work, we are interested by the correlations effect during the transition, therefore we perform all calculations in the pair approximation. Indeed, in that case our approach represents the dynamical extension of the well known Bethe-Peierls approach of the equilibrium statistical mechanics. We now have to choose an explicit form for the probabilities $P(\{s\}, t)$ as a function of the order parameters of the model and the spin variables $(s_1, s_2, \dots, s_N) = \{s\}$.

1.5

Pair Approximation

In the pair approximation, the probabilities (or the density matrix operators) $P_1(s_j; t)$ for the single spin s_j , and the pair probability $P_2(s_i; s_j; t)$ associated with a pair of neighbouring spins $s_i; s_j$ are given by:

$$P_1(s_i; t) = \frac{1}{2}(1 + m_i(t)s_i) \quad (19)$$

and

$$P_2(s_i, s_j; t) = \frac{1}{4}(1 + m_i(t)s_i + m_j(t)s_j + r_{ij}(t)s_i s_j) \quad (20)$$

with $m_i = \langle s_i \rangle$ and $r_{ij} = \langle s_i s_j \rangle$.

We now have to examine the probabilities of occupation of the configuration of clusters of $q+1$ spins, which are formed by the central spin surrounded by its q neighbours. The probability $P_{q+1}(s_b, \{s_{i+\alpha}\}; t)$, of such a cluster is approximated by using an elegant formulation due to Mamada and Takano [64], in which the authors considered $P_{q+1}(s_b, \{s_{i+\alpha}\}; t) \approx P_1(s_b; t) \times \dots \times P(s_{i+\omega}|s_b; t) \times \dots \times P(s_{i+q}|s_b; t)$, where $P(s_i|s_b; t)$ is the conditional probability at time t of s_j at fixed value of spin s_i . Using the identity $P_2(s_b, s_j; t) = P_1(s_j; t) \times P(s_j|s_b; t)$, we obtain:

$$P_{q+1}(s_1, \{s_{i+\alpha}\}; t) = P_1(s_i; t) \prod_{\alpha=1}^q \frac{P_2(s_i, s_{i+\alpha}; t)}{P_1(s_i; t)} \quad (21)$$

where the subscript α runs over the neighbouring spins of s_i . Inserting Eq. 21 in the right-hand side of Eqs. 17, 18, we obtain the closed set of motion equations of the system, presented in the next section.

1.6

Relaxation under Photo-excitation

For this first attempt, the lattice is assumed to be spatially invariant; then we put $m_i = m$ and $r_{ij} = r_{|i-j|} = r$. Substituting now the probability of flipping site i , $W_i^{\text{Therm}}(s_i)$, $W_i^{\text{Opt}}(s_i)$ and $P_{q+1}(s_i, \{s_{i+\alpha}\}; t)$ for their corresponding expressions (15–21), we obtain, after some calculations, the following evolution equations for the long- and short-range order parameters, respectively:

$$2\tau \frac{dm}{dt} = (x+x')(1-m) \left(y + y' \frac{m-r}{1-m} \right)^q - (x-x')(1+m) \left(y - y' \frac{m+r}{1+m} \right)^q + 2I_o \sigma (1-m) \quad (22)$$

and

$$\tau \frac{dr}{dt} = (x+x')(1-m) \left(y \frac{m-r}{1-m} + y' \right) \left(y + y' \frac{m-r}{1-m} \right)^{q-1} - (x-x')(1+m) \left(y \frac{m+r}{1+m} - y' \right) \left(y - y' \frac{m+r}{1+m} \right)^{q-1} + 4I_o \sigma (m-r) \quad (23)$$

with $(x+x') = \exp(b)$ and $(x-x') = \exp(-b)$, where b , y and y' are given by: $b = \beta [Gm + (1/2)kT \ln(g+/g-) - \Delta]$, $y = \cosh \beta J$, and $y' = \sinh \beta J$.

For convenience, it is useful to re-express the latter equations in terms of the fractions of the high spin molecules (n_H) and the pairs HS-LS molecules (n_{HL}), respectively $n_H(t) = (1+m(t))/2$ and $n_{HL}(t) = (1-r(t))/4$ [59]. They give, in the low-temperature region in which we are looking for the relaxation of the HS fraction, the following non-linear equations:

$$\frac{dn_{HS}}{dt} = -\frac{n_{HS}}{2\tau_o} e^{-(\beta E_a^o + b)} \left(e^{-\beta J} + 2 \sinh \beta J \frac{n_{HL}}{n_{HS}} \right)^q + 2I_o \sigma (1 - n_{HS}) \quad (24)$$

and

$$\frac{dn_{HL}}{dt} = -\frac{n_{HS}}{2\tau_o} e^{-(\beta E_a^o + b)} \left(e^{-\beta J} + 2 \cosh \beta J \frac{n_{HL}}{n_{HS}} \right) \left(e^{-\beta J} + 2 \sinh \beta J \frac{n_{HL}}{n_{HS}} \right)^{q-1} + 8I_o \sigma (n_{HS} + 2n_{HL} - 1) \quad (25)$$

The photo-excitation effect depends on the time t_w at which the light is switched on. This time has to be compared with the characteristic time t_c at

which the correlation onsets in sizeable amount. t_c should be considered as an incubation time, defined as the time at which the transition rate exhibits a sizeable departure from the linear mean-field behaviour. The t_c value is of course determined numerically. We obtain the following results:

1. $t_w < t_c$: the lifetime of the metastable HS state is increased; however, the relaxation tail is reduced. The light drives the system to the mean-field behavior. We stress on the paradoxical effect that finally *light speeds up relaxation* in the late stage of the relaxation.
2. $t_w > t_c$: in a first stage, light slows down relaxation; even, above a threshold value of intensity, an increase of the HS population may be observed. In a further stage, i.e. after some incubation process, the light starts destroying the already established correlations and the final effect is to speed up relaxation.

(Figure 10 curves (b), (c)). The paradoxical effect is remarkably rapid and efficient.

Systematic computations have shown that the above effects are exclusively associated with the short-range interaction. An extensive investigation including short- and long-range interactions is under progress.

References

1. Létard JF, Guionneau P, Rabardel L, Howard JAK, Goeta AE, Chasseau D, Kahn O (1998) *Inorg Chem* 37:4432
2. Désaix A, Roubeau O, Jeftic J, Haasnoot JG, Boukheddaden K, Codjovi E, Linares J, Nogués M, Varret F (1998) *Eur Phys J B* 6:183
3. Menendez N, Varret F, Codjovi E, Boukheddaden K, Haasnoot JG (2000) Third TMR-TOSS meeting (Leiden, May 2000)
4. Boukheddaden K, Shteto I, Hoo B, Varret F (2000) *Phys Rev B* 62:14,806
5. Varret F, Boukheddaden K, Jeftic J, Roubeau O (1999) ICMM '98 (Seignosse, France, Sept 1998). *Proceedings: Mol Cryst Liq Cryst* 335:561
6. Hauser A (1986) *Chem Phys Lett* 124:543
7. Hauser A, Gülich P, Spiering H (1986) *Inorg Chem* 25:4245
8. Hauser A (1992) *Chem Phys Lett* 192:65
9. Hauser A, Jeftic J, Romstedt H, Hinek R, Spiering H (1999) *Coord Chem Rev* 190/192:471–491
10. Decurtins S, Gülich P, Köhler CP, Spiering H, Hauser A (1984) *Chem Phys Lett* 139:1
11. Decurtins S, Gülich P, Hasselbach KM, Spiering H, Hauser A (1985) *Inorg Chem* 24:2174
12. Gülich P, Hauser A, Spiering H (1994) *Angew Chem Int Ed* 33:2024
13. Hauser A (1991) *Coord Chem Rev* 111:275
14. Hauser A (1991) *J Chem Phys* 94:2741
15. Gülich P, Garcia Y, Woike T (2001) *Coord Chem Rev* 219/221:839
16. McGarvey JJ, Lawthers I (1982) *J Chem Soc* 906
17. Enachescu C, Linares J, Varret F (2001) *J Phys Condens Matter* 13:2481

18. Ogawa Y, Koshihara S, Koshino K, Ogawa T, Urano C, Takagi H (2000) *Phys Rev Lett* 84:3181
19. Enachescu C, Constant H, Codjovi E, Linarès J, Boukheddaden K, Varret F (2001) *J Phys Chem Solids* 62:1409
20. Enachescu C, Oetliker U, Hauser A (2002) *J Phys Chem* 37:9540
21. Varret F, Boukheddaden K, Codjovi E, Linarès J (2001) 4th TMR-TOSS meeting (Bordeaux, May 2001)
22. Hoo B, Boukheddaden K, Varret F (2000) *Eur Phys J B* 17:449
23. Boukheddaden K, Shteto I, Hoo B, Varret F (2000) *Phys Rev B* 62:14,796
24. Boukheddaden K (2000), Thèse d'Habilitation, Université de Versailles
25. Boukheddaden K, Varret F, Salunke S, Linarès J, Codjovi E (2002) International Conference on Photo-Induced Phase Transitions (Tsukuba, Japan, Nov 2001), *Proceedings: Phase Transitions* 75:733
26. Ogawa Y, Ishikawa T, Koshihara S, Boukheddaden K, Varret F (2002) *Phys Rev B* 66:073104
27. Renz F, Spiering H, Goodwin H, Gütlisch P (2000) *Hyperfine Interact* 126:155
28. Montant S, Chastanet G, Létard S, Marcen S, Létard JF, Freysz E (2002) Fifth TMR-TOSS Meeting (Seeheim, March 2002)
29. Shimamoto N, Ohkosi SK, Sato O, Hashimoto K (2002) *Chem Lett* 4:486
30. Hauser A (1995) *Comments Inorg Chem* 17:17
31. Martin JP, Zarembowitch J, Bousseksou A, Dworkin A, Haasnoot JG, Varret F (1994) *Inorg Chem* 18:2617
32. Constant-Machado H, Linarès J, Varret F, Haasnoot JG, Martin JP, Zarembowitch J, Dworkin A, Bousseksou A (1996) *J Phys I France* 6:1203
33. Jetic J, Matsarki M, Hauser A, Goujon A, Codjovi E, Linarès J, Varret F (2001) *Polyhedron* 20:1599
34. Létard JF, Chastanet G, Nguyen O, Marcen S, Marchivie M, Guionneau P, Chasseau D, Gütlisch P (2002) In: Verdaguer M, Linert W (eds) *Monatshefte für Chemie*. Springer, Berlin Heidelberg New York
35. Chastanet G, Enachescu C, Varret F, Ader JP, Létard JF (2002) Fifth TOSS Meeting (Seeheim, March 2002)
36. Varret F, Constant-Machado H, Dormann JL, Goujon A, Jetic J, Nogués M, Bousseksou A, Klokishner S, Dolbecq A, Verdaguer M (1998) International Conference on Applied Mossbauer Effect, ICAME '97, *Proceedings. Hyperfine Interact* 113:37
37. Codjovi E, Morscheidt W, Jetic J, Linarès J, Nogués M, Goujon A, Roubeau O, Constant-Machado H, Desaix A, Bousseksou A, Verdaguer M, Varret F (1999) *Proceedings of ICMM '98* (Seignosse, France) *Mol Cryst Liq Cryst* 335:1295
38. Varret F, Nogués M, Goujon A (2001) In: Miller J, Drillon M (eds) *Magnetism: molecules to materials*, vol 2. Wiley WCH, pp 257–291
39. Roubeau O, Haasnoot JG, Codjovi E, Varret F, Reedijk J (2002) *Chem Mater* 14:2559
40. Spiering H, Kohlhaas T, Romstedt H, Hauser A, Bruns-Yilmaz C, Kusz J, Gütlisch P (1999) *Coord Chem Rev* 190/192:629
41. a) Wajnflasz J, Pick R (1971) *J Phys Coll* 32:C1–91; b) Bousseksou A, Nasser J, Linarès J, Boukheddaden K, Varret F (1992) *J Phys I* 2:1381
42. Real JA, Bolvin H, Bousseksou A, Dworkin A, Kahn O, Varret F, Zarembowitch J (1992) *J Am Chem Soc* 114:4650
43. Linarès J, Spiering H, Varret F (1999) *Eur Phys J B* 10:271
44. Doniach S (1978) *J Chem Phys* 68:11
45. Goujon A, Roubeau O, Varret F, Dolbecq A, Bleuzen A, Verdaguer M (2000) *Eur Phys J B* 14:115

46. Varret F, Goujon A, Boukheddaden K, Nogués M, Bleuzen A, Verdaguer M (2002) International Symposium on Cooperative Phenomena of Assembled Metal Complexes (Osaka, Japan, Nov 2001) Proceedings (2002). *Mol Cryst Liq Cryst* 379:333
47. Goujon A, Varret F, Escax V, Bleuzen A, Verdaguer M (2001) ICMM'00 (San Antonio, Texas) Proceedings (2001). *Polyhedron* 20:1347
48. Hôo B (2001) Thèse de Doctorat, Université de Versailles
49. Hauser A (1998) *J Phys Chem Solids* 59:1353
50. Garcia Y, Ksenofontov V, Levchenko G, Schmitt G, Gütllich P (2000) *J Phys Chem B* 104:5046
51. Codjovi E, Menendez N, Jeftic J, Varret F (2001) *C R Acad Sci Paris* 4:181
52. Varret F, Enachescu C, Boukheddaden K, Codjovi E, Linarès J (2002) Final TMR-TOSS Meeting (Seeheim, March 2002)
53. Koshihara S, Takahashi Y, Sakai H, Tokura Y, Luty T (1999) *J Phys Chem B* 103:2592
54. Romstedt H, Hauser A, Spiering H (1998) *J Phys Chem Solids* 59:265
55. Linarès J, Enachescu C, Boukheddaden K, Varret F (2003) Proceedings ICMM'02 (Valencia, Spain), *Polyhedron* 22:2453
56. Jeftic J, Hauser A (1997) *J Phys Chem B* 101:10,262
57. Bousseksou A, Molnar G, Tuchagues JP, Menendez N, Codjovi E, Varret F (2003) *Compt Rend Acad Sci Paris (Chimie)* 6:329
58. Varret F, Bleuzen A, Boukheddaden K, Bousseksou A, Codjovi E, Enachescu C, Goujon A, Linarès J, Menendez N, Verdaguer M (2002) *Pure Appl Chem* 74:2159
59. Boukheddaden K, Linarès J, Spiering H, Varret F (2000) *Eur Phys J B* 15:317
60. Willenbacher N, Spiering H (1988) *J Phys C* 21:1423; Spiering H, Willenbacher N (1989) *J Phys Cond Matter* 1:10,089
61. Bousseksou A, Constant-Machado H, Varret F (1995) *J Phys I* 5:747
62. Glauber RJ (1968) *J Math Phys* 4:294
63. Ludwig KF, Park B (1992) *Phys Rev B* 46:5079
64. Mamada H, Takano S (1968) *J Phys Soc Japan* 25:675

Nuclear Decay Induced Excited Spin State Trapping (NIESST)

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Dedicated to Professor Rudolf L. Mößbauer on the occasion of his 75th birthday.

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Abstract Mössbauer Emission Spectroscopy (MES) has been employed in studies of chemical and physical after-effects of the electron capture process $^{57}\text{Co}(\text{EC})^{57}\text{Fe}$ in inorganic compounds. The ^{57}Co labelled compounds are used as the Mössbauer source at variable temperatures vs a single-line absorber such as $\text{K}_4[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ kept at room temperature. The recorded ME spectrum yields information on the electronic and molecular structure of species containing the nucleogenic ^{57}Fe in its first nuclear excited state (14.4 keV, $\tau_M \approx 140$ ns lifetime). The after-effects observed in this time window refer to changes of charge and spin state, radiolysis products, metal-ligand bond rupture, long-lived metastable spin states and low energy excitations in spin-orbit coupling or Zeeman manifolds.

Long-lived metastable spin states of $^{57}\text{Fe}(\text{II})$ have been observed in time-integral ME spectra of ^{57}Co labelled coordination compounds, the corresponding iron(II) compounds of which are classified as strong-field and intermediate field (spin crossover) compounds. Their lifetimes have been measured using a MES coincidence spectrometer and found, at

comparable temperatures, to be very similar to those observed of metastable Fe(II)-HS states after laser excitation (LIESST). The so-called *inverse energy gap law*, first introduced by Buhks et al. and later applied by A. Hauser to describe the relaxation of metastable LIESST states, also applies to the relaxation of metastable spin states generated by “nuclear decay-induced excited spin state trapping (NIESST)”. We therefore conclude that both phenomena, LIESST after optical excitation and NIESST after nuclear decay, follow the same relaxation mechanism.

Keywords Mössbauer emission spectroscopy · Chemical and physical after-effects of nuclear decay · Metastable spin states · Relaxation of NIESST and LIESST states

List of Abbreviations

MAS	Mössbauer absorption spectroscopy
MES	Mössbauer emission spectroscopy
TIMES	Time-integral Mössbauer emission spectroscopy
TDMES	Time-differential Mössbauer emission spectroscopy
EC	Electron capture decay
NIESST	Nuclear decay-induced excited spin state trapping
LIESST	Light-induced excited spin state trapping
HS	High spin
LS	Low spin
τ_M	Lifetime of the nuclear excited level involved in the Mössbauer effect (ca. 140 ns in the case of ^{57}Fe)
τ_L	$(\hbar/2\pi\hbar)(\Delta E)^{-1}$, Larmor precession time for nuclear electric quadrupole interaction or nuclear magnetic dipole interaction with hyperfine interaction energy ΔE
τ_e	Lifetime of after-effect species resulting from $^{57}\text{Co}(\text{EC})^{57}\text{Fe}$ decay
phen	1.10-Phenanthroline
bipy	2,2'-Bipyridine
pmi	2-Pyridinalmethyimine
pic	2-Picolylamine
ptz	1-Propyl-tetrazole
terpy	2,2':6',2''-Terpyridine

1

Introduction

The actual roots of NIESST experiments are found in studies of chemical reactions of energetic atoms produced by nuclear transformations, so-called hot atom chemistry, which began with the work of Szilard and Chalmers in 1934 [1]. Since then research activities have focused mainly on the elucidation of the mechanisms of “after-effects” following the nuclear decay of radioisotopes in gaseous, liquid and solid phases of organic and inorganic compounds [2, 3]. While work on gas phases on the one hand and insulating compounds on the other hand was rather successful even in the early stages of hot atom chemistry, mechanistic studies of solid coordination compounds and systems with high electrical conductivity proved to be much

more cumbersome due to the lack of suitable techniques for the analysis of short-lived metastable species.

The situation changed with the discovery of “recoilless nuclear resonance fluorescence” (Mössbauer effect) in the late 1950s. In fact, Mössbauer spectroscopy has so far proven to be the most valuable spectroscopic tool for the study of chemical and physical after-effects [4, 5]. While in conventional Mössbauer *absorption* spectroscopy (MAS) [6, 7], one uses a suitable radioactive source with a single gamma transition line between the unsplit nuclear ground and excited states to study the hyperfine interactions in the absorber material of interest, one reverses the technique in Mössbauer *emission* spectroscopy (MES) and uses a known single-line absorber to restore resonance with the gamma ray transition lines of the source under study. Thus, in MES experiments the recorded Mössbauer spectrum yields information about the electronic and molecular structure of the nucleogenic species during the lifetime of the excited nuclear (Mössbauer) state. The elegant feature of this technique is that the chemical and physical after-effects are being produced in the Mössbauer source compound and, at the same time, analysed spectroscopically in a nondestructive manner. A variety of nuclear decay processes have been studied this way, but by far the most extensively investigated nuclear decay process is the electron capture decay of $^{57}\text{Co}(\text{EC})^{57}\text{Fe}$ in inorganic compounds, primarily coordination compounds. Among the various kinds of after-effects is the observation of metastable spin states in ^{57}Co doped coordination compounds, a phenomenon which has been termed “Nuclear Decay-Induced Excited Spin State Trapping”, abbreviated as NIESST, in analogy to the phenomenon of “Light-Induced Excited Spin State Trapping (LIESST)”. While in LIESST experiments the long-lived metastable spin states are created optically with an external light source, NIESST makes use of the nuclear decay as an intrinsic excitation source to generate the metastable spin states trapped in the “time window” of Mössbauer spectroscopy. There is experimental evidence that the relaxation mechanisms are the same in both phenomena. Examples, exclusively dealing with the $^{57}\text{Co}(\text{EC})^{57}\text{Fe}$ decay process, are discussed in this account. We begin with a description of the various after-effects which may follow the nuclear decay of radioactive atoms in solids. The main section deals with MES experiments, both time-integral (TIMES) and time-differential (TDMES) on iron(II) and cobalt(II) coordination compounds of different ligand field strength. The chapter concludes with a report on recent NIESST experiments in various systems.

2

Chemical and Physical After-Effects of $^{57}\text{Co}(\text{EC})^{57}\text{Fe}$ Decay

2.1

 ^{57}Co Electron Capture Decay and Immediate Consequences

The radioactive ^{57}Co nucleus decays by capturing a K-electron or, to a lesser extent, an L-electron and emitting a neutrino of 0.7 eV and thereby populating the 136.5 keV excited state of ^{57}Fe ; cf. the nuclear decay scheme of ^{57}Co in Fig. 1. The recoil energy of 4.6 eV of the neutrino emission is far below the displacement threshold determined by the chemical bond energy of typically 25 eV. Therefore, the physico-chemical consequences—called after-effects—arise from the electronic de-excitation of the nucleogenic ^{57}Fe species. If, e.g. the ^{57}Co atom is in the divalent state, immediately after the electron capture a highly excited $^{57}\text{Fe}^{2+}$ ion with a hole in the inner shell region is present. In times of about 10^{-15} s after the nuclear decay the electron hole in the K or L shell moves outwards via radiative processes (X-rays of up to several keV) or non-radiative Auger-processes (Auger electrons of several keV). The branching ratio of these processes and their relative probabilities were estimated by Pollak [8]. He also proposed that these processes may result in highly charged species up to $^{57}\text{Fe}^{7+}$. A more detailed description of the fast de-excitation processes following immediately the nuclear decay is given in [5].

The highly charged $^{57}\text{Fe}^{n+}$ ions trap electrons from the nearby surroundings producing further holes. The recombination processes are determined by various properties of the lattice such as mobility of the holes and electrons, imperfections and radiolysed molecules, resulting from X-ray emissions, as electron traps, electron capture cross sections of the holes and all

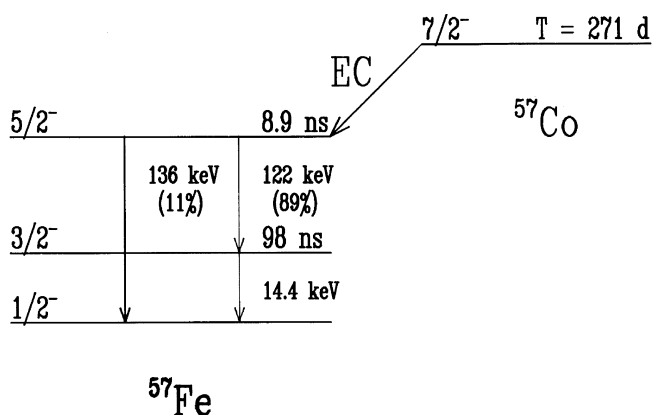


Fig. 1 Nuclear decay scheme of ^{57}Co

acceptors including the $^{57}\text{Fe}^{n+}$. The primary recombination processes are believed to take place in times less than 10^{-14} s. Thereafter, the lattice around the nucleogenic ion is heated due to the energy loss of the Auger electrons and due to the recoil energy from the neutrino emission. This local heat of the “hot spike” is dissipated into the lattice by the onset of atomic vibrations with frequencies of typically 10^{13} s $^{-1}$.

It is assumed that all these energies dissipate in less than 10^{-10} s, i.e. long before the time-window of Mössbauer spectroscopy opens. The 136 keV level of ^{57}Fe decays with a lifetime of 1.2×10^{-8} s and populates the 14.4 keV level opening the Mössbauer time-window of $\tau_M \approx 140$ ns. The small recoil energy of 0.14 eV of the emitted 122 keV γ -quantum also dissipates immediately before the Mössbauer time-window opens.

2.2

After-Effects Observed by Mössbauer Emission Spectroscopy

Like any other spectroscopic method, Mössbauer spectroscopy [6, 7] possesses a characteristic time scale (time-window) of the measurement, which is determined by the mean life time $\tau_M \approx 140$ ns (half life $\tau_{1/2} = 98$ ns) of the first excited nuclear state (14.4 keV state) involved in the Mössbauer effect. For the measurement of hyperfine interactions (electric quadrupolar and magnetic dipolar) of energy $\Delta E \approx 10^{-8}$ eV, the characteristic time scale corresponds to the relevant Larmor precession time $\tau_L = (\hbar/2\pi)(\Delta E)^{-1}$. If the environment (electronic and/or molecular structure) of the nucleogenic ^{57}Fe species changes dynamically in the course of after-effect relaxation, the observed spectra depend specifically on the mean life time τ_e of the metastable nucleogenic species relative to τ_M and τ_L . In the slow relaxation limit, $\tau_e \gg \tau_M$, the measurement reveals a quasi-static situation, and the observed spectrum shows resolved resonance lines originating from relatively long-lived metastable species. In the fast relaxation limit, $\tau_e \ll \tau_M$, the observed spectrum reveals the nucleogenic species in its ground state.

The chemical state of the nucleogenic ^{57}Fe atom, analysed by time-integral Mössbauer emission spectroscopy, has been found to depend strongly on the surrounding host lattice. In conducting material (metals and alloys), rapid electron recombination and annealing of lattice structural defects take place in times much shorter than τ_M , and after-effects are generally not observable in the Mössbauer emission spectra of such systems. In insulating substances (inorganic and metal-organic compounds), the situation regarding the nature of after-effect products and their lifetimes is different. Ligand molecules coordinated to the parent ^{57}Co and the nucleogenic ^{57}Fe central atom, respectively, may be radiolysed by emission of X-rays and Auger electrons leading to electron deficiency and/or bond rupture. Parallel with or subsequent to electron recombination of the highly charged central metal ion, a process which is considered fast also in insulating systems, secondary

reactions take place between the autoradiolysis products and the central ion. Intramolecular electron transfer and redox reactions depending on the redox potentials of the nucleogenic central ion and the (possibly radiolysed) ligand molecules are the types of processes to be expected. The extent of autoradiolysis in the ligand sphere has been found to depend strongly on the nature of the ligands. Small ligand molecules such as water are less radiation resistant than the electronically flexible aromatic systems such as phenanthroline [9–11]. Metal-ligand bond rupture due to Coulombic repulsion with and without subsequent structural rearrangement of the inner coordination sphere resulting in significant changes of the ligand field potential at the central ion are further possible secondary reactions, which may decisively determine the final chemical state (e.g. trapping metastable spin states) of the nucleogenic atom.

The various types of after-effects observed in the ^{57}Fe Mössbauer emission spectra of ^{57}Co -labelled compounds may be classified in the following way:

1. *Change of charge state* of ^{57}Fe , if it deviates by one or more units from the charge state of the ^{57}Co atom in the parent compound used as the Mössbauer source. This effect may result from either incomplete electron recombination following the Auger cascade or from intramolecular electron transfer (metal-to-ligand) following the creation of ligand radicals by autoradiolysis.
2. *Change of inner coordination sphere* of an $[\text{FeL}_n]$ complex molecule arising from secondary reactions of the nucleogenic central ion with an autoradiolysed ligand: the reaction $[\text{}^{57}\text{Co}(\text{H}_2\text{O})_6]^{2+} \rightarrow [\text{}^{57}\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ is an example for this “ligand replacement effect”.
3. *Metal-Ligand bond rupture* and subsequent rearrangement of the inner coordination sphere (“linkage isomerism”). The inversion of a cyanide ligand following the EC decay in the complex $[\text{}^{57}\text{Co}(\text{CN})_6] \rightarrow [\text{}^{57}\text{Fe}(\text{CN})_5(\text{NC})]^{3-}$ is an example [12]. Numerous examples of classes 1, 2 and 3 after-effects have been studied and are reported in the literature [3, 13].
4. *Change of spin state*, if the spin multiplicity of the nucleogenic ^{57}Fe ion in the $[\text{}^{57}\text{FeL}_n]$ complex differs from that of the corresponding $[\text{}^{57}\text{FeL}_n]$ in its ground state, determined e.g. by Mössbauer absorption spectroscopy (MAS) under the same conditions (“spin isomerism”). This type of after-effect, termed “Nuclear Decay-Induced Excited Spin State Trapping (NIESST)” in analogy to the LIESST phenomenon is the main topic of this chapter.
5. *Long-lived low energy excitations* within the ligand field ground state. The observation of the non-thermalized populations of spin-orbit levels of ^{57}Fe in a $\text{ZnS}/^{57}\text{Co}$ source [14] and the non-thermalized populations of the Zeeman levels of the $^6\text{A}_1\text{g}$ ground state of nucleogenic Fe(III) resulting from EC decay of ^{57}Co doped into LiNbO_3 as Mössbauer source [15] are examples of this class of after-effects.

3 Early NIESST Experiments with Complexes of Different Ligand Field Strength

3.1

Strong Field Complexes

The first MES studies with ^{57}Co labelled coordination complexes with phenanthroline ligands as Mössbauer source vs $\text{K}_4[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ as a single-line absorber were performed some 35 years ago in our laboratory. The phenanthroline complexes were chosen because their Fe(II) complexes offer a wide range of ligand field strengths depending on the particular ligand sphere. E.g. $[\text{Fe}(\text{phen})_3](\text{ClO})_4$ is a typical low-spin compound with $^1\text{A}_1$ ground state, $[\text{Fe}(2\text{-CH}_3\text{-phen})_3](\text{ClO})_4$ or $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ are known to be spin crossover compounds with temperature-dependent $^1\text{A}_1 \leftrightarrow ^5\text{T}_2$ transitions, and $[\text{Fe}(2\text{-Cl-phen})_3](\text{ClO})_4$ is a high-spin compound with $^5\text{T}_2$ ground state. Thus these complexes represent members of *strong-field*, *intermediate-field*, and *weak-field* coordination compounds of iron(II). As will be discussed below, the ligand field strength plays an important role in the relaxation mechanism of nucleogenic ^{57}Fe species, specifically the NIESST states.

The first observation of trapped excited spin states arising from the ^{57}Co (EC) ^{57}Fe decay was made with the ^{57}Co labelled tris-phenanthroline compound [16]. The system $[\text{M}(\text{phen})_3](\text{ClO}_4)_2$ with $\text{M} = ^{57}\text{Fe}_x/\text{Co}_{1-x}$, $x=0.001$ was studied by temperature dependent Mössbauer absorption spectroscopy, and the one with $\text{M} = ^{57}\text{Co}_x/\text{Co}_{1-x}$, $x=0.001$ by time-integral Mössbauer emission spectroscopy (TIMES). A selection of spectra for both series is shown in Fig. 2.

The Mössbauer absorption spectra for the compound with $\text{M} = ^{57}\text{Fe}_x/\text{Co}_{1-x}$, $x=0.001$ in Fig. 2a, recorded with a usual single-line source such as $^{57}\text{Co}/\text{Rh}$ kept at room temperature, show the same quadrupole doublet at all temperatures under study; the quadrupole splitting and the isomer shift values are typical for iron(II) in the LS state and are identical to those of the neat iron complex compound. Thus the hyperfine interactions in the $[\text{Fe}(\text{phen})_3]^{2+}$ complex molecule embedded in the host lattice of the corresponding cobalt compound are within experimental error the same as in the neat iron compound. As the tris-phenanthroline complex of cobalt(II) is high-spin with a $^4\text{T}_1$ ground state, whereas that of the iron(II) complex is low-spin with a $^1\text{A}_1$ ground state, it is obvious that the hyperfine interactions felt by the central $^{57}\text{Fe}(\text{II})$ ion are determined primarily by the immediate coordination sphere and are virtually unaffected by the next-nearest environment.

If the Co(II) compound is doped with radioactive $^{57}\text{Co}(\text{II})$ and used as a Mössbauer source against the single-line absorber $\text{K}_4[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$, emission spectra are obtained as shown in Fig. 2b. Down to ca. 250 K the emission spectra are much the same as the absorption spectra and show essentially only the typical Fe(II)-LS ($S=0$) doublet (A) and a small temperature-inde-

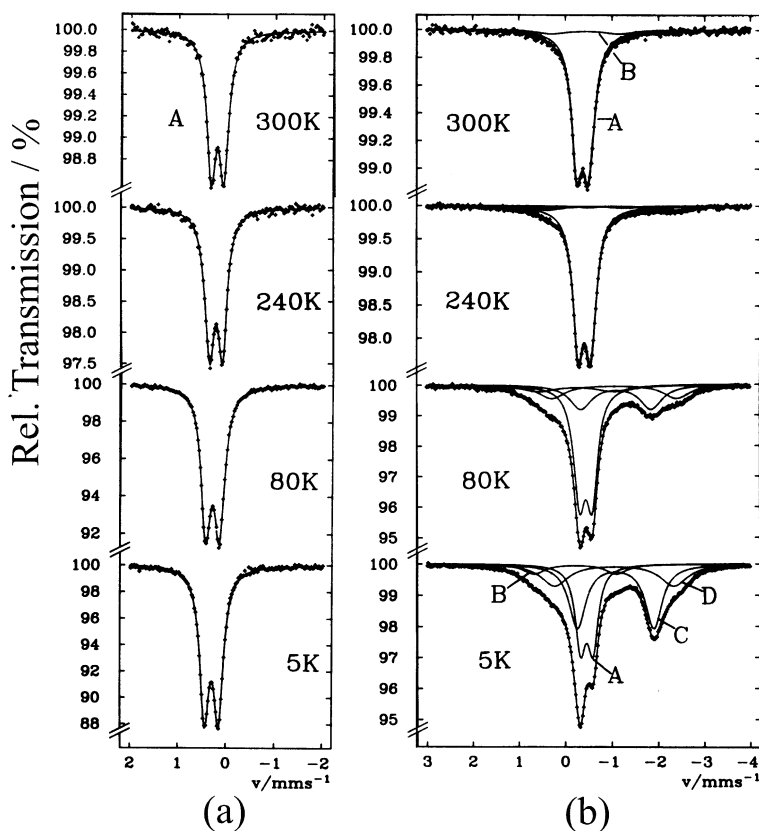


Fig 2 **a** ^{57}Fe Mössbauer absorption spectra of $[\text{}^{57}\text{Fe}/\text{Co}(\text{phen})_3](\text{ClO}_4)_2$ as a function of temperature vs $^{57}\text{Co}/\text{Rh}$ as source (295 K). **b** Time-integral ^{57}Fe Mössbauer emission spectra of $[\text{}^{57}\text{Co}/\text{Co}(\text{phen})_3](\text{ClO}_4)_2$ as source as a function of temperature vs $\text{K}_4[\text{Fe}(\text{CN})_6]$ as absorber (295 K). Assignment: A, Fe(II)-LS; B, Fe(III)-LS; C, Fe(II)-HS1; D, Fe(II)-HS2. In a the source was moved relative to the absorber; in b the absorber was moved relative to the fixed source mounted in the cryostat. For direct comparison the sign of the velocities (x-axis) must be changed either in a or in b [4]

pendent fraction of Fe(III)-LS (B), arising from the loss of a valence electron after the nuclear decay. As the hyperfine interaction of the $^{57}\text{Fe}(\text{II})$ -LS atom with its environment, as reflected by the LS quadrupole splitting, is the same in both the emission and the absorption spectra at all temperatures down to 4.2 K, it is clear that for this fraction of the nuclear events corresponding to the intensity of the LS doublet, there is no observable chemical or physical after-effect; the nucleogenic ^{57}Fe atom is found in its normal electronic and lattice structural environment as expected for a $[\text{Fe}(\text{phen})_3]^{2+}$ complex ion.

The quadrupole doublet B was assigned, on the basis of its isomer shift and quadrupole splitting values, to an Fe(III)-LS species with $S=1/2$. This assignment was confirmed in an emission experiment with the sample placed

in an applied magnetic field; the measured internal hyperfine field was found to be ca. 300 kOe, which is typical for iron(III) compounds with $S=1/2$ ground state [4, 17]. The relative intensity of this species was ca. 10% and remained practically constant over the whole temperature range. This species was assigned to a class I after-effect.

At temperatures below 250 K, two more resonance doublets (C and D in Fig. 2b) appeared in the emission spectra of ^{57}Co labelled $[\text{Co}(\text{phen})_3](\text{ClO}_4)_2$ with increasing intensities at the expense of the Fe(II)-LS doublet. The doublets C and D were assigned to arise from Fe(II)-HS ($S=2$) states. At 4.2 K, according to their area fractions, about half of the nucleogenic ^{57}Fe ions were observed to be “trapped” in metastable Fe(II)-HS states in a formally strong ligand field, with lifetimes comparable to or longer than the Mössbauer time-window τ_M of ca. 10^{-7} s. The *anomalous spin states* (doublets C and D) were originally attributed, on the basis of the large difference in quadrupole splitting, to the two substates $^5\text{A}_1(\text{D}_3)$ and $^5\text{E}(\text{D}_3)$ of the $^5\text{T}_2(\text{O}_h)$ state split by an axially distorted (D_3) cubic ligand field [18]. Doublet C with the smaller quadrupole splitting was assigned to a trigonally elongated octahedron (^5E state), and doublet D with the larger quadrupole splitting to a trigonally compressed octahedron ($^5\text{A}_1$ state).

Very similar findings were observed later with other strong-field complexes, $^{57}\text{Co}(\text{pmi})_3(\text{ClO}_4)_2$ ($\text{pmi}=2$ -pyridinalmethylimine) [19], $^{57}\text{Co}(\text{phen})_2(\text{CN})_2$ [19] and $^{57}\text{Co}(\text{bpy})_3(\text{ClO}_4)_2$ ($\text{bpy}=\alpha,\alpha'$ -bipyridyl) [20], where again the labelled cobalt complexes are high-spin with $^4\text{T}_1$ ground state, but the corresponding iron complexes are low-spin with $^1\text{A}_1$ ground state. As the temperature was lowered, trapped divalent nucleogenic ^{57}Fe species in the HS state appeared with increasing intensity in the Mössbauer emission spectra at the expense of the $^{57}\text{Fe}(\text{II})$ -LS state.

3.2

Intermediate Field (Spin Crossover) Complexes

If the ligand field strength of the host compound is somewhat lowered as in the ^{57}Co -labelled complex $^{57}\text{Co}(\text{phen})_2(\text{NCS})_2$, the iron(II) analogue of which is known to exhibit thermal $\text{LS}(S=0) \leftrightarrow \text{HS}(S=2)$ spin crossover with a transition temperature $T_{1/2} \approx 180$ K [21, 22], one obtains emission spectra as shown in Fig. 3 [23].

On the left of Fig. 3, temperature-dependent Mössbauer absorption spectra of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ clearly demonstrate the occurrence of a sharp spin transition around 180 K from Fe(II)-HS above to Fe(II)-LS below this temperature. On the right of Fig. 3 are shown emission spectra of $^{57}\text{Co}(\text{phen})_2(\text{NCS})_2$ as the Mössbauer source recorded at four different temperatures vs $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ as a Mössbauer absorber (kept at room temperature). Clearly, the dominant or even only signal observed at all temperatures from 296 K down to 4.2 K is the Fe(II)-HS quadrupole doublet, even at temperatures below ca. 180 K, where thermal spin transition occurs to

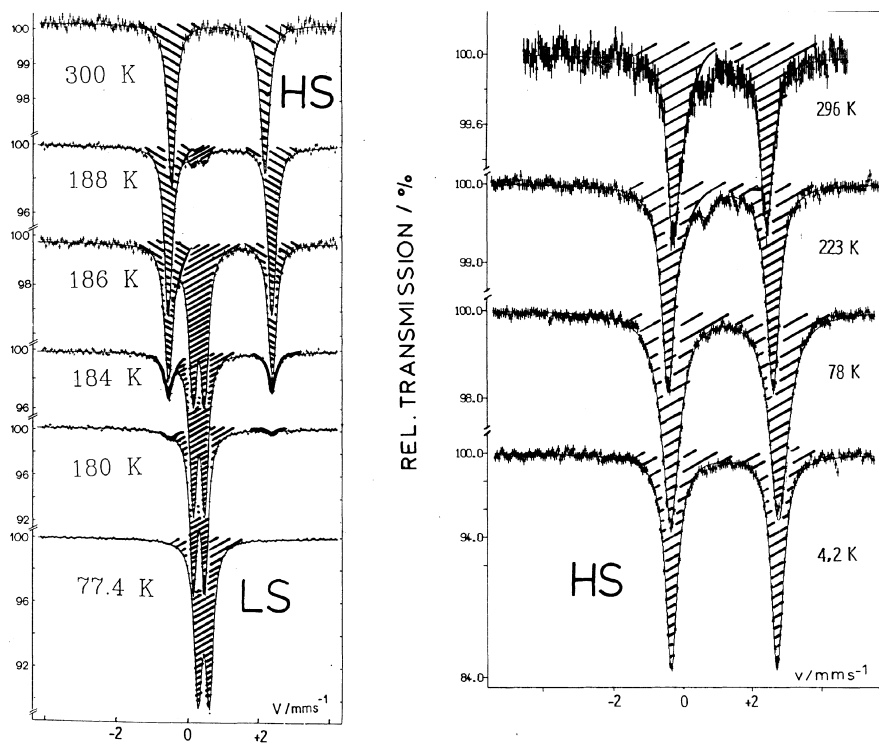


Fig 3 (Left) ^{57}Fe Mössbauer absorption spectra of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ as a function of temperature vs $^{57}\text{Co}/\text{Rh}$ as source (295 K). (Right) Time-integral ^{57}Fe Mössbauer emission spectra of $[\text{Co}(\text{phen})_2(\text{NCS})_2]$ as source as a function of temperature vs $\text{K}_4[\text{Fe}(\text{CN})_6]$ as absorber (295 K). Assignment: The quadrupole doublet with the larger splitting (ca. 3 mm s^{-1}) refers to the Fe(II)-HS state, the one with the smaller splitting (ca. 0.5 mm s^{-1}) to the Fe(II)-LS state [23]

the Fe(II)-LS ground state in the iron(II) complex. Similar behaviour was observed in the Mössbauer emission spectra of $[\text{Co}(\text{bipy})_2(\text{NCS})_2]$ [23], $[\text{Co}(\text{Co}(2\text{-CH}_3\text{-phen})_3)(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}]$ [24], $[\text{Co}(\text{Co}(2\text{-CH}_3\text{O-phen})_3)(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}]$ [25], $[\text{Co}(\text{Co}(2\text{-pic})_3)\text{Cl}_2 \cdot \text{EtOH}]$ [26, 27] and $[\text{Co}(\text{Co}(\text{ptz})_6)(\text{BF}_4)_2]$ [28], where Co(II) again possesses a $^4\text{T}_1$ ground state in all cases, but all the corresponding iron(II) complexes exhibit thermal spin crossover. Obviously, in all these Fe(II) spin crossover systems metastable Fe(II)-HS states originating from the ^{57}Co nuclear decay are trapped and observed, to nearly 100% of all decay events, in the “Mössbauer window” of ca. 100 ns after nuclear decay, whereas the ground state of Fe(II) in the same ligand surroundings at comparable temperatures below the spin transition temperature is LS ($^1\text{A}_1$). Thus the Mössbauer emission studies of the ^{57}Co labelled spin crossover compounds enabled direct identification of the excited state as the $^5\text{T}_2(\text{O}_h)$ HS state. The lifetimes of the trapped HS states are definitely longer

than τ_M , and the initial population (at the opening time of the Mössbauer window) is close to unity, $n_{HS}(t=0)=1$.

Wei et al. reported a MES study of the systems $[^{57}\text{Co}(\text{ppi})_2(\text{NCS})_2]$ ($\text{ppi}=\text{N-phenyl-2-pyridinalimine}$) and $[^{57}\text{Co}(\text{bpi})_2(\text{NCS})_2]$ ($\text{bpi}=\text{N-benzyl-2-pyridinalimine}$) [29]. The corresponding iron(II) compounds show spin crossover behaviour. From the temperature dependent Mössbauer absorption spectra it is inferred that the ligand field strength is somewhat stronger in the ppi system than in the bpi system; at 78 K, the ppi complex of iron(II) shows still ca. 50% HS and 50% LS state, whereas the bpi complex of iron(II) shows only HS behaviour at all temperatures under study. Interestingly, the Mössbauer emission spectrum of the ppi complex shows a mixture of nucleogenic $^{57}\text{Fe}(\text{II})\text{-HS}$ and $^{57}\text{Fe}(\text{II})\text{-LS}$ states (ca. 3:1 ratio) at 78 K, whereas that of the bpi complex shows, as expected for a weak field complex, only $\text{Fe}(\text{II})\text{-HS}$ at all temperatures down to 78 K.

3.3

Weak Field Complexes

If the ligand field strength of an octahedral iron(II) complex with nitrogen donating ligands of the above kind is reduced further such that the HS state is

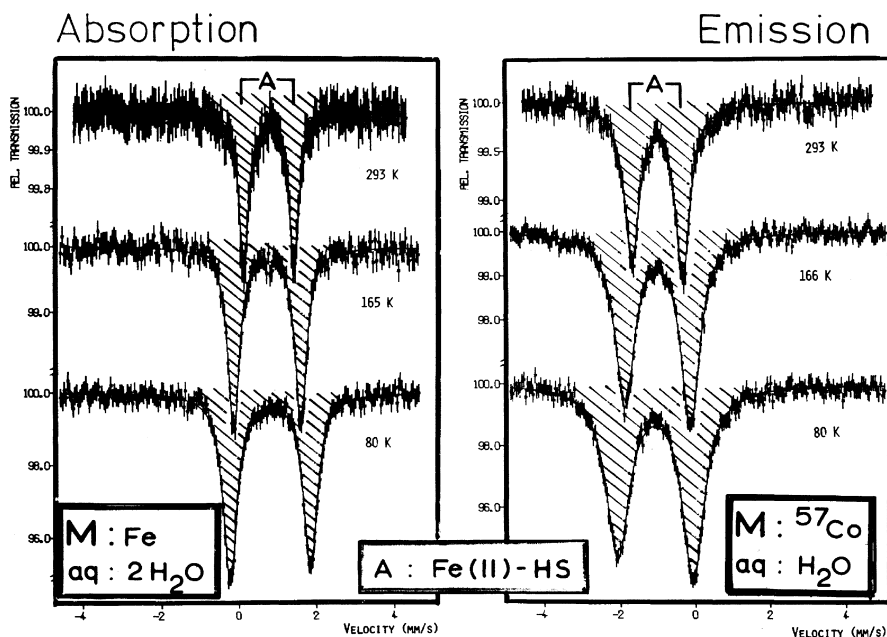


Fig 4 (Left) ^{57}Fe Mössbauer absorption spectra of $[\text{Fe}(\text{2-Cl-phen})_3](\text{ClO}_4)_2 \cdot \text{aq}$ as a function of temperature vs $^{57}\text{Co}/\text{Rh}$ as source (295 K). (Right) Time-integral ^{57}Fe Mössbauer emission spectra of $[^{57}\text{Co}/\text{Co}(\text{2-Cl-phen})_3](\text{ClO}_4)_2 \cdot \text{aq}$ as source as a function of temperature vs $\text{K}_4[\text{Fe}(\text{CN})_6]$ as absorber (295 K). The only quadrupole doublet observed in both the absorption and emission spectra at all temperatures refers to the $\text{Fe}(\text{II})\text{-HS}$ state [30, 31]

stabilized exclusively, one should expect that the only $^{57}\text{Fe(II)}$ species observed in the emission spectra of the corresponding ^{57}Co labelled source compound would be HS independent of temperature. This has been fully confirmed by measuring the Mössbauer absorption and emission spectra of $[\text{M(2-Cl-phen)}_3](\text{ClO}_4)_2$ ($\text{M} = ^{57}\text{Fe}, ^{57}\text{Co}$) [30, 31]; cf. Fig. 4. The substitution of the hydrogen atom in the 2-position of the phen ligand reduces the basicity of the coordinating nitrogen atom, which in turn weakens the metal-ligand bond strength such that the iron(II) compound becomes high-spin at all temperatures down to 4.2 K [31, 32]. The quadrupole splitting observed in both the absorption and emission spectra is the same; even its temperature function is the same. Therefore, possible structural damage of the nearby surroundings as a consequence of the nuclear decay has either annealed within times shorter than τ_{M} , or it is so small that it is not “felt” by the ^{57}Fe nucleus. The only difference between the absorption and emission spectra is the broader line width in the emission spectra (which is often observed in emission spectra, most likely due to lattice inhomogeneities in the source compound).

3.4

Matrix Influence

NIESST experiments have also been carried out with $[\text{}^{57}\text{Co}_x\text{M}_{1-x}(\text{phen})_3](\text{ClO}_4)_2$ ($\text{M} = \text{Fe, Ni, Co, Zn}$; $x = 0.001$) as Mössbauer sources vs $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ as absorber, in order to investigate the matrix influence, particularly the effect of different M^{2+} radii leading to different local pressure, on the relaxation rate of the metastable NIESST state ($^5\text{T}_2$). At a given temperature, the intensity of the nucleogenic $^{57}\text{Fe(II)}$ -HS resonances was found to increase with increasing M^{2+} radius in the series $\text{M}^{2+} = \text{Fe}$ (61 pm in LS state) $< \text{Ni}$ (70 pm) $< \text{Co}$ (74 pm) $< \text{Zn}$ (75 pm) [4, 17]. A selection of relevant emission spectra recorded at 4.2 K is shown in Fig. 5.

In view of the fact that the Fe(II) -HS ion has the largest M^{2+} radius, 78 pm, of all metal ions involved in this study, it is expected that the host with the smallest M^{2+} ion, which is the Fe(II) -LS ion with a M^{2+} radius of 61 pm, should have the lowest probability of formation of $^{57}\text{Fe(II)}$ -HS after NIESST. This is indeed the case as can be seen from the Mössbauer emission spectra depicted in Fig. 5. The intensities of the quadrupole doublets HS 1 and HS2, recorded at a given temperature (4.2 K in this case) increase with increasing M^{2+} radius, i.e. in the above order. In Fig. 6 are plotted the relative intensities of the Fe(II) -HS states (sum of HS1 and HS2) as a function of temperature as derived from the area fractions of the Fe(II) -HS quadrupole doublets for all four host lattices under study. The increase of the HS intensities is highest in the Zn host with the largest M^{2+} radius, and lowest in the Fe compound with the smallest M^{2+} radius. Interestingly, whereas the intensities change continuously in the Fe, Ni and Zn matrices, the HS intensity in the case of the Co host shows a sharp increase with decreasing temperature

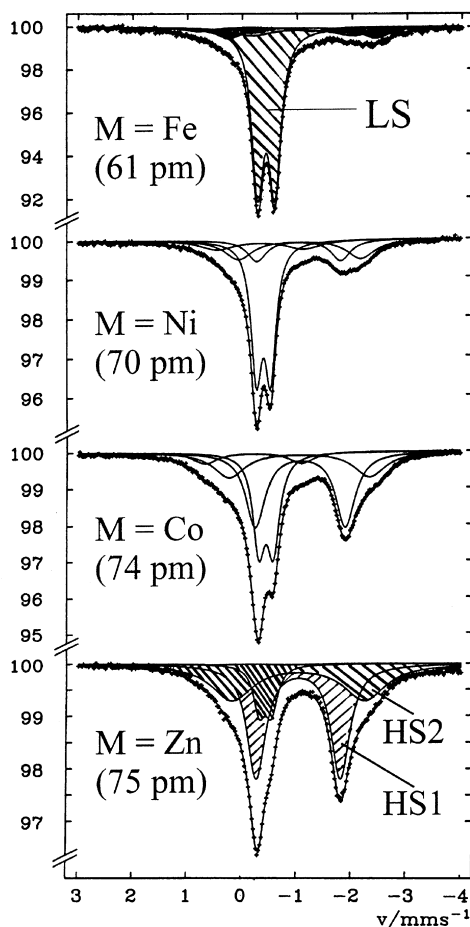


Fig 5 ^{57}Fe Mössbauer emission spectra of $[\text{}^{57}\text{Co}/\text{M}(\text{phen})_3](\text{ClO}_4)_2$ vs $\text{K}_4[\text{Fe}(\text{CN})_6]$ recorded at 4.2 K. The spectra show increasing intensities of the nucleogenic $^{57}\text{Fe}(\text{II})$ -HS doublets with increasing M^{2+} radius due to decreasing local pressure [4]

down to ca. 170 K, then merges into a plateau down to ca. 30 K and then increases sharply again. In a separate X-ray powder diffraction study between 300 and 90 K a drastic lattice contraction near 170 K was observed [17]. The matrix influence as derived from these investigations can be explained qualitatively on the basis of the different local pressure exerted by the different sizes of the M^{2+} ions: the smaller the M^{2+} radius, the less space is available for the formation of nucleogenic $^{57}\text{Fe}(\text{II})$ -HS species and the higher the tendency to relax immediately down to the $\text{Fe}(\text{II})$ -LS state, i.e. the shorter is the lifetime of the HS state. We shall see later that these observations can be put

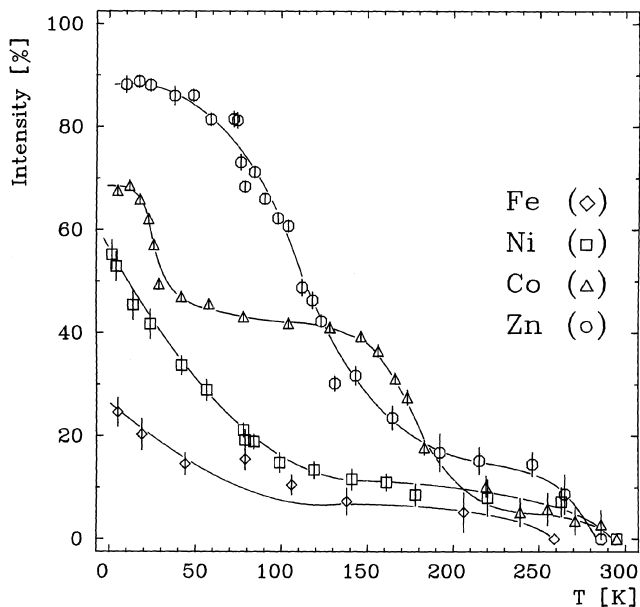


Fig 6 Intensity of the $^{57}\text{Fe(II)}$ -HS quadrupole doublets relative to the sum of the Fe(II) -HS and Fe(II) -LS intensities observed in the ^{57}Fe Mössbauer emission spectra of the system $[\text{}^{57}\text{Co}_x/\text{M}_{1-x}(\text{phen})_3](\text{ClO}_4)_2$ ($x=0.001$; $\text{M}=\text{Fe, Ni, Co, Zn}$) as a function of temperature [4, 17]

on a more solid footing within the framework of the LIESST mechanism and the key feature therein, namely the *inverse energy gap law*.

4 Lifetime Measurements of Trapped HS States by Time-Differential Mössbauer Emission Spectroscopy

4.1 Experimental Results

So far we have described experiments with *Time-Integral Mössbauer Emission Spectroscopy* (TIMES), where the spectra are recorded by collecting the 14.4 keV gamma quanta resulting from the decaying first excited nuclear level of ^{57}Fe in the source compound, irrespective of their individual lifetimes. This is also the usual technique in ^{57}Fe Mössbauer absorption spectroscopy with a commercially available source like $^{57}\text{Co}/\text{Rh}$ and an iron-containing compound under study as absorber. The fact that TIME spectra of ^{57}Co -labelled complexes corresponding to strong-field iron complexes, like $[\text{}^{57}\text{Co}/\text{Co}(\text{phen})_3](\text{ClO}_4)_2$, exhibited resonance signals of trapped Fe(II) -

HS species in the low-temperature region, with increasing intensity as the source material was cooled further, was the stimulus to design and construct a *delayed-coincidence spectrometer* for *Time-Differential Mössbauer Emission Spectroscopy* (TDMES). The goal was to determine the initial population of the metastable Fe(II)-HS states at the opening of the Mössbauer window and to measure their actual lifetimes in the Mössbauer time window τ_M . A first description of such a delayed-coincidence spectrometer with a time-resolution of 13 ns (ca. 10% of the lifetime of the 14.4 keV Mössbauer level) and its successful operation for lifetime measurements on the polycrystalline $[^{57}\text{Co}/\text{Co}(\text{phen})_3](\text{ClO}_4)_2$ system as a Mössbauer source at variable temperatures was communicated by Grimm et al. [18]. The TDME spectra recorded for four different time windows between 0 and 210 ns at four different temperatures (10, 25, 47 and 80 K) and corrected for random coincidences showed clearly a significant increase in the relative intensity of the metastable $^{57}\text{Fe}(\text{II})$ -HS states with decreasing time delay after the nuclear decay. The derived lifetimes of the $^{57}\text{Fe}(\text{II})$ -HS states were found to be 390 ns (10 K), 300 ns (25 K), 205 ns (47 K) and 100 ns (80 K), and their initial population (at the time of opening the Mössbauer window) was found to be 1.0 at all three temperatures. The temperature dependence of the lifetimes is plotted in Fig. 7 as $\log(s/\tau)$ vs $10^3 \text{ K}/T$.

The graph shows the four data points derived from the time-delayed coincidence measurements and two (at 4.2 and 223 K) from time-integral measurements. At around 220 K the lifetime was found to rise steeply with decreasing temperature and to become nearly temperature-independent below 25 K. At higher temperatures the function $\log(1/\tau)$ vs T^{-1} is linear. This behaviour is indicative of a tunnelling relaxation mechanism with Arrhenius type thermal assistance at higher temperatures. The dashed line in Fig. 7 was calculated using a model which accounts for an Arrhenius type process at high temperatures and T-independent tunnelling at low temperatures [18]. The initial populations of the metastable Fe(II)-HS states (at the time of opening the Mössbauer window) were assumed to be 100% in the application of this model.

In a first attempt to explain the formation mechanism for the anomalous spin states [18], two possibilities were suggested. First, in times shorter than τ_M , the anomalous spin states are adjusted as ground states in a weakened metastable ligand field resulting from the creation of defects in the ligand sphere. This metastable ligand sphere relaxes within the Mössbauer time window τ_M to the normal strong-field of the tris-phen complex and induces spontaneous spin state conversion from HS to LS. Second, the defects in the ligand sphere relax relatively fast restoring the strong ligand field before the Mössbauer time window opens. The HS states are trapped as metastable states and decay via electronic relaxation processes to the LS state within the Mössbauer time window. With regard to the Tanabe-Sugano diagram for d^6 complexes the former relaxation scheme was termed *horizontal* and the lat-

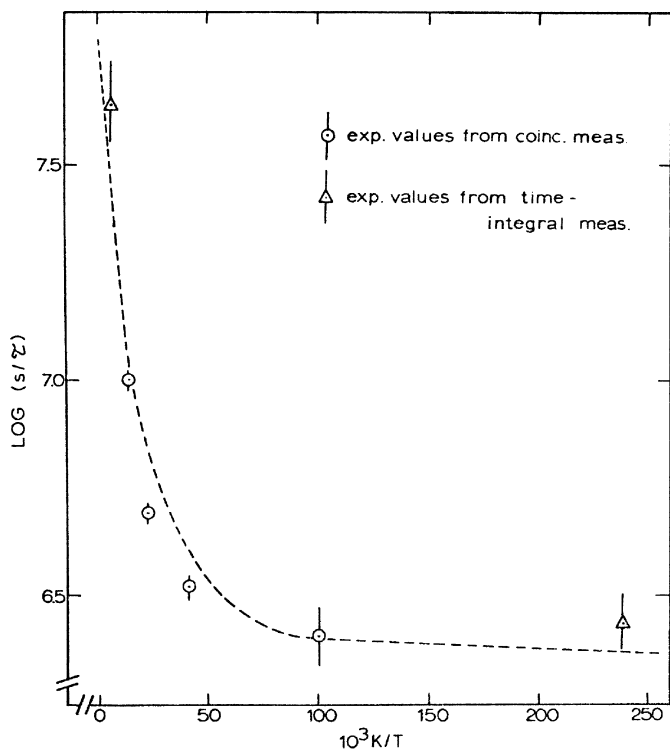


Fig 7 $\text{Log}(s/\tau)$, where τ is the lifetime of the metastable Fe(II)-HS states, vs. $10^3 K/T$ (T =temperature). The dashed line was calculated using a model which accounts for an Arrhenius type process at elevated temperatures and T -independent tunnelling in the low temperature regime [18]

ter *vertical* relaxation,. In the latter case it was argued that the rate-determining process takes place radiationless by creation of phonons, and that the only way of overcoming the highly spin forbidden $\Delta S=2$ transition down to the $^1A_1$ state of $^{57}\text{Fe(II)-LS}$ is by involving the $^3T_{1,2}$ states via spin-orbit coupling. We shall see next that support for this relaxation mechanism has been provided from studies of the related LIESST phenomenon.

With the discovery of the “*Light Induced Excited Spin State Trapping* (LIESST)” in 1984 [33, 34], where long-lived metastable Fe(II)-HS states were first observed by irradiation of an iron(II) spin crossover complex with a light source, a new basis was available for better understanding of the relaxation mechanism for the metastable Fe(II)-HS states created by nuclear decay of ^{57}Co (NIESST effect). It was suggested that it follows the same (*vertical*) decay mechanism as for the metastable LIESST states, i.e. via two successive intersystem crossing processes involving the ligand-field triplet states. Although the lifetimes derived from the TDMES and optical excita-

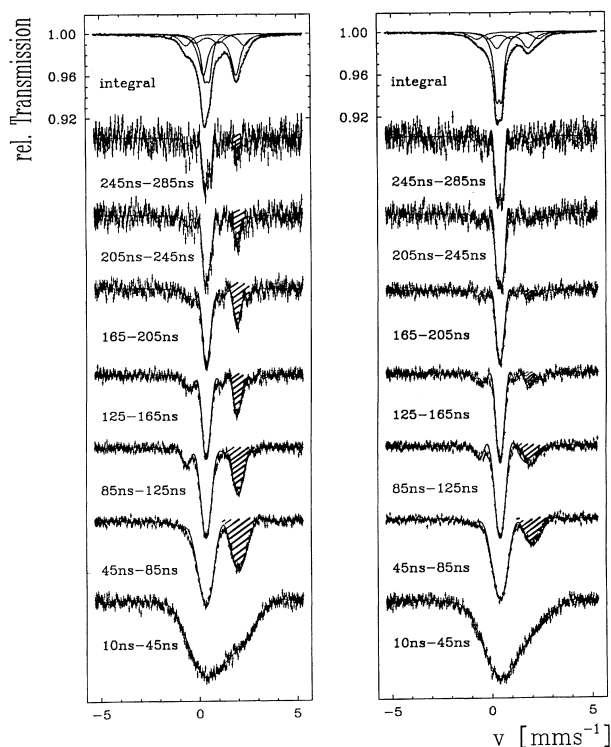


Fig 8 Time dependent ^{57}Fe Mössbauer emission (TDME) spectra of $^{57}\text{Co}/\text{Co}(\text{phen})_3(\text{ClO}_4)_2$ recorded at 40 K (left) and 80 K (right) vs $\text{K}_4[\text{Fe}(\text{CN})_6]$ as absorber (295 K) [37]

tion measurements were quite comparable, the relative initial populations of the trapped Fe(II)-HS states in the case of strong-field complexes, however, were considerably different (1.0 in NIESST, and significantly lower in LIESST). This discrepancy, together with the hope of being able to follow the decay kinetics of the two nucleogenic Fe(II)-HS states separately, has encouraged us to repeat the TDMES experiments with a much improved coincidence spectrometer [35, 36]. The new spectrometer had a much higher count rate (factor 20) and the use of a microcomputer system allowed us to record 256 time-resolved spectra simultaneously, covering a time range of about 400 ns with a resolution of ca. 3 ns.

Using this new setup, the system $^{57}\text{Co}/\text{Co}(\text{phen})_3(\text{ClO}_4)_2$ was re-investigated [37], and two series of selected TDME spectra recorded at 40 and 80 K with comparable time windows in each series are displayed in Fig. 8. With reference to the resonance signal at about 2 mm s^{-1} , which represents the high velocity components of the Fe(II)-HS quadrupole doublets, two important features become apparent. First, the relative intensity of this signal increases with decreasing delay times after the nuclear decay. Second,

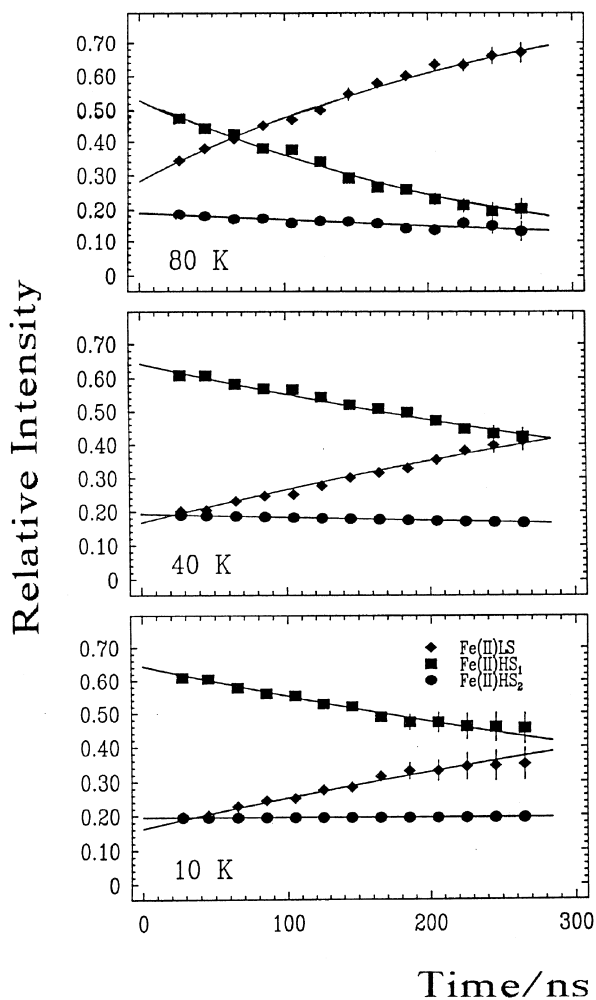


Fig 9 Time dependence of the relative intensities of the metastable Fe(II)-HS1 and Fe(II)-HS2 states and the Fe(II)-LS state derived from the TDME spectra of $[\text{}^{57}\text{Co}/\text{Co}(\text{phen})_3](\text{ClO}_4)_2$ recorded at 10, 40 and 80 K [37]

for comparable time windows the relative intensity of this signal decreases with increasing temperature. Interestingly, this signal, like the Fe(II)-LS signal near zero velocity, broadens considerably with shorter delay times after the nuclear decay; this broadening effect is a consequence of the Heisenberg Uncertainty Principle. The time dependence of the relative intensities of the Fe(II)-LS state and the separate Fe(II)-HS1 and Fe(II)-HS2 states derived from the TDME spectra recorded at 10 K, 40 K and 80 K are shown in Fig. 9.

The lifetimes of the metastable Fe(II)-HS states determined in this re-investigation were higher by a factor of 1.5–2 compared to those of the earlier TDMES study by Grimm et al. [18]; the new data were found to be 645 ns (10 K), 660 ns (40 K) and 260 ns (80 K) for the Fe(II)-HS1 state, and $>10^4$ ns (10 K), ~ 2500 ns (40 K) and 800 ns (80 K) for the Fe(II)-HS2 state [37]. These differences were ascribed to a slightly different source preparation. It has been proposed that the slow decay rate for the Fe(II)-HS2 state (at 40 K a factor of 40 slower than for the Fe(II)-HS1 state) is determined by the relaxation of the metastable ligand sphere (probably with a long-lived defect from radiolysis such as a broken bond or an electron hole, which explains also the difference in the quadrupole splitting), while the faster decay kinetics of the Fe(II)-HS1 state is determined by electronic processes in an intact strong-field lattice site. The lifetimes of the Fe(II)-HS1 state are very comparable to those determined by laser excitation of $[\text{Fe}(\text{phen})_3]^{2+}$ complexes embedded in a Nafion foil [5]. The relative initial populations, which could be determined separately for the three nucleogenic species, were found to be 0.16 (10 K), 0.14 (40 K) and 0.22 (80 K) for the Fe(II)-LS state, 0.55 (10 K), 0.57 (40 K) and 0.49 (80 K) for the Fe(II)-HS1 state, and 0.17 (10 K), 0.17 (40 K) and 0.17 (80 K) for the Fe(II)-HS2 state. Thus, they are quite different from the 100% initial populations found in the previous TDME experiments [18]. The relative initial population of the HS states of the complex obtained by optical excitation was estimated to be ca. 80% in the case of the strong-field $[\text{Fe}(\text{phen})_3]^{2+}$ complexes embedded in a Nafion foil [5].

In order to confirm these results, we have conducted similar experiments using nearly identical samples of another strong-field system under entirely comparable conditions in the MES study and the optical excitation study. The compound $[\text{Mn}(\text{bipy})_3](\text{PF}_6)_2$ was chosen as a matrix for ^{57}Co -labelling as a source for TDME measurements on the one hand and for Fe-doping of a single crystal for optical relaxation measurements after laser excitation on the other hand. The $[\text{Mn}(\text{bipy})_3](\text{PF}_6)_2$ matrix was chosen for several reasons. First, the tris-bipy ligand sphere is known to form Fe(II)-LS complex molecules with $^1\text{A}_1$ ground state, not only when prepared as the neat iron compound, but also when Fe(II) is doped in low concentration into a tris-bipy coordination compound with any transition metal ion irrespective of the spin state, as was discussed in the case of the tris-phen complexes above. This was confirmed by conventional Mössbauer absorption measurements. Therefore, $^{57}\text{Co}/\text{Mn}(\text{bipy})_3](\text{PF}_6)_2$ as a Mössbauer source was expected to behave very similarly to the related tris-phen complexes discussed above, with regard to both the time-integral and time-differential measurements. Second, the absence of charge transfer bands of the Mn complex in the visible region allowed us to measure the lifetime of the transient HS state of the Fe(II) dopant optically. Third, the paramagnetic behaviour of the Mn metal sites causes fast fluctuation of the spin of the aliovalent Fe(III) state by magnetic spin-spin coupling, so that in MES experiments the line shape of the

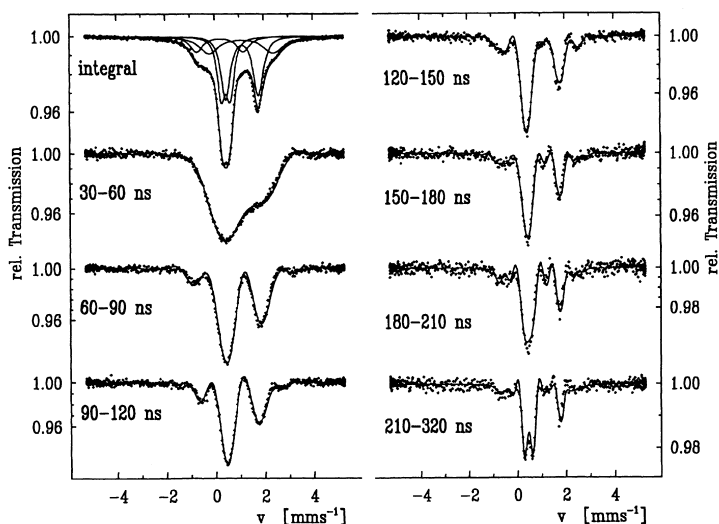


Fig 10 Time-integral ^{57}Fe Mössbauer emission (TIME) spectrum (top) and time-differential ^{57}Fe Mössbauer emission (TDME) spectra of $[\text{}^{57}\text{Co}/\text{Mn}(\text{bipy})_3](\text{PF}_6)_2$ recorded at 83 K vs $\text{K}_4[\text{Fe}(\text{CN})_6]$ as absorber (295 K) [38]

Fe(III) doublet (which shows up to a considerable extent in most emission spectra of strong-field complexes) could be treated as Lorentzian within the fast relaxation limit. Time-integral (TIME) measurements with a $40\text{-}\mu\text{Ci}$ source of $[\text{}^{57}\text{Co}/\text{Mn}(\text{bipy})_3](\text{PF}_6)_2$ were carried out over the temperature range from 4.2 K to room temperature [38, 39]. The spectra resembled closely those obtained from the tris-phen complexes described above, with resonances of the same four iron species: $^{57}\text{Fe(II)-LS}$ with decreasing intensity, Fe(II)-HS1 and Fe(II)-HS2 with increasing intensities on lowering the temperature, and a temperature-independent fraction of Fe(III)-LS ($S=1/2$). Time-differential (TDME) measurements were performed at 83, 104 and 170 K. A measuring time of ca. two weeks was needed to obtain spectra of the quality shown in Fig. 10.

As in the case of the TDME spectra of the tris-phen source, the signal appearing near 2 mm s^{-1} shows clearly the decay of the HS excited state with increasing time delay after the nuclear decay of ^{57}Co . The lifetimes derived for the two temperatures of 83 and 104 K are inserted in Fig. 11 together with the data of the lifetime measurements by laser excitation of a single crystal of $[\text{Mn:Fe}(0.05\%)(\text{bipy})_3](\text{PF}_6)_6$ [38]. As can be seen from Fig. 11, where the logarithm of the decay rate $k_{\text{H/L}}$ (s^{-1}) of the transient electronic states are plotted as a function of $1/T$, the two data points (500 ns at 80 K and 110 ns at 104 K) derived from TDME measurements match very well those from the laser excitation measurements. Thus it can be safely concluded that the fast relaxing transient electronic state of the nucleogenic $^{57}\text{Fe(II)}$

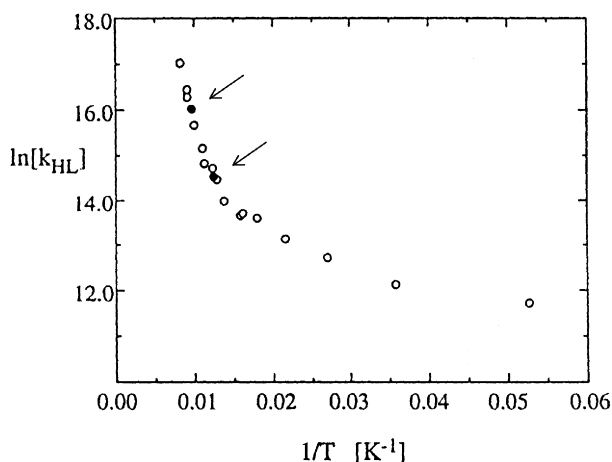


Fig 11 The logarithm of the decay rate k_{HL} (s^{-1}) of the transient electronic state in single crystals of $[Mn:Fe(0.05\%)(bipy)_3](PF_6)_2$ after laser excitation at 532 nm (*open circles*) and from TDMES of $[^{57}Co/Mn(bipy)_3](PF_6)_2$ (*arrows*) vs. $1/T$ [38]

species, Fe(II)-HS1, is identical to the metastable excited state from laser excitation. The second HS state, Fe(II)-HS2, the quadrupole splitting of which is nearly twice as large, did not decay in this matrix within the Mössbauer time window τ_M up to room temperature [38, 39]. As in the case of the trisphen complex, this doublet was attributed to a distorted environment resulting either from a defect or a missing electron in the ligand sphere as a consequence of the nuclear decay (type I after-effect), which would weaken the ligand field strength and therefore stabilize the HS state.

The initial populations derived from the TDME experiments turned out to be nearly independent of temperature up to ca. 40 K. At 80 K, it changes by ca. 10% in the case of Fe(II)-HS1, whereas it is constant for Fe(II)-HS2. It has been proposed [5] that the branching ratio, being a property of the relaxation cascade before the opening of the Mössbauer time window (τ_M), is determined by the transient temperature of the “thermal spike” relative to the lattice temperature. We believe that the transient temperature of the thermal spike determines the branching ratios at low lattice temperatures, and only at lattice temperatures higher than the transient one does a lower population of the Fe(II)-HS state result. On these grounds and in view of the different excitation energies involved in the LIESST and NIESST phenomena it cannot be expected that the initial populations in optical and in MES experiments are the same.

4.2

Formation and Decay Mechanism of NIESST States

We recall that the ^{57}Fe Mössbauer spectroscopic techniques described above have their characteristic time windows. In the usual time-integral technique (TIMES) the 14.4 keV γ -quanta from the decaying first excited nuclear level are collected without any time-differentiation in a window of about 140 ns corresponding to the mean lifetime of the 14.4 keV nuclear state of ^{57}Fe . In the TDMES technique the nuclear decay events are recorded in smaller time windows of typically 40 ns covering a total range of about 100–500 ns, with a resolution of less than 5 ns. Resonance lines with time-dependent intensities and broadening effects (in addition to those due to the Heisenberg Uncertainty Principle) in the TDME spectra are diagnostic of formation and relaxation processes with rates corresponding to lifetimes in the 100–500 ns range. Metastable after-effect species with lifetimes shorter than 100 ns after the nuclear decay of ^{57}Co cannot be resolved by conventional ^{57}Fe Mössbauer spectroscopy. Nevertheless, there are data and arguments, partly from model calculations and partly by extrapolation of experimental findings back to $t=0$ at nuclear disintegration, which can be used to construct the following qualitative time sequence of after-effects following the $^{57}\text{Co}(\text{EC})^{57}\text{Fe}$ decay in chemical compounds [4], leading ultimately to the Mössbauer time windows with spin and charge state relaxation therein.

- $t=0$ s: $^{57}\text{Co}(\text{EC})^{57}\text{Fe}$ decay, immediately followed by dilatation of electron shells, emission of conversion and Auger electrons and X-rays, leading to
- ⇒ Highly charged species
 - ⇒ Radiolysis of ligands leading to electron deficiency and ligand radicals
 - ⇒ Local heating
 - ⇒ Electronic excitation
- $t \approx 10^{-15}$ s: Electron recombination
- ⇒ Normal and aliovalent charge states
 - ⇒ Excited ligand field states
 - ⇒ Local pressure (size effect)
 - ⇒ Vibrational excitation
- $t \approx 10^{-13}$ s: Lattice vibrational relaxation
- ⇒ Fast relaxation of local heat (*thermal spikes*) and pressure
 - ⇒ Geometrical rearrangement of ligand sphere and
 - ⇒ New bond formation, both leading to change of ligand field potentials
- $t \approx 10^{-12}$ s: Fast optical transitions (spin and parity allowed)
- ⇒ Fast relaxation of excited CT and ligand field states
 - ⇒ Fast intra-molecular electron transfer and
 - ⇒ Fast redox reactions, both leading to stabilization of aliovalent charge states

- $t \approx 10^{-11}$ s: Slow relaxation of local heat
 $\Rightarrow$ Cooling down of “thermal spikes”
- $t > 10^{-9}$ s: Time-Differential Mössbauer Emission Spectroscopy (TDMES)
 $\Rightarrow$ Lifetime measurements of transient after-effect species,
 i.e. decaying aliovalent charge states and excited spin states,
 in the time range of 5–500 ns
- $t \approx 10^{-7}$ s: Time-Integral Mössbauer Emission Spectroscopy (TIMES)
 $\Rightarrow$ Observation of long-lived aliovalent charge states and excited
 spin states, resulting from after-effects described in section 2.2
 in the “Mössbauer time window” $\tau_M \approx 10^{-7}$ s.

The TDMES measurements described in the previous section have proven that metastable nucleogenic Fe(II)-HS states exist even on the nanosecond time scale [18, 38, 39] with initial populations of around 80%. The lifetimes of such metastable spin states are very similar to those found in lifetime measurements after optical excitation. This lends support to the conclusion that the relaxation of nucleogenic metastable $^{57}\text{Fe(II)-HS}$ states follows the same mechanism as that proposed for LIESST. It is this identity which has led us to denote this special after-effect phenomenon as *nuclear-decay-induced excited spin state trapping*, abbreviated as NIESST. The difference obviously lies mainly in the excitation step, which is optical excitation using an external light source in LIESST, and the nuclear decay event as an intrinsic molecular excitation source in NIESST. The decay scheme developed for LIESST [34, 40] and reverse-LIESST [41] shown in Fig. 12 explains the relaxation mechanism for both phenomena LIESST and NIESST.

Relaxation of the LIESST state has been described in detail in the Chapter by Hauser in this volume. LIESST is initiated by irradiating the sample with green light (514 nm of an Ar ion laser) at sufficiently low temperatures into the $^1\text{A}_1 \rightarrow ^1\text{T}_{1,2}$ absorption bands with two subsequent fast intersystem crossing steps via the spin triplet states populating finally the metastable spin quintet state $^5\text{T}_2$. NIESST is initiated by the nuclear decay event $^{57}\text{Co(EC)}^{57}\text{Fe}$, which releases much higher energy initially, much of it is transmitted to the electron shells leading to highly excited and—very shortly after the nuclear decay—highly positively charged species. Fast electron recombination occurs forming *normal* charge states (e.g. $^{57}\text{Fe(II)}$) in NIESST experiments with $^{57}\text{Co(II)}$ compounds) and to some extent *aliovalent* charge states (usually differing by no more than one unit from the charge state of the parent nuclide) on the nanosecond time scale. Highly excited Fe(II) ions with d^6 electron configuration populate, according to the relevant Tanabe-Sugano diagram, excited spin singlet, triplet and quintet states in an octahedral ligand field. It is expected that spin-allowed ($\Delta S=0$) transitions will feed promptly the stable ground state $^1\text{A}_1$ and the metastable $^5\text{T}_2$ state contributing to their *initial populations* (at the time the Mössbauer window opens). These states, however, are not only populated through prompt transitions, but also via the

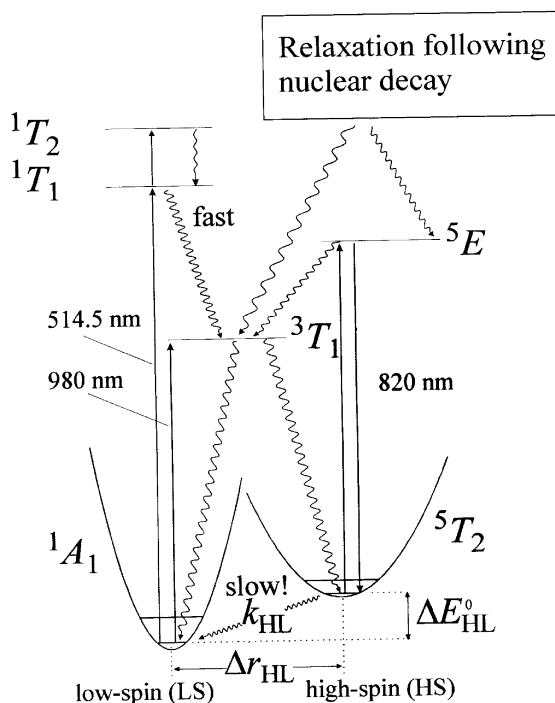


Fig 12 Relaxation scheme for light-induced excited spin state trapping (LIESST) and nuclear decay-induced excited spin state trapping (NIESST) [40]

double intersystem crossing processes $^1T_{1,2} \rightarrow ^3T_1 \rightarrow ^5T_2$ and $^5E \rightarrow ^3T_1 \rightarrow ^1A_1$, respectively; these decay pathways have been found to be very fast due to second-order spin-orbit coupling of the $^3T_1$ state to the spin quintet and the spin singlet states, respectively. The decay kinetics of the metastable $^5T_2$ state can be described by a nonadiabatic multiphonon relaxation model as discussed in the previous chapter by A. Hauser. The two quantities which determine the decay rate k_{HL} are the energy difference between the lowest vibronic levels, ΔE_{HL}^0 , and the difference between the metal-ligand bond distances of the metastable HS state and the LS ground state, Δr_{HL} . The larger Δr_{HL} , the longer the lifetime of the metastable $^5T_2$ state. However, since this quantity is limited to roughly 10% only, which is known from crystal structure determination (the Fe(II)-to-donor atom distance is typically 220 pm in the HS state and 200 pm in the LS state), its importance for the decay kinetics is only marginal. More important is the quantity ΔE_{HL}^0 which depends on the ligand field strength felt by the nucleogenic $^{57}\text{Fe(II)}$ -HS ion when it has reached the $^5T_2$ state. The weaker the ligand field strength, the smaller is ΔE_{HL}^0 and the longer is the lifetime of the metastable $^5T_2$ state (*reduced energy gap law*). This agrees with the experimental results, where the population

of the $^5T_2$ state is found to be much more pronounced in the Mössbauer emission spectra of spin crossover complexes (with intermediate ligand field strength) than in a strong-field system like $[M(\text{phen})_3]^{2+}$ or $[M(\text{bipy})_3]^{2+}$. The “*reduced energy gap law*” for radiationless transitions, originally introduced by Buhks et al. [42] was demonstrated by Hauser [43] to be obeyed also by LIESST state relaxation in Fe(II) spin crossover complexes. The good agreement between the lifetime data from LIESST and NIESST relaxation studies indicates that it is also obeyed in the NIESST state relaxation mechanism.

5

Other NIESST Experiments

More recent NIESST experiments have been performed with the systems $[^{57}\text{Co}/\text{Co}(\text{bpy})_3][\text{MCr}(\text{ox})_3]$ ($M=\text{Li}, \text{Na}$) and $[^{57}\text{Co}/\text{Co}(\text{bpy})_3][\text{Mn}^{\text{II}}_2(\text{ox})_3]$ as Mössbauer sources. These systems possess a cubic structure, where the ^{57}Co -labelled cationic complex molecules are accommodated in cavities of slightly differing dimensions [44]. The a axis is smallest (15.387 Å) in the network with Li^+ and largest in that with $\text{Mn}(\text{II})$. Thus it is expected that in the former case the relaxation of the nucleogenic $^{57}\text{Fe}(\text{II})$ -HS state after NIESST will be faster due to the somewhat higher local pressure as compared to the latter case. This has indeed been observed in the Mössbauer emission spectra. The intensity of the $^{57}\text{Fe}(\text{II})$ -HS resonances at a given temperature is larger in the system with $\text{Na}^+\text{Cr}^{3+}$ than in that with $\text{Li}^+\text{Cr}^{3+}$, but is largest in the host with $(\text{Mn}^{2+})_2$ [45, 46]. These results are again consistent with the “*reduced energy gap*” law.

The NIESST effect was recently studied for the first time in Co(II) spin crossover compounds, namely $[^{57}\text{Co}/\text{Co}(\text{terpy})_2]\text{X}_2 \cdot n\text{H}_2\text{O}$ ($\text{X}=\text{ClO}_4^-$, $n=1/2$, $\text{X}=\text{Cl}^-$, $n=5$), where terpy is the tridentate ligand terpyridine. The perchlorate salt shows thermal spin crossover with $T_{1/2}$ around 200 K and a high spin fraction of nearly 100% at room temperature, whereas the chloride salt apparently possesses a somewhat stronger ligand field giving rise to thermal spin transition at much higher temperatures (the HS fraction starts to rise around 200 K, reaches ca. 20% at 320 K and obviously would increase further) [47]. Conventional Mössbauer absorption measurements were performed on the corresponding systems doped with 5% Fe(II), which was found to be in the LS ($S=0$) state at all temperatures under study [47]. The emission spectra of the ^{57}Co labelled cobalt complexes were measured using a new home-made resonance detector, which operates as a conversion electron detector with count rates 10–20 times higher than those of a conventional detector. At room temperature, the nucleogenic ^{57}Fe ions were found to have relaxed to the stable $^1A_1$ LS ground state. On lowering the temperature metastable Fe(II)-HS resonance lines appear in the spectra with increas-

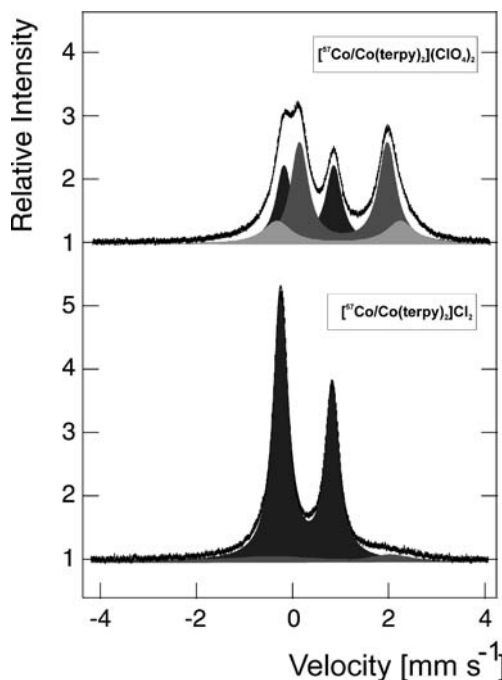


Fig 13 Time-integral ^{57}Fe Mössbauer emission (TIME) spectra of $[\text{}^{57}\text{Co/Co(terpy)}_2]\text{A}_2$ ($\text{A}=\text{ClO}_4^-$, Cl^-), recorded at 100 K with a conversion electron detector. Assignment: *Black doublet*, Fe(II)-LS; *dark grey and light grey doublets*; Fe(II)-HS [47]

ing intensities. The perchlorate derivative with the weaker ligand field strength shows, at comparable temperatures, a considerably higher amount of Fe(II)-HS fraction than the chloride derivative with the stronger ligand field. The emission spectra recorded at 100 K and displayed in Fig. 13 demonstrate this effect very clearly.

For a comparative study on a related system with even weaker ligand field strength at the central metal ion, temperature dependent NIESST experiments were carried out with ^{57}Co doped into the high spin compound $[\text{Mn(terpy)}_2](\text{ClO}_4)_2 \cdot 1/2\text{H}_2\text{O}$. As expected, the $^{57}\text{Fe(II)-HS}$ fraction derived from the emission spectra of the manganese host with the weakest ligand field is the highest one for these three systems at comparable temperatures as is evident from the graphs in Fig. 14.

It can be seen that in the relaxation scheme in Fig. 12, ΔE_{HL}^0 takes on increasing values in the order $\text{Mn/ClO}_4 < \text{Co/ClO}_4 < \text{Co/Cl}$ corresponding to the increasing ligand field strength in the same ordering. The $^{57}\text{Fe(II)-HS}$ fraction, at a given temperature, decreases in the reverse order, in full agreement with the “reduced energy gap law”.

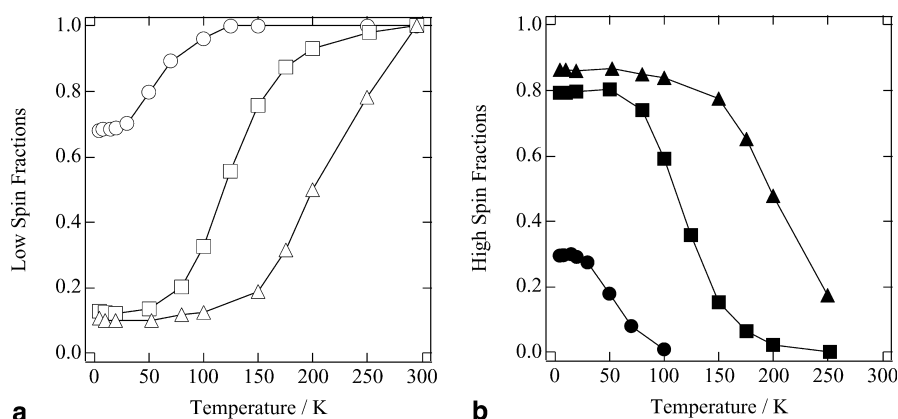


Fig 14 Temperature dependence of the (a) Fe(II)-LS fraction (*open symbols*) and (b) Fe(II)-HS1 fraction (*filled symbols*) of $[^{57}\text{Co}/\text{Co}(\text{terpy})_2]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ (*spheres*), $[^{57}\text{Co}/\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot 1/2\text{H}_2\text{O}$ (*squares*), and $[^{57}\text{Co}/\text{Mn}(\text{terpy})_2](\text{ClO}_4)_2 \cdot 1/2\text{H}_2\text{O}$ (*triangles*) [47]

NIESST studies have also been performed on $[^{57}\text{Co}/\text{Co}(\text{py})_2\text{Ni}(\text{CN})_4]$ ($\text{py}=\text{pyridine}$) [48]. The corresponding 2D cyano coordination Fe(II)-Ni(II) polymer is known to display an abrupt thermal spin transition $^1\text{A}_1 \leftrightarrow ^5\text{T}_2$ around 190 K with a hysteresis width of 12 K [49]. The diamagnetic Ni^{II} ions are arranged in square planar configuration whereas Fe(II) ions have octahedral surroundings. The emission spectra recorded below 80 K consisted of three components ascribed to two Fe(II)-HS states and one Fe(III)-LS state.

6 Conclusion

Mössbauer spectroscopy using ^{57}Co labelled cobalt(II) coordination compounds (usually with $^4\text{T}_1$ ground state) versus a single-line absorber like $\text{K}_4[\text{Fe}(\text{CN})_6]3\text{H}_2\text{O}$, originally conducted to investigate in a nondestructive manner the chemical and physical after-effects following the electron capture decay of $^{57}\text{Co}(\text{EC})^{57}\text{Fe}$ in solid state, have led to the first observation of metastable electronic states of $^{57}\text{Fe}(\text{II})$ generated from $^{57}\text{Co}(\text{II})$ compounds with strong and intermediate ligand field strength. In comparison with conventional Mössbauer absorption spectroscopy of the corresponding iron(II) complexes with LS or spin crossover behaviour, the *anomalous* resonance lines in the emission spectra have been identified as excited Fe(II)-HS states. With a specially designed and constructed coincidence spectrometer, the lifetimes of the excited spin states could be determined with time-differential Mössbauer emission spectroscopy. The very good agreement of the results with data derived from optical lifetime measurements by laser excita-

tion on related systems led to the conclusion that the metastable spin states created in both phenomena, i.e. by *light-induced excited spin state trapping* (LIESST) and *nuclear decay-induced excited spin state trapping* (NIESST) follow the same relaxation mechanism and can be described by the same non-classical model, namely a nonadiabatic multiphonon relaxation. The parameter in this relaxation model that is of utmost importance for the lifetimes of the metastable Fe(II)-HS states in both phenomena is the energy difference ΔE_{HL}^0 between the lowest vibronic levels of the metastable $^5\text{T}_2$ state and the $^1\text{A}_1$ ground state potentials. ΔE_{HL}^0 correlates with the ligand field strength. In weak or intermediate ligand fields, ΔE_{HL}^0 is small, the low temperature tunnelling rate is small too, the lifetime may become very long (in the order of days around 4 K), and relaxation occurs only through thermally activated tunnelling. In strong ligand field complexes, corresponding to the analogous iron(II) complexes with LS behaviour, ΔE_{HL}^0 is large, the low temperature tunnelling rate increases exponentially with this energy difference, and the lifetime of the metastable Fe(II)-HS state shortens considerably. Thus, the stronger the ligand field, the larger ΔE_{HL}^0 , the shorter the lifetime of the metastable Fe(II)-HS state. This so-called *inverse energy gap law*, which is discussed in detail for LIESST in the previous chapter by A. Hauser, also describes the NIESST relaxation kinetics.

It has been demonstrated in NIESST experiments, where the host lattice was varied in a systematic manner, e.g. by offering more or less space to accommodate the nucleogenic ^{57}Fe ion, that the smaller the space, the lower is the population of the Fe(II)-HS state observed at a given temperature and thus the shorter is the lifetime of the metastable Fe(II)-HS state. Responsible for this is the build-up of local pressure, which causes a horizontal and vertical shift of the LS and HS potentials relative to each other, thereby increasing ΔE_{HL}^0 and thus the tunnelling rate, in much the same way as A. Hauser describes in the previous chapter the self-accelerated cooperative HS $\rightarrow$ LS relaxation through the dynamical build-up of internal pressure. It seems quite appropriate to think of possible applications of NIESST for probing the dimensions of cavities or tubes in nanostructured materials.

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References

1. Szilard L, Chalmers TA (1934) *Nature* 134:462
2. Tominaga T, Tachikawa E (1981) *Modern hot-atom chemistry and its applications*. Springer, Berlin Heidelberg New York
3. Matsuura T (ed) (1984) *Hot atom chemistry*. Kodanski, Tokyo
4. Sano H, Gütlich P (1984) In: Matsuura T (ed) *Hot atom chemistry*. Kodanski, Tokyo, p 265
5. Spiering H, Alflen M, Gütlich P, Hauser A, Hennen C, Manthe U, Tuczek F (1990) *Hyperfine Interact* 53:113
6. Greenwood NN, Gibb TC (1971) *Mössbauer spectroscopy*. Chapman and Hall, London
7. Gütlich P, Link R, Trautwein AX (1978) *Mössbauer spectroscopy and transition metal chemistry*. Inorganic Chemistry Concepts Series, no 3. Springer, Berlin Heidelberg New York
8. Pollak H (1962) *Phys Status Solidi* 2:270
9. Friedt JM, Danon J (1980) *At Energ Rev* 18:4
10. Gütlich P, Odar S, Fitzsimmons BW, Erickson NE (1968) *Radiochim Acta* 10:147
11. Misroch MB, Schramm CJ, Nath A (1976) *J Chem Phys* 65:1982
12. Fenger J, Olsen J (1974) *J Chem Soc Dalton* 319
13. Adloff JP (1973) *Effets chimiques des transformations nucléaires*. Report no CRN/CNPA 74-28 and subsequent annual reports. Université de Strasbourg, France
14. Bonville P, Garcin C, Gerard A, Imbert P, Jehanno G (1981) *Phys Rev B* 23:4293, 4310
15. Tuczek F, Spiering H, Gütlich P (1990) *Hyperfine Interact* 62:109
16. Ensling J, Fitzsimmons BW, Gütlich P, Hasselbach (1970) *Angew Chem* 9:637
17. Grimm R, Gütlich P (1983) *Lab Rep*, Chemistry Dept, University of Mainz
18. Grimm R, Gütlich P, Kankleit E, Link R (1977) *J Chem Phys* 67(12):5491
19. Ensling J, Fleisch J, Gütlich P, Fitzsimmons BW (1977) *Chem Phys Lett* 45(1):22
20. Sanchez JP, Llabador Y, Friedt JM (1973) *J Inorg Nucl Chem* 35:2557
21. Madeja K, König E (1963) *J Inorg Nucl Chem* 25:377
22. Baker WA, Bobonich HM (1964) *Inorg Chem* 3:1184
23. Ensling J, Gütlich P, Hasselbach KM, Fitzsimmons BW (1976) *Chem Phys Lett* 42:232
24. Fleisch J, Gütlich P (1976) *Chem Phys Lett* 42:237
25. Fleisch J, Gütlich P (1977) *Chem Phys Lett* 45:29
26. Fleisch J, Gütlich P, Köppen H (1980) *Radiochem Radioanal Lett* 42:279
27. Gütlich P, Köppen H (1980) *J Phys (Paris)* 41-C:311
28. Hennen C (1986) Master's thesis, University of Mainz, Dept of Chemistry
29. Wei HH, Ho LZ (1982) *Radiochem Radioanal Lett* 55:29
30. Fleisch J, Gütlich P (1977) *Chem Phys Lett* 45:29
31. Fleisch J, Gütlich P, Hasselbach KM (1976) *Inorg Chim Acta* 17:51
32. Reiff W, Long G (1974) *Inorg Chem* 13:2150
33. Decurtins S, Gütlich P, Köhler CP, Spiering H, Hauser A (1984) *Chem Phys Lett* 105:1
34. Decurtins S, Gütlich P, Hasselbach KM, Spiering H, Hauser A (1985) *Inorg Chem* 24:2174
35. Albrecht R, Alflen M, Gütlich P, Kajcsos Z, Schulze R, Spiering H, Tuczek F (1987) *Nucl Instrum Methods A* 257:209
36. Alflen M, Hennen C, Tuczek F, Spiering H, Gütlich P, Kajcsos Z (1989) *Hyperfine Interact* 47:115
37. Hennen C, Alflen M, Spiering H, Gütlich P (1990) *Hyperfine Interact* 56:1527
38. Deisenroth S, Hauser A, Spiering H, Gütlich P (1994) *Hyperfine Interact* 93:1573

39. Deisenroth S (1996) PhD Thesis, Chemistry Dept, University of Mainz
40. Gütlich P, Hauser A, Spiering H (1994) *Angew Chem Int Ed* 33:2024
41. Hauser A (1986) *Chem Phys Lett* 24:543
42. Buhks E, Navon G, Bixon M, Jortner J (1980) *J Am Chem Soc* 102:2918
43. Hauser A (1995) *Comments Inorg Chem* 17:17
44. Sieber R, Decurtins S, Stoeckli-Evans H, Wilson C, Yufit D, Howard JAK, Capelli SC, Hauser A (2000) *Chem Eur J* 6: 361
45. Chameko V (2001) In partial fulfilment of the Ph.D. thesis, Univ Mainz, first presented at the Workshop "Molecular Photomagnetism", Seeheim, 2001
46. Chameko V, Bron M, Gütlich P, Decurtins S (To be published)
47. Oshio H, Spiering H, Ksenofontov V, Renz F, Gütlich P (2001) *Inorg Chem* 40(6):1143
48. Sato T, Ambe F, Kitazawa T, Sano H, Takeda M (1997) *Chem Letters* 12:1287
49. Kitazawa T, Gomi Y, Takahashi M, Takeda M, Enomoto M, Miyazaki A, Enoki T (1996) *J Mater Chem* 6:119

Ligand-Driven Light-Induced Spin Change (LD-LISC): A Promising Photomagnetic Effect

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Abstract “Ligand-driven light-induced spin change” (LD-LISC) is a photomagnetic effect based on the modulation of the ligand-field strength of a suitable spin-crossover complex through a photochemical reaction on the ligand. It allows one to switch the electronic spin state of the metal ion by means of light over a broad range of temperatures possibly including room temperature. Among the photochemical reactions capable of triggering the spin conversion reversibly, we have firstly selected *cis-trans* isomerization. The occurrence of the LD-LISC effect was shown in several iron(II) or iron(III) complexes. On varying the molecular components, the working temperature and excitation wavelengths were modulated so that the effect could be observed at room temperature upon irradiation of the sample with visible light. The experiments were performed on compounds either in solution or included in polymeric matrices.

Keywords Spin crossover · Ligand-driven spin change · Photomagnetism · Photoisomerization · Langmuir-Blodgett film

1 Introduction

The electronic lability of transition-metal complexes in which a reversible change of the spin multiplicity of the metal-ion may be induced by an external stimulus makes these systems potentially suitable for practical applications in the area of molecular electronics. In particular, the memory effect

resulting from the possible bistable behavior of these complexes suggests the potential for future exploitation in information storage or display devices [1].

The spin-crossover (SCO) phenomenon provides the best documented examples of such compounds [2]. If the high-spin (HS) $\leftrightarrow$ low-spin (LS) interconversion is controlled by an intensive variable such as temperature or pressure, the prerequisite for bistability is the existence of hysteresis, which may occur in the solid state provided that intersite interactions are strong enough. However, a quasi-bistability can also be observed in photodriven spin changes. This is illustrated by the LIESST (light-induced excited spin-state trapping) and reverse-LIESST effects, where the LS-to-HS and reverse transitions induced in Fe(II) SCO complexes take place at a temperature sufficiently low for the metastable HS state to have a virtually infinite lifetime [2a, 2c, 3]. The systems are said to be photoswitchable [2i]. Also, on varying temperature or light intensity while maintaining irradiation, light-induced thermal [4] and optical [4b] hystereses can be detected.

With the aim to design photoswitchable materials with higher working temperatures than those (lower than ~ 80 K) reported to date together with long-lifetime photoexcited states, we have been focusing for several years on a novel strategy that we have named “Ligand-Driven Light-Induced Spin Change” (or LD-LISC) [5–7]. The method consists of using a photosensitive ligand, in order to trigger the metal-ion spin interconversion through the variation of the ligand-field (LF) strength resulting from the reversible photochemical modification of this ligand.

In contrast with the SCO process, where the structures of ligands are essentially unaffected, the LD-LISC effect is accompanied by a pronounced structural change of the photoresponsive ligands. Moreover, the two approaches are basically different, in that the two electronic levels involved in the spin conversion are: i) for SCO systems, the lowest-lying HS and LS levels of a given molecule in a close energy proximity (the energy gap being of the order of thermal energies); ii) for LD-LISC systems, the HS and LS ground states, respectively, of the homologous molecules formed with each of the two isomers of the photoreactive ligand.

The photochemical transformation chosen to drive the metal-ion SCO is *cis-trans* photoisomerization. This has long been used to exert photocontrol on chemical systems and, in particular, to operate artificial molecular-level machines [8]. With appropriately selected ligands, the *cis-trans* conversion (and hence the SCO process) can not only be reversible with successive irradiations at two suitable wavelengths, but also ensure long-lifetime excited states. In addition, the LD-LISC effect shows specific properties that open up appealing perspectives for possible exploitation in information processing devices:

- It may apply to any metal ion capable of undergoing a SCO.
- Depending on the nature of the systems under investigation, it can be observed in an extended temperature range going from low to rather high temperatures, the upper limit being determined only by the thermal stability of the samples.
- Apart from *cis-trans* photoisomerization, any reversible ligand photoexcitation leading to a significant variation of the LF strength may be used to drive the $HS \leftrightarrow LS$ interconversion, therefore broadening the scope of the study of LD-LISC.

In addition, it can be emphasized that, in relation to the search for practical applications, stimulation by light is certainly the most promising way to control the spin crossover phenomenon [1d]: the process is rapid—compared with thermo- and piezo-excitations, easy to tune, and its molecular nature allows one to anticipate the possibility to ultimately address molecules individually in the solid state. Moreover, various non-destructive read-out methods can be used to characterize the resulting state of the systems, i.e., to report the “written” data. However, a number of drawbacks associated with ligand photoexcitation may possibly be encountered. They may result, in particular, from a significant optical absorption of solid samples—which might prevent light from penetrating into the bulk, a low efficiency of the process or an accumulation of by-products that might rapidly compromise the operation of the system. We shall see hereafter that these disadvantages can be reduced or even excluded by the use of appropriate photoresponsive ligands and adapted experimental conditions.

The following section is devoted to the basic concept of the LD-LISC effect [7]. In subsequent sections, we report the observation of the photomagnetic effect: first at 140 K, in an iron(II) complex embedded in a cellulose acetate matrix [9], then at room temperature, in both an iron(II) complex [10] and an iron(III) complex [11] in acetonitrile solutions. Finally, we will present the preliminary results of an approach to induce the LD-LISC effect in a Langmuir-Blodgett film, that is, the observation of a thermally induced SCO in an amphiphilic iron(II) complex containing photoisomerizable ligands [12].

2 Basic Concept of LD-LISC

As seen above, the LD-LISC approach may allow one to control reversibly the metal-ion spin state, in molecular complexes containing a photosensitive ligand, by exciting this ligand with light.

A prerequisite for the effect to be observed is that the two complexes C_A and C_B formed with the ligand photoisomers L_A and L_B , respectively, show

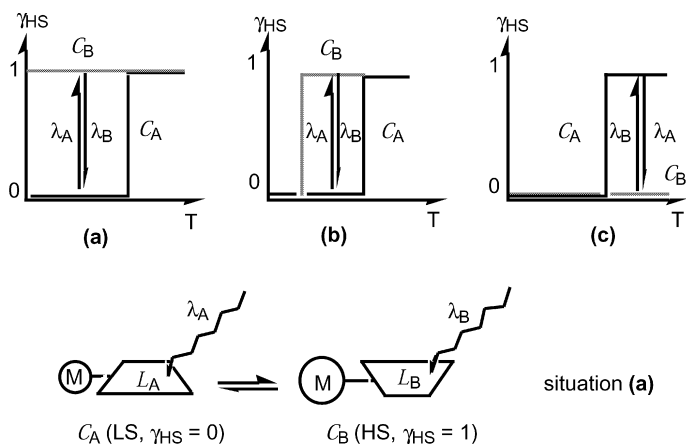


Fig. 1a–c Relative magnetic behavior of C_A and C_B homologous complexes favoring the observation of the LD-LISC effect. Schematic mechanism of this effect in the situation (a). γ_{HS} =HS fraction; T =temperature; C_A =SCO complex formed with the L_A isomer of the photosensitive ligand; C_B =complex formed with the L_B isomer; λ_A and λ_B =wavelengths used to trigger $C_A \rightarrow C_B$ and $C_B \rightarrow C_A$ conversions, respectively; M =metal ion

different magnetic behavior as a function of temperature. In the temperature range where the metal ion can be either in the LS or in the HS state according to the configuration of the photoreactive ligand, a spin-state interconversion should occur upon successive irradiations of the system at two wavelengths λ_A and λ_B .

A convenient way to achieve this is to design a metal environment in order that at least one of the complexes (C_A for instance) exhibits a thermally-induced SCO; in Fig. 1, this property is depicted in the form of the temperature-dependence of the HS fraction γ_{HS} . It follows that the magnetic properties of C_A are particularly sensitive to relatively slight variations of the LF strength. Consequently, C_B is expected either to be in the HS state ($\gamma_{HS}=1$, Fig. 1a) or the LS state ($\gamma_{HS}=0$, Fig. 1c) at any temperature, or to exhibit a SCO at a lower (Fig. 1b) or higher temperature than C_A . In each case, there is a temperature range in which ligand photoexcitation may result in a change of the metal-ion spin state. The mechanism of the process at the molecular scale is shown schematically in the lower part of Fig. 1 for the situation (a). Of course, C_A - C_B pairs of complexes with fully HS and LS magnetic behavior, respectively, should also be good candidates for the LD-LISC effect to be observed. However, if they exist, such pairs cannot be easily designed: the relevant ligand-field strengths must lie on both sides of the range corresponding to SCO complexes, which on the one hand is very difficult to achieve and on the other hand requires the change in LF strength upon ligand photoconversion to be unusually large.

The photochemical process we first selected to operate the LD-LISC effect, that is *cis-trans* photoisomerization, was applied up to now to molecules containing the photoreactive group $-\text{CH}=\text{CH}-\text{Ph}$. This choice was dictated by the fact that the energy barrier between the two isomers is then expected to be high enough to prevent any thermal interconversion from occurring up to temperatures higher than room temperature [13]. This should allow the molecular systems to be bistable and therefore to be prepared and handled in their two isomeric forms.

Hereafter, the *cis* and *trans* ligand isomers and the relevant complexes will be labelled as L_c and L_t , C_c and C_t , respectively.

3

LD-LISC in Iron(II) Complexes

The first attempts to detect the LD-LISC effect were carried out by using 4-styrylpyridine ($\text{py}-\text{CH}=\text{CH}-\text{Ph}$, denoted stpy) as the photoisomerizable ligand. Complexes of the type $[\text{Fe}(\text{stpy})_4(\text{X})_2]$, with $\text{X}=\text{an anionic ligand}$, were synthesized, for they were considered capable of undergoing a thermally-induced SCO or to act as precursors in the syntheses of SCO species, by analogy with the complex $[\text{Fe}(\text{py})_4(\text{NCS})_2]$ in which the mere replacement of two pyridine rings by a suitable bidentate ligand leads to SCO complexes [14].

$[\text{Fe}(\text{stpy})_4(\text{NCS})_2]$ was the first system whose C_t and C_c isomers were found to display the relative magnetic properties required for the observation of the LD-LISC effect [7]. C_t exhibits a thermally induced ST, centered around 108 K and taking place between ~ 165 K and 90 K, while C_c remains in the HS state at any temperature. It follows that the working temperature (T_w) cannot be much higher than 90 K. Comparison of the molecular structures of the two isomers in their HS form (see Fig. 2) [7] calls for several remarks: i) iron(II) ions have similar pseudo-octahedral $[\text{N}_6]$ environments, formed with the nitrogen atoms of the two NCS groups in *trans*-position and those, nearly coplanar, of the four stpy moieties; ii) L_c ligands deviate more strongly from planarity than L_t ones, which may lead to a lower π -acceptor character of the former and, consequently, to a stabilization of the HS state in C_c , compared with C_t ; iii) last but not least, the volume per molecular unit in the crystal is found to be higher by $\sim 1\%$ in HS C_t ($1212 \text{ \AA}^3$) than in HS C_c ($1201 \text{ \AA}^3$), thus showing that the LD-LISC effect, which in this system involves LS C_t and HS C_c isomers, should give rise to a *lower* volume change than the spin-state switch between LS C_t and HS C_t alone.

However, in spite of the fact that the above system displays appropriate magnetic and structural properties for LD-LISC to be observed, the low value of T_w should result in very weak photoisomerization quantum yields, in consequence of both the competitive processes and the pronounced rigidity of the matrices used for incorporating the solid-state compounds [15].

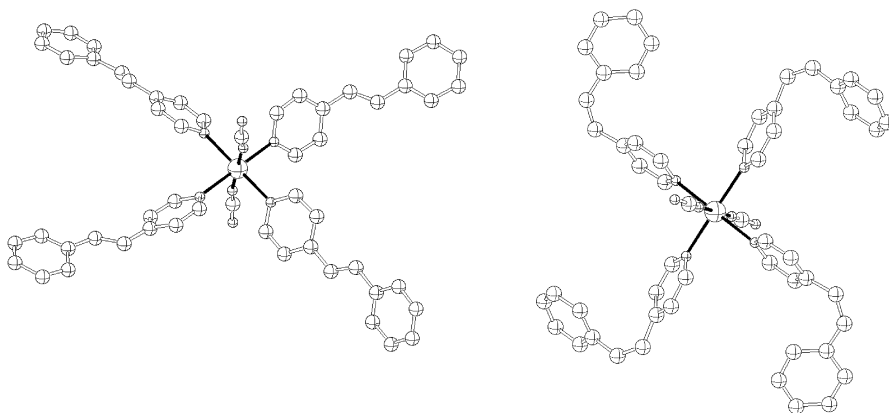


Fig. 2 Molecular structures of $[\text{Fe}(\text{trans-stpy})_4(\text{NCS})_2]$ (C_t) and $[\text{Fe}(\text{cis-stpy})_4(\text{NCS})_2]$ (C_c) at 293 K. Hydrogen atoms were omitted for clarity

3.1

First Observation of the Effect, at 140 K

With the aim of shifting the ST of the C_t isomer to higher temperatures and hence to increase the value of T_w , new systems of the type $[\text{Fe}(\text{L})_4(\text{X})_2]$ were investigated [9]. In these systems, L is 4-styrylpyridine or a derivative in which the phenyl ring is either 4-substituted or replaced by another aromatic group; X is NCBPh_3^- or NCBH_3^- , these anionic ligands being known to significantly increase the transition temperature ($T_{1/2}$) of SCO compounds, compared with NCS^- [16]. All C_t complexes do exhibit an SCO behavior. As T_w has to be as high as possible and the HS-to-LS transformation of C_t at this temperature must be close to complete (in order that the spin-change detecting signal be large enough), the best candidate for the possible observation of the LD-LISC effect turns out to be $[\text{Fe}(\text{stpy})_4(\text{NCBPh}_3)_2]$.

In this compound, the anionic ligands are expected to be *trans*-located with regard to the four Fe-N(stpy) bonds, for the ν_{CN} IR absorption (near 2190 cm^{-1}) is a single and sharp band. Hence, the molecular structures of the two isomers should closely resemble those of $[\text{Fe}(\text{stpy})_4(\text{NCS})_2]$ (see Fig. 2). The magnetic behavior of solid samples of C_c and C_t is shown in Fig. 3a in the form of the temperature dependence of the product $\chi_M T$ (χ_M =molar magnetic susceptibility). C_c is HS at any temperature and the ST exhibited by C_t , centered around 190 K, takes place between ~ 250 and 140 K. The latter temperature was adopted as the working temperature for the photostimulation.

The experiments were further carried out on both C_t and C_c isomers embedded in cellulose acetate matrices, by using UV-vis absorption spectrometry as the detecting technique [9].

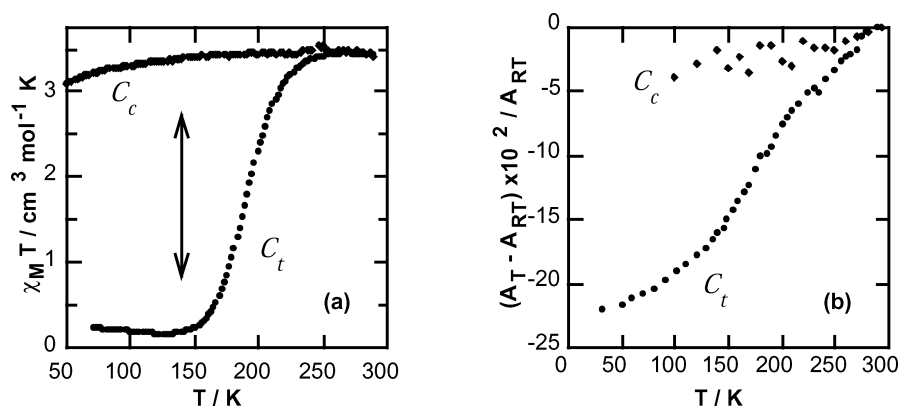


Fig. 3 **a** Temperature dependence of $\chi_M T$ for polycrystalline samples of the C_t and C_c isomers of $[\text{Fe}(\text{stpy})_4(\text{NCBPh}_3)_2]$. **b** Temperature dependence of the relative variation of absorbance, at 342 nm, for these isomers embedded in cellulose acetate films

The preliminary step consisted in controlling the magnetic behavior of the two compounds in their polymeric host. This was carried out by following the temperature dependence of the absorbance (A) of the samples, at a wavelength (342 nm) associated with the metal-to-ligand charge transfer. The curves showing the relative variation of A as a function of T closely resemble the $\chi_M T$ vs T plots obtained with polycrystalline samples (see Fig. 3b). The only difference is that the spin conversion exhibited by C_t , centered around 185 K, is less cooperative than the previous one, presumably a consequence of the dilution of the compound in the polymeric matrix. It is worth noting that this HS-to-LS transformation can be visually observed in the most concentrated samples, for it is accompanied by an orange-to-red color change. In contrast, the C_c isomer, which does not undergo SCO, retains the yellow color of the HS form at any temperature.

The photoexcitation of 4-styrylpyridine ligands was performed at 140 K, by irradiating the C_t and C_c samples at $\lambda_{\text{exc}}=322$ and 260 nm, respectively. Figure 4a,b shows the spectra of the starting isomers and those of the resulting photostationary states. They clearly provide evidence of *trans*→*cis* (a) and *cis*→*trans* (b) ligand photoisomerizations. As these transformations are expected to be the only detectable photoreactions [17], the composition of the photostationary states can be approximated from the simulation of their spectra with linear combinations of C_t and C_c spectra. Irradiations of C_t and C_c are found to lead to ~62% of C_c and ~67% of C_t , respectively.

Since, at 140 K, iron(II) ions are HS in C_c and predominantly LS in C_t (see Fig. 3b), ligand isomerization should result in a change of the spin state of most of these ions. This assumption was corroborated by following the temperature dependence of the relative variation of absorbance for each isomer, before and after irradiation. Figure 4c shows the results obtained for

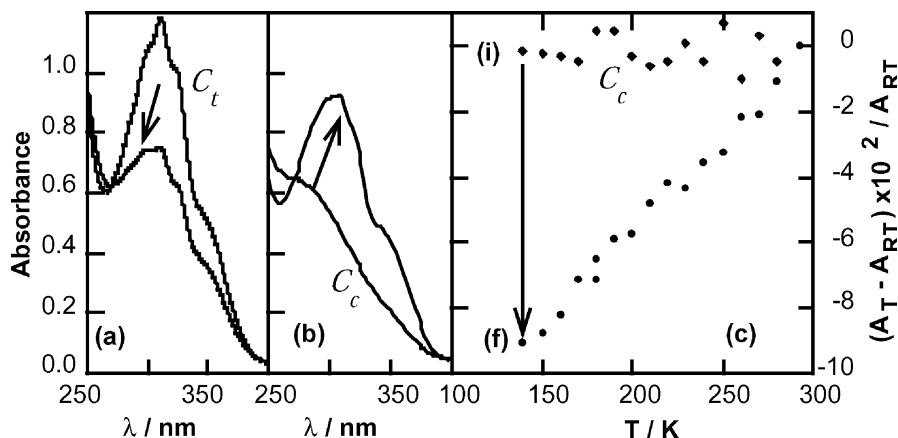


Fig. 4 a, b Absorption spectra of C_t (a) and C_c (b) in similarly concentrated cellulose acetate films, and of the relevant photostationary states obtained after irradiation of the samples at 140 K with $\lambda_{exc}=322$ nm (a) and 260 nm (b). c Temperature dependence of the relative variation of absorbance at 344 nm, for a C_c -containing cellulose acetate film before (i) and after (f) irradiation with $\lambda_{exc}=260$ nm at 140 K

C_c : on increasing temperature, the C_t complex resulting from the photoconversion of HS C_c exhibits a thermal SCO, which confirms that iron(II) ions were at least partly in the LS state at 140 K. At this temperature, the LD-LISC effect can also be visually detected, for the HS $C_c \rightarrow$ LS C_t transformation is accompanied by a yellow-to-red color change.

3.2

Observation of the Effect at 293 K

For LD-LISC to be observed at a higher temperature than the working temperature used for $[\text{Fe}(\text{stpy})_4(\text{NCBPh}_3)_2]$, an increase in the LF strength is required. This can be achieved by replacing the set of monodentate (pyridine derivative) ligands by bidentate (e.g. a 2,2'-bipyridine derivative) ligands, which should increase the 10Dq parameter through a stronger π -back bonding interaction from the metal ion (d_π) to the ligand (π^*) orbitals.

In Fig. 5 is shown the C_t complex $[\text{Fe}(\text{trans-msbpy})_2(\text{NCS})_2]$ that has been synthesized and investigated (*trans-msbpy*=4-methyl-4'-*trans*-styryl-2,2'-bipyridine) [10]. The molecules of this compound are organized around the coordination core $[\text{Fe}(\text{bpy})_2(\text{NCS})_2]$, known to give rise to a number of SCO systems, and include the photoactive group ($-\text{CH}=\text{CH}-\text{Ph}$). Depending on the procedure used for the synthesis, the compound can be isolated in the form of two powdered species, with different aspects (crystalline/amorphous character, color), solubilities and magnetic properties, that may be ascribed either to diastereoisomeric species or to distinct crystalline structures. The

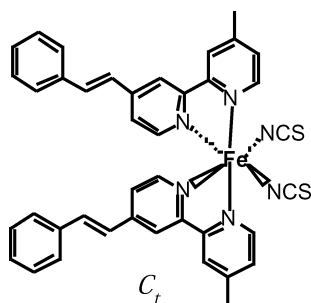


Fig. 5 Schematic representation of the C_t molecule $[\text{Fe}(\text{trans-msbpy})_2(\text{NCS})_2]$

temperature dependence of the χ_{MT} product shows gradual SCO processes for both solid samples. As expected, the curves are found to be shifted toward higher temperatures ($T_{1/2} \sim 264$ and 380 K) in comparison with those of $[\text{Fe}(\text{stpy})_4(\text{X})_2]$ species.

The study was later on performed with the solid C_t isomer for which $T_{1/2} \sim 264$ K, because of its solubility in the usual organic solvents. The χ_{MT} vs T plot for this complex in acetonitrile solution, determined from Evans NMR measurements, does show the existence of a spin equilibrium. However, this is now centered at a temperature high enough for C_t to be almost diamagnetic at 293 K ($\chi_{\text{MT}} = 0.17 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$).

Taking advantage of this characteristic, we have performed the photoisomerization of *trans*-msbpy (L_t) in CH_3CN solutions of L_t and C_t at room temperature. For uncoordinated L_t , the *trans* $\rightarrow$ *cis* isomerization is easily detected from the evolution of the UV-vis spectra and the ^1H NMR data (formation of $\geq 70\%$ of L_c , with $\lambda_{\text{exc}} = 312$ nm). This photochemical reaction is also identified upon irradiation of the C_t solution with $\lambda_{\text{exc}} = 334$ nm (see Fig. 6). In this case, the main features deduced from the data are (i) the possible occurrence of a $C_t \leftrightarrow C_c$ interconversion (isosbestic points in UV and vis spectral ranges); (ii) the formation of an excess of C_c ($> 55\%$); (iii) the generation of HS iron(II) ions concomitantly with the C_t -to- C_c transformation (weak NIR band assigned to the d-d transition of these ions). This set of observations indicates that a significant amount of C_t , in the LS state before irradiation, is photoconverted into an HS C_c complex at room temperature. This assertion has been confirmed by a qualitative study performed with a SQUID magnetometer. The net increase in magnetization observed after irradiation of an acetonitrile solution of C_t is consistent with the fact that iron(II) ions are partly converted from the LS state to the HS state.

It follows that, for the first time, evidence is provided for the LS-to-HS photoconversion of iron(II) ions at *room temperature*. This result shows that the working temperature can be modulated by the fine-tuning of the LF strength based on the choice of the molecular components.

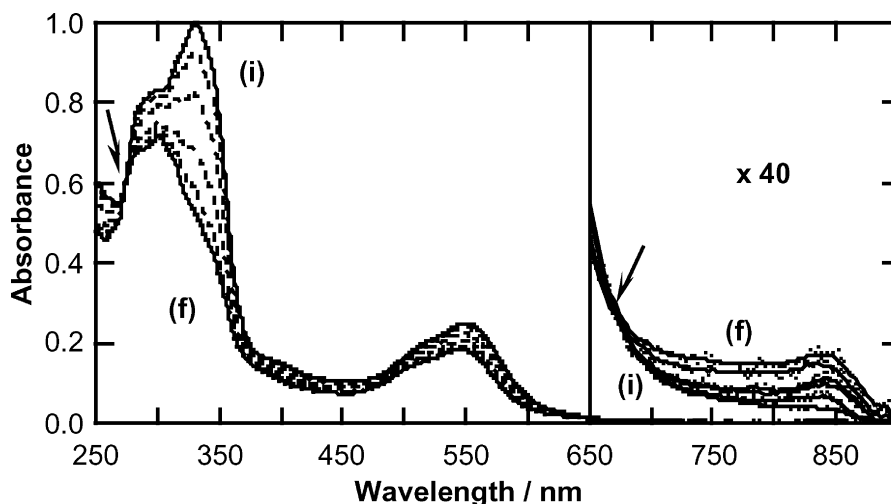


Fig. 6 Evolution of the UV-vis spectrum of a 1.9×10^{-5} mol/l CH_3CN solution of C_t upon irradiation with $\lambda_{\text{exc}}=334$ nm; i: initial spectrum, f: spectrum of the photostationary state

3.3

Towards the LD-LISC Effect in a Langmuir-Blodgett Film

To realize the optical addressing of systems in the solid state, it is of prime importance to solve the problem of optical density in relation to the sample thickness. This can be overcome by developing transparent solids that can be shaped into thin layers. Among the possible approaches, we have chosen to use the Langmuir-Blodgett technique. It should be noted that in LB multilayer structures, which consist of highly ordered and densely packed assemblies of molecules, the SCO exhibited by the starting species may be modified and even suppressed, since SCO characteristics strongly depend on particular ordering and intermolecular interactions.

Taking advantage of the magnetic behavior of $[\text{Fe}(\text{trans-msbpy})_2(\text{NCS})_2]$ at room temperature, we have synthesized the related amphiphilic C_t complex $[\text{Fe}(\text{trans-hsbpy})_2(\text{NCS})_2]$ (*trans-hsbpy*=4-heptadecyl-4'-*trans*-styryl-2,2'-bipyridine) by adding long alkyl chains onto the organic ligand backbone. The magnetic properties of a polycrystalline sample of C_t , depicted in Fig. 7a, show that the compound exhibits a gradual SCO centered around 295 K [12a].

To prepare a stable monolayer of this amphiphilic complex, we have used a formamide/KCN aqueous solution mixture as the subphase, in order to prevent dissociation reactions from taking place at the air/water interface [12b]. The multilayer film obtained by successive transfers of monolayers on a substrate has been characterized by variable temperature FTIR spectrometry. As the frequency of the ν_{CN} stretching mode of NCS^- ligands depends on

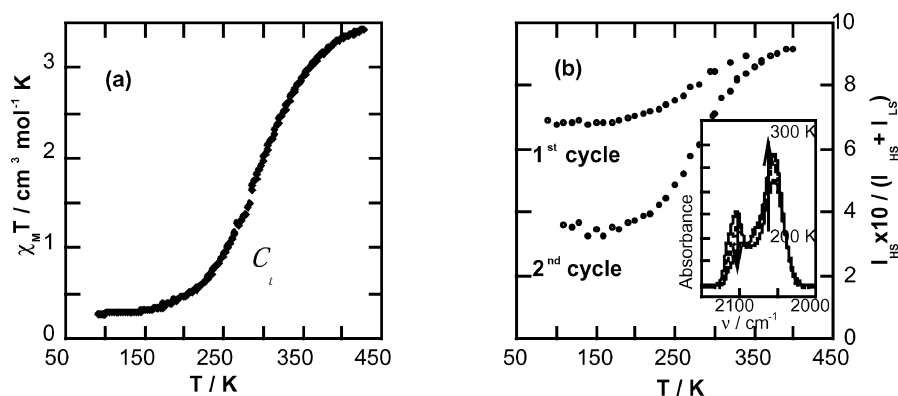


Fig. 7 a Temperature dependence of $\chi_M T$ for a bulk sample of $[\text{Fe}(\text{trans-hsbpy})_2(\text{NCS})_2]$. b Temperature dependence of the $I_{\text{HS}}/(I_{\text{HS}}+I_{\text{LS}})$ ratio for the LB film, I_{HS} and I_{LS} being the intensities of the ν_{CN} IR peaks within the ranges 2000–2090 cm^{-1} and 2090–2150 cm^{-1} , respectively. The second cycle was obtained after annealing the film at $T=340$ K. *Inset*: thermal evolution (from 200 to 300 K) of the ν_{CN} IR peaks

the spin state of the metal ion, the relative intensity of the bands associated with LS and HS forms allows one to follow the spin state conversion (see the inset in Fig. 7b). A first thermal cycle (see Fig. 7b), from 300 to 80 K and back to 300 K, shows that $\sim 30\%$ of the iron(II) ions undergo a thermal spin equilibrium whose characteristics are similar to those of the polycrystalline sample, while the others remain HS. The latter behavior may be ascribed to the distortion of molecules under the effect of strains within the LB film. This interpretation is corroborated by the second thermal cycle (see Fig. 7b) obtained after annealing the film at $T \geq 340$ K. The thermal treatment, that leads to a loss of the layer structure and of the intralayer organization, appears to favor the SCO behavior in consequence of the structural relaxation allowing the molecules to recover their regular shape. This shows that changes in the host matrix may significantly control the spin conversion process.

Irradiation of the organized film at room temperature with $\lambda=340$ nm gives rise to the typical variations in UV absorption associated with the *trans*→*cis* isomerization of the coordinated photosensitive ligand. However, the IR data show the concomitant disappearance of the ν_{NC} bands and hence the degradation of the complex. It is noteworthy that, if a similar treatment is performed on the material obtained after evaporating the solvent, this degradation reaction is found to be reduced.

The above features show that the LD-LISC effect cannot be observed under the conditions used for the experiments. Nevertheless, they suggest several strategies for further attempts: i) utilization of complexes more stable in the presence of water than $[\text{FeL}_2(\text{NCS})_2]$ type species; ii) elaboration of less

densely packed LB films; (iii) dilution of the amphiphilic complex with molecules capable of acting as separators; (iv) use of the semi-amphiphilic method (based on polyelectrolytes and ionic complexes). Moreover, as far as organized media are required, attempts to trigger LD-LISC in complexes intercalated within lamellar materials would be advisable. Preliminary results have already been obtained with this approach [18].

4

LD-LISC at 293 K in an Iron(III) Complex

In order to improve further the conditions for observing the LD-LISC effect, we later focused our interest on the C_t complex $[\text{Fe}(\text{salten})(\text{Mepepy})]\text{BPh}_4$, where H_2salten stands for N,N' -bis[(2-hydroxyphenyl) methylene]-4-azaheptane-1,7-diamine and Mepepy is the photosensitive pyridine derivative *trans*-1-(pyridin-4-yl)-2-(*N*-methylpyrrol-2-yl)ethene (see Fig. 8a) [11]. This choice was dictated by several reasons: i) the homologous compound $[\text{Fe}(\text{salten})(\text{py})]\text{BPh}_4$ undergoes a thermal SCO centered at $T_{1/2} \sim 320$ K [19]; ii) the spin state conversion is faster in iron(III) than in iron(II) ions [2g], which should increase the rate of the photomagnetic process; iii) there is only one photoreactive ligand per metal ion, which is expected to enhance the efficiency of the photochemical reaction, compared with the previous experiments, and to prevent the possible formation of diastereoisomers; iv) the incorporation of a substituent containing a pyrrole ring into this ligand leads to a shift of the $\pi\text{-}\pi^*$ absorption band toward longer wavelengths and hence opens up the possibility of converting the L_t ligand into the L_c one with visible light.

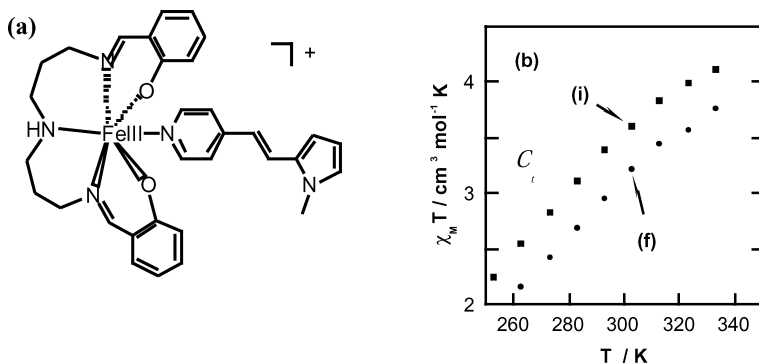


Fig. 8 a Scheme of the cation $[\text{Fe}(\text{salten})(\text{Mepepy})]^+$ in the C_t complex. b Temperature dependence of $\chi_M T$ for a CD_3CN solution of $[\text{Fe}(\text{salten})(\text{Mepepy})]\text{BPh}_4$ (C_t), before irradiation (i) and in the steady state (f)

[Fe(salten)(Mepepy)]BPh₄ undergoes a gradual thermally-induced SCO both in the solid state ($T_{1/2} \sim 308$ K) and in solution ($T_{1/2} \sim 270$ K). Rather than choosing a working temperature at which all iron(III) ions are in the HS or the LS state, we have attempted to detect the photomagnetic effect in solution at room temperature, despite the fact that the initial complex is then a mixture of HS C_t (predominantly) and LS C_t forms. Irradiation of an acetonitrile solution of this complex with $\lambda_{\text{exc}} = 405$ nm induces the *trans*→*cis* isomerization of the L_t ligand. This inference is drawn from the behavior of a solution of pure L_t under the same experimental conditions: the evolution of the UV spectra upon the photochemical process is similar to that observed for the complex and the photostationary state is then shown, by UV-vis and ¹H NMR measurements, to contain an excess of L_c isomer (66%).

The effect of irradiation on the magnetic properties of a solution of C_t (CD₃CN, 10⁻³ M) was followed by the Evans NMR method (see Fig. 8b). The room temperature χ_{MT} value is found to decrease until the steady state is reached, which does account for a HS C_t→LS C_c conversion. Moreover, the temperature dependence of χ_{MT} shows that the steady state exhibits a reversible thermal SCO, shifted toward higher temperature compared with that of the starting complex. So, for the first time, the *trans*→*cis* photoisomerization of the ligand is found to result in a HS-to-LS conversion of the metal ion. This may be at least partly accounted for by the fact that the strong π -donor character of the methyl-pyrrole moiety decreases as the complex changes from L_t to L_c, leading to an increase in the LF strength.

To sum up, in this molecular system, the spin state conversion revealed by the slight but clearly detectable decrease of the χ_{MT} product is driven, at room temperature, by the *trans*→*cis* photoisomerization of a single ligand with visible light.

Close analogues of this complex have been recently prepared with both L_t and L_c ligand isomers [20, 21]. The photo-induced spin change is currently being investigated for compounds embedded in polymeric thin films [21].

5 Conclusions

LD-LISC affords a promising example of the strategies leading to photomagnetic effects in inorganic compounds [1d, 2a, 2i, 22]. This approach, based on the coupling between the switching properties of SCO complexes and those of photoactive ligands, enables the spin state of the metal ion to be optically controlled on the molecular scale.

The above studies reveal a number of positive features. By suitably tuning the LF strength and using a photoresponsive ligand L capable of undergoing a thermally irreversible *cis*-*trans* photoisomerization, one can trigger

LD-LISC at *room temperature* between two *stable states*. Also depending on the nature of L, the effect may be induced by *visible light*, without *any noticeable formation of by-products*. Moreover, the SCO characteristics of the systems can be controlled to some extent by variation of the metal ion undergoing SCO. Finally, it is significant that, in a number of situations (predictable on the basis of crystal volume measurements on C_t and C_c complexes in the same spin state), the volume change associated with LD-LISC may be *lower* than that resulting from the metal-ion spin state conversion alone. This feature may be of relevance to the use of solid-state samples. Hence, if the availability of various non-destructive read-out methods is also taken into account, it clearly appears that LD-LISC could play a prominent part in optical information technology, particularly in optical switching (intrinsic property), optical memories (thermal stability of both ligand isomers) and display devices (photochromism).

These promising findings prompt us now to take advantage of the molecular nature of the photomagnetic process to seek materials with a high recording density. Consequently, it appears advisable to focus on the LD-LISC effect in the solid state. As already mentioned, LD-LISC experiments have already been performed on solid compounds encapsulated in polymeric films. However, the problem of sample thickness requires that future work be directed to the development of thin layer materials [1d, 23]. Our initial attempts to drive ligand *cis-trans* photoisomerization in a Langmuir-Blodgett film have failed, but we can expect to observe this phenomenon under different experimental conditions. Moreover, the question of the interdependence of the molecular and bulk characteristics could be addressed through the comparative investigation of the complexes in the form of different physical arrangements (crystals, thin layers, etc.) or in various host matrices. With this in mind, SCO complexes either intercalated within lamellar matrices (bulk materials and thin layers) or inserted into polyelectrolytes are presently under investigation [18]. With respect to the actual photochemical process, our purpose is now to explore other ways to improve its efficiency, in particular by using photosensitizers, and to test the fatigue of the complexes upon repeated *cis-trans* interconversion cycles. Regarding the latter point, it is worth noting that the degradation of the systems is expected to be reduced in the solid state, where side-effect photoreactions are minimized.

Future developments might be based on photoreactions other than *cis-trans* photoisomerization [23], for example photochromic keto-enol tautomerism. Initial attempts based on the photocyclization of diarylethenes are presently being undertaken by the Louvain and Mainz groups [24]. Moreover, the nature of the spin-changing metal ion could be varied. We have recently obtained preliminary results with a pentacoordinate cobalt(II) complex formed with a $[N_2O_2]$ Schiff-base and a photoisomerizable styrylpyridine derivative [25].

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References

1. a) Zarembowitch J, Kahn O (1991) *New J Chem* 15:181; b) Kahn O, Kröber J, Jay C (1992) *Adv Mat* 4:718; c) Kahn O, Jay-Martinez C (1998) *Science* 279:44; d) Varret F, Noguès M, Goujon A (2001) In: Miller J, Drillon M (eds) *Magnetism: molecules to materials*, vol II. Wiley-VCH, p 257
2. a) Gütllich P, Hauser A, Spiering H (1994) *Angew Chem Int Ed* 33:2024; b) Kahn O (1993) *Molecular magnetism*. VCH New York; c) Hauser A (1991) *Coord Chem Rev* 111:275; d) König E (1991) *Struct Bond* 76:51; e) Toftlund H (1989) *Coord Chem Rev* 94:67; f) Beattie JK (1988) *Inorg Chem* 32:1; g) König E (1987) *Prog Inorg Chem* 35:527; h) Gütllich P, Hauser A, Spiering H (1999) In: Solomon EI, Lever ABP (eds) *Inorganic electronic structure and spectroscopy*, vol II. Wiley, New York, p 575; i) Gütllich P, Garcia Y, Woike T (2001) *Coord Chem Rev* 219/221:839; j) Gütllich P, Garcia Y, Spiering H (2003) In: Miller JS, Drillon M (eds) *Magnetism: molecules to materials*, vol IV. Wiley-VCH Weinheim, p 271
3. a) Decurtins S, Gütllich P, Spiering H, Hauser A (1985) *Inorg Chem* 24:2174; b) Gütllich P, Hauser A (1990) *Coord Chem Rev* 97:1; c) Hauser A (1995) *Comments Inorg Chem* 17:17
4. a) Létard JF, Guionneau P, Rabardel L, Howard JAK, Goeta AE, Chasseau D, Kahn O (1998) *Inorg Chem* 37:4432; b) Desaix A, Roubeau O, Jeftic J, Haasnoot JG, Boukheddaden K, Codjovi E, Linares J, Noguès M, Varret F (1998) *Eur Phys J B* 6:183
5. Zarembowitch J, Roux C, Boillot M-L, Claude R, Itié J-P, Polian A (1993) *Mol Cryst Liq Cryst* 234:247
6. Roux C (1992) Thesis, University Paris-Sud, France
7. Roux C, Zarembowitch J, Gallois B, Granier T, Claude R (1994) *Inorg Chem* 33:2273
8. Balzani V, Credi A, Raymo FM, Stoddart JF (2000) *Angew Chem Int Ed* 39:3348
9. Boillot M-L, Roux C, Audièrre J-P, Dausse A, Zarembowitch J (1996) *Inorg Chem* 35:3975
10. Boillot M-L, Chantaine S, Zarembowitch J, Lallemand J-Y, Prunet J (1999) *New J Chem* 23:179
11. Sour A, Boillot M-L, Rivière E, Lesot P (1999) *Eur J Inorg Chem* 2117
12. a) Boillot M-L, Soyer H (1997) *New J Chem* 21:889; b) Soyer H, Mingotaud C, Boillot M-L, Delhaès P (1998) *Langmuir* 14:5890; c) Soyer H (1998) Thesis, University of Bordeaux I, France; d) Boillot M-L, Sour A, Delhaès P, Mingotaud C, Soyer H (1999) *Coord Chem Rev* 190/192:47; e) Mingotaud C, Delhaès P, Meisel MW, Talham DR (2001) In: Miller J, Drillon M (eds) *Magnetism: molecules to materials*, vol II. Wiley-VCH, p 457
13. Fisher E, Frei Y (1957) *J Chem Phys* 27:808
14. Claude R, Real J-A, Zarembowitch J, Kahn O, Ouahab L, Grandjean D, Boukheddaden K, Varret F, Dworkin A (1990) *Inorg Chem* 29:4442
15. a) Bartocci G, Mazzucato U, Masetti F, Galianzo G (1980) *J Phys Chem* 84:847; b) Barigelletti F, Dellonte S, Orlandi G, Bartocci G, Masetti F, Mazzucato U (1984) *J*

- Chem Soc, Faraday Trans I 80:1123; c) Marconi G, Bartocci G, Mazzucato U, Spalletti A, Abbate F, Angeloni L, Castellucci E (1995) Chem Phys 196:383
16. a) Edwards MP, Hoff CD, Curnutte B, Eck JS, Purcell KF (1984) Inorg Chem 23:2616; b) Purcell KF, Edwards MP (1984) Inorg Chem 23:2620
 17. a) Zarnegar PP, Whitten DG (1971) J Am Chem Soc 93:3776; b) Zarnegar PP, Bock CR, Whitten DG (1973) J Am Chem Soc 95:4367; c) Wrighton MS, Morse DL, Pdungsap L (1975) J Am Chem Soc 95:4367
 18. a) Jaiswal A, Floquet S, Boillot M-L, Delhaès P (2002) Chem Phys Chem 12:1045; b) Floquet S, Salunke S, Boillot M-L, Clément R, Varret F, Boukheddaden K, Rivière E (2002) Chem Mater 14:4164
 19. Matsumoto N, Ohta S, Yoshimura C, Ohyoshi A, Kohata S, Okawa H, Maeda Y (1985) J Chem Soc Dalton Trans 2575
 20. Hirose S, Hayami S, Maeda Y (2000) Bull Chem Soc Jpn 73:2059
 21. Sour A, Boillot M-L, Floquet S, Rivière E (2001) ESF Workshop on Molecular Photo-magnetism (Seeheim, Germany), October 2001
 22. a) See the chapters by Hauser A et al., Hendrickson DN et al., Varret F et al. in the present book; b) Escax V, Bleuzen A, Cartier dit Moulin C, Villain F, Goujon A, Varret F, Verdager M (2001) J Am Chem Soc 123:12536; c) Ohkoshi S, Hashimoto K (2001) J Photochem Photobiol C Photochem Rev 2:71; (d) Rombaut G, Verelst M, Gohlen S, Ouahab L, Mathonière C, Kahn O (2001) Inorg Chem 41:1151
 23. a) Feringa BL, Jager WF, de Lange B (1993) Tetrahedron 49:8267; b) Irie M (2000) Chem Rev 100:1685
 24. Garcia Y, Ksenofontov V, Reiman S, Stauf S, Lang O, Tremel W, Lapouyade R, Gütlich P (2002) Seventh Spin Crossover Family Meeting (Seeheim, Germany), March 2002
 25. Tuna F, Patron L, Rivière E, Boillot M-L (2000) Polyhedron 19:1643

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- Astruc D, Blais J-C, Cloutet E, Djakovitch L, Rigaut S, Ruiz J, Sartor V, Valério C (2000) The First Organometallic Dendrimers: Design and Redox Functions. *210*: 229–259
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- Balzani V, Ceroni P, Maestri M, Saudan C, Vicinelli V (2003) Luminescent Dendrimers. Recent Advances. *228*: 159–191
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- Bertrand G, Bourissou D (2002) Diphosphorus-Containing Unsaturated Three-Membered Rings: Comparison of Carbon, Nitrogen, and Phosphorus Chemistry. *220*: 1–25
- Betzemeier B, Knochel P (1999) Perfluorinated Solvents – a Novel Reaction Medium in Organic Chemistry. *206*: 61–78
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- Brunel JM, Buono G (2002) New Chiral Organophosphorus atalysts in Asymmetric Synthesis. 220: 79–106
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- Chow H-F, Leung C-F, Wang G-X, Zhang J (2001) Dendritic Oligoethers. 217: 1–50
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- de Meijere A, Kozhushkov SI, Khlebnikov AF (2000) Bicyclopropylidene – A Unique Tetrasubstituted Alkene and a Versatile C₆-Building Block. *207*: 89–147
- de Meijere A, Kozhushkov SI, Hadjiraoglou LP (2000) Alkyl 2-Chloro-2-cyclopropylideneacetates – Remarkably Versatile Building Blocks for Organic Synthesis. *207*: 149–227
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- Drabowicz J, Mikołajczyk M (2000) Selenium at Higher Oxidation States. *208*: 143–176
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- Ehses M, Romerosa A, Peruzzini M (2002) Metal-Mediated Degradation and Reaggregation of White Phosphorus. *220*: 107–140
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- Famulok M, Jenne A (1999) Catalysis Based on Nucleic Acid Structures. *202*: 101–131
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- Zhdankin VV (2003) C-C Bond Forming Reactions. 224: 99–136
- Zhao M, see Crooks RM (2001) 212: 81–135
- Zimmermann SC, Lawless LJ (2001) Supramolecular Chemistry of Dendrimers. 217: 95–120
- Zwanenburg B, ten Holte P (2001) The Synthetic Potential of Three-Membered Ring Azaheterocycles. 216: 93–124

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