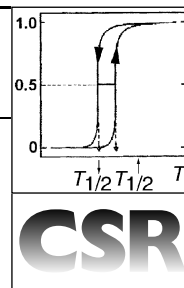


# Spin crossover phenomena in Fe(II) complexes†

Philipp Gütlich,\*<sup>a</sup> Yann Garcia<sup>a</sup> and Harold A. Goodwin<sup>b</sup>

<sup>a</sup> Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg Universität, Staudingerweg 9, D-55099 Mainz, Germany

<sup>b</sup> School of Chemistry, The University of New South Wales, UNSW Sydney 2052, Australia



Received 8th May 2000

First published as an Advance Article on the web 4th October 2000

The behaviour of spin crossover compounds is among the most striking and fascinating shown by relatively simple molecular species. This review aims to draw attention to the various ways in which spin crossover phenomena are manifested in iron(II) complexes, to offer some rationalisation for these, and to highlight their possible applications. Typical examples have been selected along with more recent ones in order to give an overall view of the scope and development of the area. The article is structured to provide the basic material for those who wish to enter the field of spin crossover.

† Dedicated to Professor F. A. Cotton on occasion of his 70th birthday.

## 1 Introduction

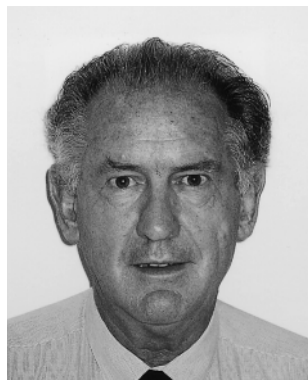
As a consequence of the splitting of the energy of the d orbitals into the  $t_{2g}$  and  $e_g$  sets in a ligand field, octahedral complexes of certain of the transition metal ions, particularly those of the first transition series with configurations  $d^4$  to  $d^7$ , may exist in either the high-spin (HS) or low-spin (LS) state, depending on the nature of the ligand field about the metal ion. In weak fields the ground state is HS where the spin multiplicity is a maximum, the d electrons being distributed over the  $t_{2g}$  and  $e_g$  sets whereas strong fields stabilise the LS state with minimum multiplicity, the  $t_{2g}$  set being completely occupied before electrons are added to the  $e_g$  set. For the  $d^6$  ion of iron(II), for example, the two states are illustrated by  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , which, with the configuration

Harold Goodwin, became a research associate at the University of Illinois in 1959. He was appointed as a lecturer at the University of New South Wales in 1960 and promoted to associate professor in 1974. In 1996, after his retirement, he was appointed as honorary visiting fellow of the school of chemistry of the UNSW. Among his many international overseas appointments, he received several fellowships, including some from the prestigious Alexander von Humboldt foundation. His main research interests focus on transition metal chemistry with particular emphasis on the electronic and structural properties of metal derivatives of nitrogen-containing heterocycles. The Royal Australian Chemical Institute cited Dr Goodwin in 1988.

Dr Yann Garcia, born in 1972 in Castres (France), studied Chemistry and Physics at the University of Bordeaux, where he undertook his doctoral studies with Professor O. Kahn in the field of spin transition molecular materials. Following completion of his doctorate in 1999, Dr Garcia joined the University of Mainz (Germany) to work with Professor P. Gütlich as a

postdoctoral fellow. His current research interests and activities focus on cooperative phenomena of spin transitions and supramolecular chemistry.

Philipp Gütlich received his doctorate in Physical Chemistry and Nuclear Chemistry from the Technische Hochschule Darmstadt in 1963. He then moved to the Nuclear Research Centre in Saclay (France) and subsequently to the Brookhaven National Laboratory (USA), where his research led him into the field of Mössbauer spectroscopy. In 1969 he completed his habilitation at the TH Darmstadt with a thesis on the Applications of Mössbauer Spectroscopy in Chemistry. He accepted the chair of Anorganische Chemie und Analytische Chemie at the University of Mainz in 1975. His main research interests focus on the electronic structures of transition metal complexes using Mössbauer Spectroscopy and other physical techniques. Professor Gütlich received the Research Award of the Japanese Society for the Promotion of Science in 1989 and in 1993, together with Professor O. Kahn, the Forschungspreis der Max-Planck-Gesellschaft. Among his many current international appointments he is the chair of the International Board on the Application of the Mössbauer effect and the co-ordinator of the TMR-network 'Thermal and Optical Switching of Molecular Spin States (TOSS)'. He has published more than 300 research papers, several books and many book chapters.



Harold A. Goodwin

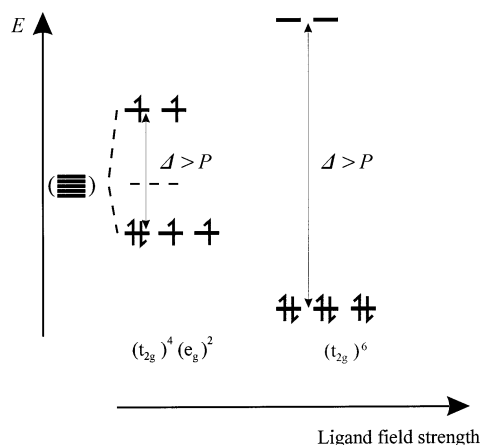


Yann Garcia



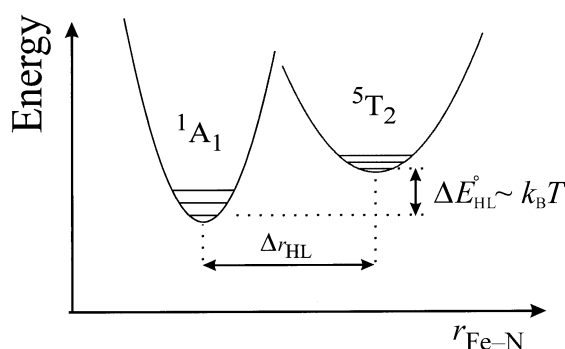
Philipp Gütlich

$t_{2g}^4 e_g^2$ , has four unpaired electrons and thus is strongly paramagnetic ( ${}^5T_{2g}$  state in octahedral symmetry), and  $[\text{Fe}(\text{CN})_6]^{4-}$  ( $t_{2g}^6 e_g^0$ ) which has no unpaired electrons ( ${}^1A_{1g}$  state) (Fig. 1). For intermediate fields the energy difference



**Fig. 1** Electronic configuration for a  $d^6$  iron(II) ion, in the HS state and equilibrium between these two states in the case of thermal spin crossover.  $\Delta$  stands for the cubic ligand field parameter and  $P$  for the mean spin-pairing energy.

( $\Delta E_{\text{HL}}^\circ$ ) between the lowest vibronic levels of the potential wells of the two states may be sufficiently small such that application of some relatively minor external perturbation effects a change in the state. This phenomenon is known as a spin transition (ST) or spin crossover (SC) and its origin is illustrated in Fig. 2. A ST will be induced thermally when



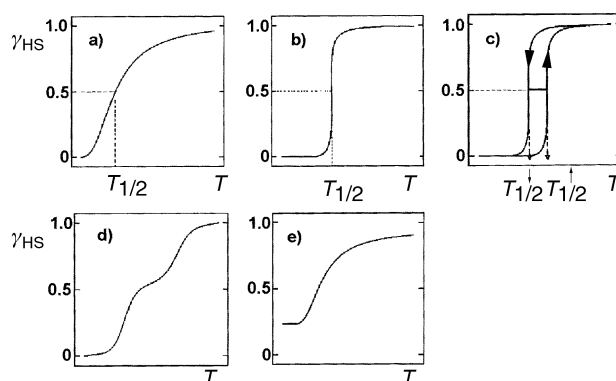
**Fig. 2** Representation of the potential wells for the  ${}^1A_1$  and  ${}^5T_2$  states of an iron(II) SC system, the nuclear coordinate being the metal-donor atom distance.

$\Delta E_{\text{HL}}^\circ \cong k_B T$  and when this criterion is met pressure- and light-induced transitions may also be observed. Although spin transitions have been observed for all the configurations listed above for the first transition series and a very limited number are known for the second transition series, by far the greatest number has been reported for iron(II). Since the properties of the iron(II) systems span the whole range of behaviour observed for ST systems, this article will draw principally on examples containing this ion to illustrate the important features of the ST phenomenon.

The relatively facile change in ground state exhibited by iron(II) in a suitably contrived ligand environment has important implications for virtually all the properties of the particular metal derivative. Spin transitions are found in natural systems, in particular in a number of haem derivatives where they can play a pivotal role in controlling biological functions.<sup>1</sup> In naturally occurring systems haemoglobin may be unique in exploiting the very significant change in the Fe-N bond lengths accompanying singlet ( ${}^1A_1$ )  $\leftrightarrow$  quintet ( ${}^5T_2$ ) conversions in

iron(II) for the purpose of efficient oxygen transport. It has been pointed out<sup>2</sup> that without application of that change in spin state, fast-moving animals could not have evolved. Spin transitions are also observed in certain minerals<sup>3</sup> and in geological processes the relationship between *pressure* and spin state is especially relevant. In synthetic systems spin transitions have been recognised since the 1930s when Cambi and co-workers first observed the phenomenon in iron(III) dithiocarbamate derivatives. Since then the field has continued to grow and the past few years in particular have seen fundamental advances in the understanding of the phenomenon and the properties associated with it. The earlier developments in iron(II) ST systems were reviewed by König in 1968,<sup>4</sup> Goodwin in 1976<sup>5</sup> and Gütllich in 1981.<sup>6</sup> Since then numerous reviews have appeared on specific aspects of the phenomenon and these are listed in the 1994 comprehensive review by Gütllich, Hauser and Spiering.<sup>7</sup>

From the measurement of the temperature-dependence of the properties of a ST system it is possible to evaluate the relative concentrations of HS and LS states as a function of temperature and thus to construct a ST curve, a plot of the HS molar fraction  $\gamma_{\text{HS}}$  vs.  $T$ , (Fig. 3). For systems in solution the behaviour follows a curve similar to that of Fig 3a and may be interpreted in terms



**Fig. 3** The nature of ST curves for SC systems in the solid state: (a) gradual; (b) abrupt; (c) with hysteresis; (d) with steps; (e) incomplete.

of a simple thermal equilibrium involving a Boltzmann distribution over all vibronic levels of the two spin states. In this instance the transition occurs essentially at the molecular level without the constraints of lattice interactions. For solid systems lattice effects assume importance and the full range of behaviour illustrated by the curves of Fig 3a-e has been observed. The transition may be gradual and continuous over an extended temperature range, similar to solution behaviour (Fig. 3a), or it may be abrupt and occur within a narrow temperature range (Fig. 3b). The transition may be associated with a thermal hysteresis loop (Fig. 3c) or be a two-step process (Fig. 3d). In certain instances the transition may be incomplete at one or both extremes of the ST curve (Fig. 3e). The curves are diagnostic of the nature of the ST and the steepness of the change, for example, is indicative of the extent of cooperativity involved in the propagation of the spin change throughout the solid lattice, *i.e.* the extent to which the electronic and structural changes in a molecule undergoing a ST influence corresponding changes in neighbouring molecules. This aspect is developed further in Section 4. When this is low the transition will be a gradual or continuous process, but as cooperativity increases the transition becomes more abrupt and may occur within a very narrow range of temperature or be associated with a phase change and/or thermal hysteresis. A transition temperature is defined as that temperature at which the fractions of HS and LS species, which take part in the transition, are equal. For transitions displaying hysteresis two transition temperatures  $T_{1/2 \downarrow}$  and  $T_{1/2 \uparrow}$  define the width of the hysteresis loop.

## 2 Principal physical techniques

The appearance of a thermally induced ST will be manifested in a strong temperature-dependence of various properties of the system, which depend on electronic structure. Perhaps the most important of these are colour, magnetism and molecular structure. Since in the HS and LS states there are different occupancies of the *anti-bonding*  $e_g$  orbitals in particular, the metal–donor atom distance is remarkably sensitive to spin-state. The change amounts to about 0.2 Å for the Fe–N bond distances as a consequence of singlet ( $^1A_1$ )  $\leftrightarrow$  quintet ( $^5T_2$ ) transitions in iron(II) systems, the Fe–N distances being longer in the HS state (with appreciable occupancy of the  $e_g^*$  orbitals) and shorter in the LS state (with empty  $e_g^*$  orbitals). For systems in the solid state this change in the molecular dimensions may bring about fundamental changes in the crystal lattice.

It is possible to monitor a transition and construct a ST curve by a variety of techniques. The measurement of magnetism is frequently employed to characterise a ST since there is a marked difference in the magnetic moments<sup>8</sup> of HS (*ca.* 5 B.M.) and LS (*ca.* 0 B.M.) iron(II) and thus a strong temperature-dependence of the magnetic moment is expected. An example is shown in Fig. 4 for  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$  (ptz = 1-propyltetrazole). Magnetism alone is not sufficient to establish the existence of a ST since it is a property of the bulk material.

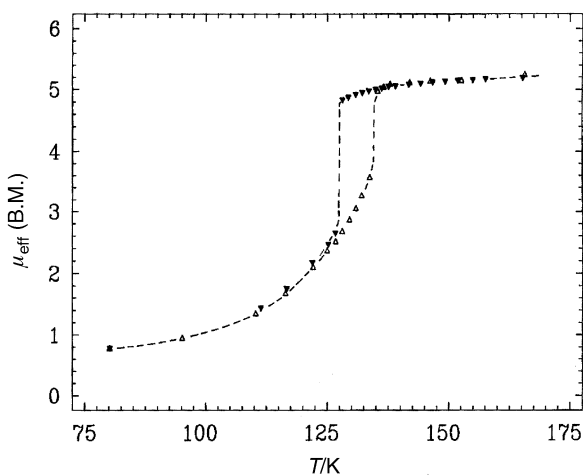


Fig. 4 Temperature-dependence of the magnetic moment for polycrystalline  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$  on slowly cooling ( $\blacktriangledown$ ) and heating ( $\triangle$ ).

Spectroscopic techniques are frequently applied to identify and characterise a ST. Iron(II) Mössbauer spectroscopy is particularly suitable since the spectral parameters associated with the HS and LS states clearly differ and the time-scale of the technique ( $10^{-7}$  s) is such as generally to allow the detection and evaluation of the separate spin states in the course of the transition. Typically, Mössbauer spectra of HS iron(II) show relatively high quadrupole splitting, ( $\Delta E_Q \approx 2\text{--}3$  mm  $\text{s}^{-1}$ ) and

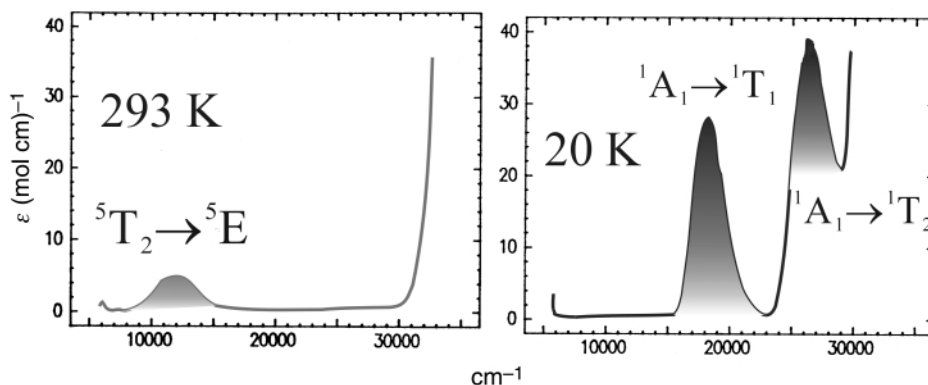


Fig. 6 Single crystal UV-vis absorption spectra for  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$  in the LS and HS states.

isomer shift, ( $\delta \approx 1$  mm  $\text{s}^{-1}$ ), while for LS iron(II) these parameters are generally smaller ( $\Delta E_Q \leq 1$  mm  $\text{s}^{-1}$ ,  $\delta \leq 0.5$  mm  $\text{s}^{-1}$ ). As an example, the temperature-dependent Mössbauer spectra of  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$  are shown in Fig. 5. For iron(II),

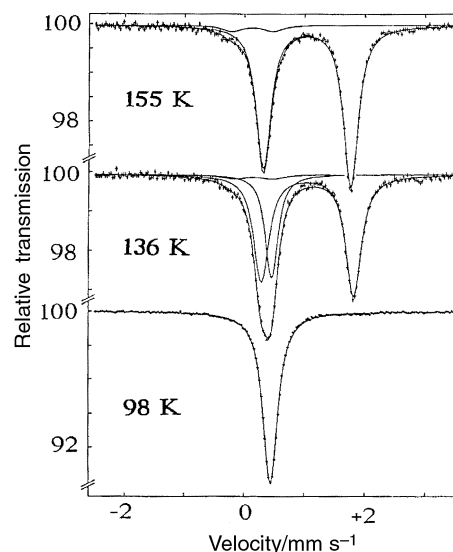


Fig. 5 Temperature-dependent  $^{57}\text{Fe}$  Mössbauer spectra for polycrystalline  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ .

the electronic spectrum for the HS ion shows one ligand field band (frequently broad or split) in the near-infrared region and arising from the  $^5T_2 \rightarrow ^5E$  transition, while for LS iron(II) two ligand field bands occur,  $^1A_1 \rightarrow ^1T_1$  and  $^1A_1 \rightarrow ^1T_2$ , the former appearing in the visible and the latter in the ultra-violet region. Charge-transfer transitions for both spin states often appear in the visible region and thus mask the ligand field transitions for the LS state but they are generally displaced to higher frequency for the HS species. Thus a thermally induced transition will usually result in strong, visible thermochromism, and this frequently provides a simple and rapid means for the ready detection of the likely occurrence of a spin transition. In certain cases the charge transfer transition in the LS form does not occur in the visible region and then the  $^1A_1 \rightarrow ^1T_1$  ligand field transition may determine the colour of the LS state. In this instance the LS  $\rightarrow$  HS transition is generally accompanied by a change from pink-violet to colourless. An example is the compound  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$  for which the optical spectra of the HS and LS states are shown in Fig. 6.<sup>7</sup>

## 3 Selected spin crossover compounds

### 3.1 Generation of the crossover situation

Although the criterion for the occurrence of a ST may appear very restrictive there is in fact a very large number ( $> 150$ ) of

systems which have been characterised. By far the majority of these are  $\text{Fe(II)}\text{N}_6$  systems where all or some of the nitrogen donors are part of heterocyclic systems. The first synthetic system,  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  (phen = 1,10-phenanthroline), was identified in 1966<sup>9</sup> and since then many other species of similar composition have been shown to undergo transitions. In addition, derivatives of simple unidentate ligands such as isoxazole and substituted tetrazoles, along with multidentate species and polynuclear systems are now known to show SC behaviour. While it is not possible to rationalise readily the great variety of ligand systems known to generate SC behaviour in iron(II), sufficient is recognised of the general features of such systems to enable the fine-tuning of the field strength of model ligands so as to bring it into the crossover region. Three strategies in particular are widely effective:

(i) The incorporation of substituents in the ligand. If the substituent is adjacent to a donor atom this will de-stabilise the singlet state by hindering the close approach of the metal atom and is illustrated by  $[\text{Fe}(\text{mephen})_3]^{2+}$  (mephen = 2-methyl-1,10-phenanthroline) which is HS at room temperature but undergoes a transition to LS at low temperatures, in contrast to the unsubstituted  $[\text{Fe}(\text{phen})_3]^{2+}$  which is LS at all accessible temperatures.<sup>10</sup> In other instances where the substituent is remote from the donor atom electronic effects may be operative and could be applied to stabilise either state.

(ii) The replacement of six-membered heterocycles by five-membered. The principal effect here is to reduce both the  $\sigma$ -donor and  $\pi$ -acceptor character of the system and hence to favour the quintet state, but steric effects are also expected to be operative since the geometry of the five-membered ring will introduce additional strain into the chelate ring. Perhaps surprisingly, the dimensions of the actual  $\text{FeN}_6$  coordination core are not usually markedly different for chelate groups containing five-membered heterocycles and those containing six-membered. The effect is illustrated by the SC behaviour of  $[\text{Fe}(\text{pyim})_3]^{2+}$  (pyim = 2-(pyridin-2-yl)imidazole), in contrast to the completely LS nature of  $[\text{Fe}(\text{bpy})_3]^{2+}$  (bpy = 2,2'-bipyridine).<sup>11</sup>

(iii) The replacement of conjugated, heterocyclic donor systems by aliphatic. The typical substitution applied here is of a 2-pyridyl group by an amino-methyl group. One of the most widely studied systems is  $[\text{Fe}(\text{pic})_3](\text{anion})_2$  (pic = 2-picolyamine) for which a variety of SC behaviour has been observed.<sup>6</sup> This approach of incorporation of the picolyamine or related structural motif has been extended widely by Toftlund<sup>12</sup> and even encompasses the sexadentate system tetrakis(2-pyridylmethyl)ethylenediamine for which the iron(II) complex perchlorate

is exceptional in showing a rate of interconversion of the quintet and singlet states sufficiently high that resolution of the two spin states on the Mössbauer timescale is not achieved.<sup>13</sup>

The tridentate ligand 2,2':6',6''-terpyridine ( $L = 1$ ) forms a LS  $[\text{FeN}_6]^{2+}$  species and many SC systems have been devised by modifying this in ways similar to those applied to the bidentate bipyridine (Fig. 7). Thus the effect of substitution is illustrated by the HS nature of salts of bis(2,6-bis-(quinolin-2-yl)pyridine)iron(II) ( $L = 2$ ) in which the benzene rings fused to the terminal pyridine rings provide a barrier to the close approach of the metal atom necessary in the LS configuration.<sup>14</sup> Introduction of a phenyl substituent adjacent to just one of the terminal N-donors ( $L = 3$ ) has been shown to lead to either a HS or a LS complex in the solid state and to a temperature- and pressure-dependent spin equilibrium in solution.<sup>15</sup> However, when phenyl or methyl substituents are present adjacent to both terminal donor atoms the  $[\text{FeN}_6]^{2+}$  derivative is entirely HS.<sup>15</sup> Replacement of the pyridine rings in terpyridine by five-membered heterocycles can also be effective in generating SC behaviour, but the effect is quite different for the terminal rings on the one hand and the central ring on the other. This arises primarily because of the steric consequences of tridentate coordination in an equatorial plane of an octahedron. The metal– $\text{N}_{\text{central}}$  distance is always the shortest and thus the replacement of the central ring has the more drastic effect. This is shown, for example, by the SC behaviour of salts of the  $[\text{FeN}_6]^{2+}$  derivative of 2,4-bis(pyridin-2-yl)thiazole ( $L = 4$ ) but the LS nature of derivatives of the isomeric ligand 2-(pyridin-2-yl)-6-(thiazol-2-yl)pyridine ( $L = 5$ ).<sup>16</sup> Even when both terminal rings are replaced by the thiazole ring, salts of the  $[\text{FeN}_6]^{2+}$  species remain LS but the system can be brought into the crossover domain by subsequent incorporation of substituents in the terminal rings (methyl or fused benzo-substitution). It is noteworthy that because of the geometry of the five-membered rings, substituents adjacent to the donor atoms are skewed away from the metal atom and steric effects are less pronounced than those of substituents adjacent to the nitrogen atom of pyridine. Thus while the  $[\text{FeN}_6]^{2+}$  derivative of 2,6-bis-(quinolin-2-yl)pyridine is HS, that of 2,6-bis(benzimidazol-2-yl)pyridine ( $L = 6$ ) or 2,6-bis(benzthiazol-2-yl)pyridine ( $L = 7$ ) shows crossover behaviour.<sup>17</sup>

The SC situation is very critically poised and modifications to a system more subtle than ligand substitution can effect fundamental changes in the electronic properties of the system. Many iron(II) SC systems are cationic and the course or even the actual occurrence of a ST can be affected by variation in the nature of the accompanying anion or by the formation of

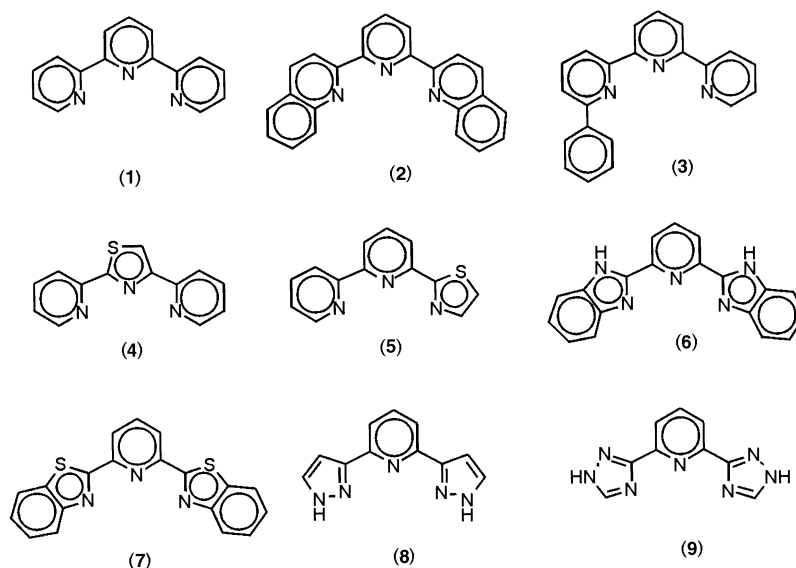


Fig. 7 Tridentate ligand systems related to 2,2':6',6''-terpyridine.

solvates. Both effects have been observed, for example, for salts of the  $[\text{Fe}(\text{pic})_3]^{2+}$  system.<sup>6</sup> The influence of solvation is observed in uncharged complexes as well. The operation of these effects is fairly widespread but rarely predictable, the one anion, for example, favouring the HS form in one system but the LS in another. Similarly hydration, while favouring the LS state in most instances, may stabilise either state. Thus while, for example,  $[\text{Fe}(\text{bpp})_2](\text{BF}_4)_2 \cdot 3\text{H}_2\text{O}$  ( $\text{bpp} = \text{bis}(2,6\text{-bis}(\text{pyrazol-3-yl})\text{pyridine})$ ) ( $L = 8$ ) is LS at room temperature, the anhydrous compound is HS. On the other hand  $[\text{Fe}(\text{btp})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  ( $\text{btp} = \text{bis}(2,6\text{-bis}(1,2,4\text{-triazol-2-yl})\text{pyridine})$ ) ( $L = 9$ ) is HS and the anhydrous salt is LS at room temperature.<sup>18</sup> These effects are determined by lattice forces and may result, for example, from outer sphere ligand field effects, hydrogen bonding interactions or changes in the ‘chemical pressure’ exerted by different lattice anions or solvate molecules.

### 3.2 Polymeric compounds

One of the main challenges in SC research is to design materials suitable for practical applications on the nanotechnological scale. For this purpose, the mere occurrence of SC itself is not a guarantee of success. For switching devices, for example, room temperature bistability conditions are required along with a very abrupt ST showing a broad hysteresis loop. For displays, a colour change is in addition necessary.<sup>19</sup> The presence of an hysteresis loop in a ST curve originates entirely from cooperative effects if there is no accompanying crystallographic phase change. The loop width is related to the strength of the cooperative interactions. Their origin is detailed in Section 4. Allowing SC centres to communicate *via* covalently bound chemical bridges, *i.e.* in a polymeric species, is an important strategy to enhance cooperativity of a given system. In this way, molecular distortions accompanying the ST can be efficiently distributed throughout the whole crystal lattice. For this reason particular attention has been directed to incorporating ST centres into polymeric species over the past ten years. Most of those studied incorporate 1,2,4-triazole as ligands.<sup>20</sup> Chains of linked ST centres, as well as two-dimensional and three-dimensional networks have been reported.<sup>19–24</sup> At the present time the  $\text{Fe}(\text{II})$ -1,2,4-triazole linear chain derivatives represent the most important class of this family.<sup>19,21</sup> Their crystal structure consists of metal centres triply bridged by 1,2,4-triazole ligands through the nitrogen atoms occupying the 1 and 2 positions, as shown recently for a related  $\text{Cu}(\text{II})$  compound.<sup>25</sup> The non-coordinated anions and any solvent molecules occupy the space between the chains. The behaviour of these systems is illustrated by  $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2$  ( $\text{NH}_2\text{trz} = 4\text{-amino-1,2,4-triazole}$ ) which undergoes an abrupt ST above room temperature and associated with a hysteresis loop of width of 35 K (Fig. 8) together with a pronounced thermochromic effect: purple (LS)  $\leftrightarrow$  white (HS).<sup>19</sup> These types of materials are currently being assessed by industrial organisations for possible practical applications. Compounds of higher dimensionality incorporate symmetric multifunctional ligands able to coordinate metal ions in several directions. The judicious use of the potentially tetradentate 4,4'-bis-1,2,4-triazole (btr) molecule resulted in the discovery of the first two-dimensional and three-dimensional ST compounds.<sup>20,22</sup> The crystal structure of  $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$  consists of planes in which the  $\text{Fe}(\text{II})$  ions are linked by btr ligands.<sup>22</sup> The thiocyanate anions are situated in *trans* position and the non-coordinated water molecules are hydrogen bonded to the peripheral nitrogen atoms of the triazole units (Fig. 9). The layers are connected by means of van der Waals forces and weak hydrogen bond bridges involving the water molecules. This compound undergoes a very abrupt ST around 134 K with a thermal hysteresis of 21 K. Replacement of the NCS anions by btr ligands in the  $\text{Fe}(\text{II})$  coordination sphere

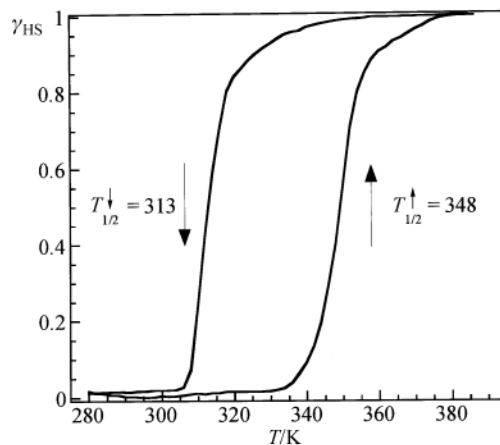


Fig. 8 Temperature-dependence of the HS molar fraction of powdered  $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2$ .

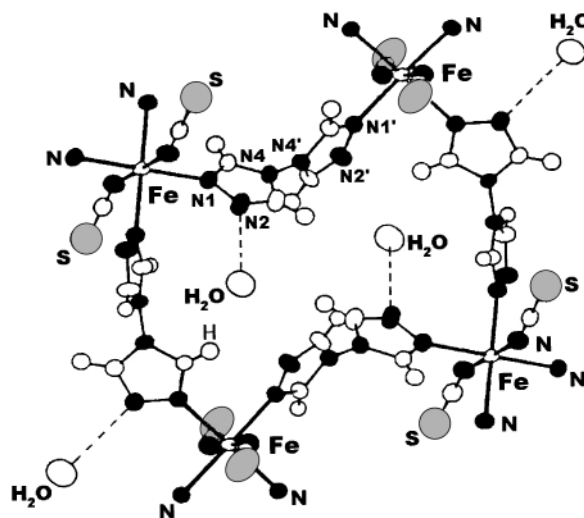


Fig. 9 Part of the crystal structure of  $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$  ( $T = 293 \text{ K}$ ).

results in an increase in the dimensionality. Thus,  $[\text{Fe}(\text{btr})_3](\text{ClO}_4)_2$  consists of a three-dimensional network. The crystal structure reveals the presence of two distinct  $\text{Fe}(\text{II})$  sites which in fact separately undergo SC behaviour below room temperature.<sup>20</sup> This leads to the observation of a two-step spin transition. The properties of  $[\text{Fe}(\text{tvp})_2(\text{NCS})_2]$  ( $\text{tvp} = \text{bis}(1,2\text{-di}(4\text{-pyridyl})\text{ethylene})$ ) are very relevant here. This compound represents the first two-dimensional molecular catenane exhibiting SC behaviour. Its crystal structure consists of two independent fully interlocked orthogonal infinite networks.<sup>23</sup>  $[\text{Fe}(\text{pyridine})_2\text{Ni}(\text{CN})_4]$  is also a two-dimensional polymeric ST compound.<sup>24</sup> It shows a discontinuous ST below room temperature with a hysteresis width of 12 K. In this system bridging cyano groups link the metal centres.

## 4 Spin crossover and the solid state [cooperative effects]

Spin transitions are observed for systems in both the solution and solid states, though the one system will not necessarily display a transition in both phases. In solution, interactions between the molecules undergoing spin change are virtually negligible and thus the course of the transition can be described by a Boltzmann approach with a temperature-dependent distribution over all HS vibronic states and the LS state. The thermal transition is in this case a molecular process and not subject to cooperative interactions. The driving force for the

transition is the considerable entropy gain of *ca.* 50–80 J mol<sup>-1</sup> K<sup>-1</sup> for the LS → HS conversion, made up of a magnetic component,  $\Delta S_{\text{mag}} = R[\ln(2S + 1)_{\text{HS}} - \ln(2S + 1)_{\text{LS}}]$ , *ca.* 13 J mol<sup>-1</sup> K<sup>-1</sup>, and a much greater vibrational entropy contribution arising from the much higher degeneracies (degrees of freedom) in the HS state.<sup>7</sup> The enthalpy change associated with the LS → HS conversion is typically in the range 6–15 kJ mol<sup>-1</sup> and is associated primarily with the rearrangement of the coordination sphere (metal–donor atom bond length increase) accompanying the LS → HS change.

In the solid state there is electron–phonon coupling between the molecules changing spin state, resulting in cooperative interactions of varying degrees, as mentioned above. Many attempts have been made to model quantitatively the different forms of ST behaviour and the nature of the underlying cooperative interactions in solid systems. One of the most successful treatments, developed by Spiering *et al.*,<sup>26</sup> takes as its basis the large change in the metal–donor atom distance (~0.2 Å) accompanying a transition in iron(II). It is proposed that such a significant change at every ‘point defect’ where a ST occurs, sets up pressure (an ‘image pressure’) which is communicated to the surroundings *via* phonon interactions. In the course of the ST process at many point defects the lattice expands and accelerates the ST in other metal centres. Thus the nature of the cooperative interactions in a solid is elastic, and in fact the model of Spiering *et al.* utilises typical quantities from elasticity theory to account for the experimental results.

Experimental proof for the existence of cooperative interactions during ST processes in solids has been observed in studies of the metal dilution effect.<sup>27</sup> This involves partial replacement of iron(II), without change of crystal structure, by a foreign metal ion, preferably zinc(II) which has the d<sup>10</sup> electron configuration and thus is magnetically silent. This affects the ST curve  $\chi_{\text{HS}}(T)$  essentially in two ways: (i) it becomes more gradual and (ii) it is displaced progressively to lower temperatures with decreasing iron concentration. In fact, at sufficiently high dilution, the ST curve reflects a simple Boltzmann distribution of the separate spin states, indicative of vanishing cooperative interactions, and resembles the curve for a system in liquid solution.

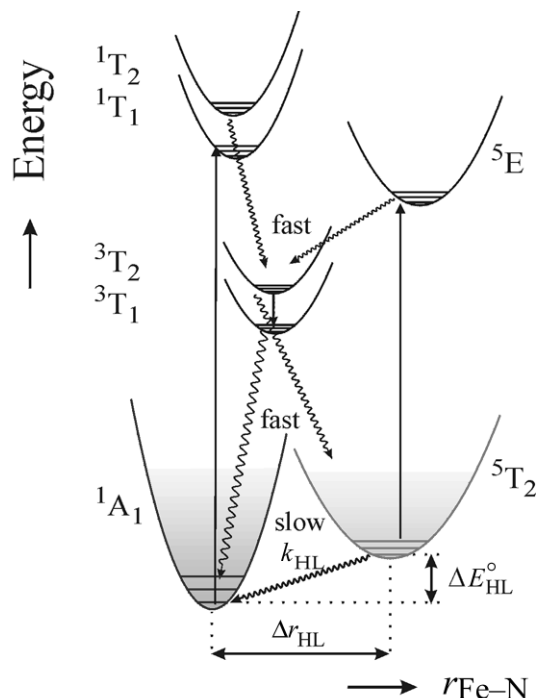
Further proof for the existence of cooperative interactions comes from optical spectroscopy of decaying long-lived HS states generated by light (LIESST effect; see Section 5).<sup>28</sup> It has been found, for example, that in a single crystal of [Fe(ptz)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub>, the <sup>1</sup>A<sub>1</sub> → <sup>1</sup>T<sub>1</sub> absorption peak shifts by *ca.* 200 cm<sup>-1</sup> relative to its original position at *ca.* 18000 cm<sup>-1</sup> as it grows in intensity during the decay of the metastable HS state. The reason is a non-linear build-up of ‘chemical pressure’ inside the crystal during the HS relaxation process. It is slow in the beginning, but accelerates with increasing concentration of iron(II) LS centres. The normalised <sup>5</sup>T<sub>2</sub> → <sup>1</sup>A<sub>1</sub> relaxation curves of such decay kinetics show sigmoidal behaviour,<sup>29</sup> which further indicates the existence of cooperative interactions. Similar studies of the decay kinetics in a diluted single crystal such as [Fe<sub>0.1</sub>Zn<sub>0.9</sub>(ptz)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> gave entirely different results. The recovery curve  $\chi_{\text{LS}}(t)$  is now single-exponential,<sup>29</sup> and there is no observable shifts in energy of the growing <sup>1</sup>A<sub>1</sub> → <sup>1</sup>T<sub>1</sub> absorption peak; both features are indicative of vanishing cooperative interactions in a diluted crystal, where the average iron(II)–iron(II) distance has become so large that the spin state changing centres no longer ‘communicate’ with each other.

Cooperativity of a ST is shown in the solid state and, if pronounced, may lead to thermal hysteresis. Since this effect is one of the most significant features of SC systems in relation to their possible practical application, considerable effort has been devoted to understanding the means by which the ST is propagated throughout the crystal. Strong cooperativity would be expected to be most likely in polymeric systems and indeed has been observed in these, most notably in the rigid triazole systems mentioned above. Hydrogen bonding has long been

considered to provide a likely mechanism for communication between metal centres. There are many SC systems where the ligand incorporates hydrogen bonding sites in addition to the donor atoms and thus such bonding may link the complex entities directly or *via* interaction with solvent molecules or anions. A further promising means of enhancing cooperativity would seem to be *via*  $\pi$  stacking interactions. These are believed to be the principal source of the cooperativity in [Fe(dpp)<sub>2</sub>(NCS)<sub>2</sub>]<sub>2</sub>·py (dpp = dipyrro[3,2-a:2'3'-c]phenazine).<sup>30</sup>

## 5 Effect of light

In the mid eighties it was accidentally observed that an Fe(II) SC compound in the LS state was converted by light into the metastable HS state and this had a virtually infinite lifetime at sufficiently low temperatures.<sup>31</sup> This phenomenon became known as the LIESST effect (Light-Induced-Excited-Spin-State-Trapping). Later it was found that the reverse process is also possible.<sup>32</sup> The mechanism for these photo-switching processes, which turned out to be a common feature of most Fe(II) SC systems, is sketched in Fig. 10. Green light (514 nm of



**Fig. 10** Schematic illustration of LIESST and reverse LIESST of a d<sup>6</sup> complex in the SC range. Spin allowed d–d transitions are denoted by arrows and the radiationless relaxation processes by wavy lines.

an Ar ion laser) is used for the spin allowed excitation <sup>1</sup>A<sub>1</sub> → <sup>1</sup>T<sub>1</sub> with <sup>1</sup>T<sub>1</sub> lifetimes typically of nanoseconds. A fast relaxation cascading over two successive intersystem crossing steps, <sup>1</sup>T<sub>1</sub> → <sup>3</sup>T<sub>1</sub> → <sup>5</sup>T<sub>2</sub>, populates the metastable <sup>5</sup>T<sub>2</sub> state. Radiative relaxation <sup>5</sup>T<sub>2</sub> → <sup>1</sup>A<sub>1</sub> is forbidden, and decay by thermal tunnelling to the ground state <sup>1</sup>A<sub>1</sub> is slow at low temperatures. Reverse LIESST is achieved by application of red light (*ca.* 820 nm) whereby the <sup>5</sup>T<sub>2</sub> state is excited to the <sup>5</sup>E state with two subsequent intersystem crossing processes, <sup>5</sup>E → <sup>3</sup>T<sub>1</sub> → <sup>1</sup>A<sub>1</sub>, leading back to the LS ground state. As demonstrated later by Hauser, photoswitching from LS to HS is also possible *via* <sup>1</sup>A<sub>1</sub> → <sup>3</sup>T<sub>1</sub> → <sup>5</sup>T<sub>2</sub> transitions using red light of 980 nm. Although LIESST was first observed in a single crystal of the SC compound [Fe(ptz)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> it was shown later that it can be induced in SC molecules embedded in polymer films and in KBr pellets. It is worth mentioning in this context that LIESST has also been observed for the conversion of a HS ground state to the metastable LS state by red light.<sup>33</sup>

Detailed studies of relaxation of LIESST-generated states have yielded clear evidence for cooperative interactions in the neat crystalline compound, but vanishing cooperativity in a metal-diluted system.<sup>29,34</sup> As already mentioned above, two important features establish the existence of cooperativity: (i) the sigmoidal shape of the LIESST state relaxation curve; (ii) shift of the  $^1A_1 \rightarrow ^3T_1$  absorption band by *ca.* 200  $\text{cm}^{-1}$  during  $^1A_1$  ground state recovery. A build-up of internal pressure, dependent on the LS fraction, causes self-acceleration of relaxation of the LIESST state and is responsible for these typical features.

The effect of light on SC systems is being pursued very actively and a number of new phenomena have recently been reported. These include: Light-Induced Thermal-Hysteresis (LITH), the effect of generating a hysteresis in the ST curve after LIESST, and subsequent constant irradiation with light;<sup>35</sup> Light-Induced Perturbation of a Thermal Hysteresis (LIPTH), whereby the hysteresis associated with a thermal ST is shifted to either lower or higher temperatures under irradiation with light of different wavelengths;<sup>36</sup> Ligand-Driven-Light-Induced Spin Change (LD-LISC) is another remarkable light effect, whereby irradiation affords a *cis-trans* isomerisation of the coordinated ligand, *e.g.* of stilbenoid type, with subsequent ST at the Fe(II) centre as a consequence of a change in ligand field strength.<sup>37</sup> This effect has so far been observed only in liquid solution, presumably because of the major mechanical forces involved in the *cis-trans* conversion. In this context attention is drawn to a fascinating photomagnetic switching in an analogue of Prussian Blue, where light-induced electron transfer between  $\text{Co}^{\text{III}}\text{-NC-Fe}^{\text{II}}$  ( $S = 0, S = 0$ ) and  $\text{Co}^{\text{II}}\text{-NC-Fe}^{\text{III}}$  ( $S = 3/2, S = 1/2$ ) entities causes spontaneous changes of spin states and thus changes of magnetisation; either the forward or reverse process is readily induced by light of different wavelengths.<sup>38</sup> It should be mentioned that it is also possible to trap spin states using soft X-rays.<sup>39</sup>

## 6 Effect of pressure

The course of a ST is sensitive to the external pressure because of the difference in volume of the HS and LS species involved in the transition. The primary effect of an increase in pressure is a favouring of the LS state in which the metal-donor atom distances are shorter. This generally results in a displacement of the transition temperature to higher values and this implies in effect an increase in the zero-point energy separation  $\Delta E^{\circ}_{\text{HL}}$  in Fig. 2. The study of the effect of pressure on ST systems has been pursued for many years and has been applied recently to elucidate subtle effects associated with the transitions and to gain insight into mechanistic aspects of them. The first study of this kind related to tris(dithiocarbamate)iron(III) systems and the pronounced pressure-dependence of the magnetism observed for this system was taken as strong evidence for the postulate of a spin change deduced from anomalous temperature-dependence of the magnetism together with spectroscopic properties.<sup>40</sup>

The pioneering work of Drickamer and coworkers on the effect of pressure on the spin state of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  and related iron(II) ST systems involved measurement of the pressure-dependence of Mössbauer spectra and provided unequivocal evidence for the HS  $\rightarrow$  LS conversion with increase in pressure.<sup>41</sup> Aspects of Drickamer's early work, in particular the unexpected partial LS  $\rightarrow$  HS transition observed at very high pressures remain contentious. In a later study, Usha, Srinivasin and Rao studied the temperature-dependence of the magnetism of the systems  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  and  $[\text{Fe}(\text{bpy})_2(\text{NCS})_2]$  at varying pressures.<sup>42</sup> For the phenanthroline complex the transition is displaced to higher temperature and

becomes more gradual as the pressure is increased. For the bipyridine complex somewhat different behaviour is observed. While an increase in LS fraction is observed at temperatures above the transition temperature, the actual transition temperature decreases with increasing pressure due, it is proposed, to an increase in the strength of the coupling of the d electrons in the quintet state complex. For both systems there is a general increase in the fractions of LS and HS species at the upper and lower extremities, respectively, of the temperature range, a result of the overall flattening-out of the transition. These latter effects have been observed also in systems in which the transitions are associated with a distinct thermal hysteresis. An additional effect noted for these in some instances has been changes in the width of the hysteresis loop with increasing pressure. Both a decrease (for  $[\text{Fe}(2\text{-pic-ND}_2)_3]\text{Cl}_2 \cdot \text{EtOD}$ <sup>43</sup> and for  $[\text{Fe}(\text{bt})_2(\text{NCS})_2]$ <sup>44</sup> (bt = 2,2'-bi-2-thiazoline)) and an increase (for  $[\text{Fe}(\text{phy})_2]\text{X}_2$  with phy = 1,10-phenanthroline-2-carbaldehyde-phenylhydrazone) in the width of these loops have been observed, the latter being rationalised in terms of a pressure-dependence of the bulk modulus of the compound.<sup>45</sup> For the polymeric chain compound  $[\text{Fe}(\text{hyetrz})_3](3\text{-nitrophenylsulfonate})_2$  with hyetrz = 4-2'-hydroxyethyl-1,2,4-triazole, the situation is different. The steepness of the ST curves remains constant along with the hysteresis width. This lends support to the assertion that the cooperative interactions in this system are confined within the iron(II) triazole chain.<sup>21</sup>

The crystal structure of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  at high pressure and ambient temperature, when the complex is completely LS, has been reported. Significantly, the space group is the same and the overall molecular dimensions are very similar to those of the structure of the LS form produced at low temperature and ambient pressure.<sup>46</sup> Thus, in this instance at least, the net effects of an increase in pressure and a decrease in temperature are essentially the same. In certain instances a pressure-induced phase transition is believed to be the likely source for the apparent reversal of the normal HS  $\rightarrow$  LS conversion with increase in pressure if the transition temperature in the new phase is lower than that in the original phase.<sup>47</sup>

Studies of the effect of pressure of the equilibrium constant for the LS  $\leftrightarrow$  HS system in solution have yielded values of  $\Delta V$  for the process of the order of 25  $\text{\AA}^3$ . The pressure-dependence of the kinetics of HS  $\rightarrow$  LS relaxation processes has been examined in a number of instances, enabling evaluation of the activation volume  $\Delta V^{\ddagger}_{\text{HL}}$ , and typically values of  $-10$  to  $-20$   $\text{\AA}^3$ , for systems in both solution and the solid state have been obtained.<sup>48</sup> At low temperatures where the HS  $\rightarrow$  LS relaxation occurs by a tunnelling mechanism, the application of an external pressure of 20 kbar has been found to have the extraordinary effect of increasing the rate by almost eight orders of magnitude for the system  $[\text{Zn}_{1-x}\text{Fe}_x(6\text{-mepy})_3\text{tren}](\text{PF}_6)_2$  where  $(6\text{-mepy})_3\text{tren} = \text{tris}(4\text{-}(2\text{-pyridyl})\text{-3-aza-3-butenyl})\text{amine}$ .<sup>49</sup>

The effect of pressure on natural oxide and silicate sources of iron as experienced in the earth's crust and mantle is predicted to be related to the pressure-induced changes detected for synthetic systems such as those described above, and indeed a ST has been detected in the mineral gillespite.<sup>50</sup> Even the relatively simple substance iron(II) sulfide has recently been shown to undergo a pressure-induced HS  $\rightarrow$  LS transition,<sup>51</sup> and transitions have been observed in a number of perovskite-type structures containing cobalt(III).<sup>52</sup>

## 7 Effect of nuclear decay

The nuclear decay of radioactive atoms embedded in a compound is known to lead to various chemical and physical 'after effects' such as redox processes, bond rupture, formation

of metastable states and others.<sup>53</sup> One of the most elegant ways of investigating such after effects in solid compounds exploits the Mössbauer effect and has been termed ‘Mössbauer Emission Spectroscopy’ (MES) or Mössbauer source experiments.<sup>54</sup> For instance, the electron capture (EC) decay of <sup>57</sup>Co into <sup>57</sup>Fe, denoted <sup>57</sup>Co(EC)<sup>57</sup>Fe, in cobalt or iron compounds has been widely explored. Usually the <sup>57</sup>Co labelled compound is used as the Mössbauer source *versus* a single-line absorber material such as K<sub>4</sub>[Fe(CN)<sub>6</sub>]. The recorded spectrum yields information on the chemical state of the nucleogenic <sup>57</sup>Fe at *ca.* 10<sup>-7</sup> s, which is approximately the lifetime of the 14.4 keV level of <sup>57</sup>Fe, after nuclear decay.<sup>55</sup>

Using this technique the temperature-dependent Mössbauer emission spectra of <sup>57</sup>Co labelled cobalt(II) and iron(II) coordination compounds with strong, intermediate, and weak ligand fields have been examined. Among the most interesting results are the formation of metastable HS states of <sup>57</sup>Fe(II) in strong and intermediate ligand fields as exemplified by the following two cases: [Fe(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>, a typical LS compound at room temperature and below; [Fe(phen)<sub>2</sub>(NCS)<sub>2</sub>], a typical SC system. The main component in the emission spectra of [<sup>57</sup>Co/Co(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> refers to [<sup>57</sup>Fe(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>. At temperatures down to *ca.* 200 K the spin state is LS but below *ca.* 200 K new signals, clearly indicative of <sup>57</sup>Fe(II) in HS state, appear with increasing intensity at the expense of the <sup>57</sup>Fe(II)-LS signals. Thus, in the case of a strong ligand field environment such as (phen)<sub>3</sub>, where Fe(II)-LS is the thermodynamically stable state, the metastable state <sup>57</sup>Fe(II)-HS can only be detected in the low temperature regime with lifetimes of the order of 10<sup>-7</sup> s.<sup>54</sup> Interestingly, there is no significant difference if one uses the paramagnetic [Co(phen)<sub>3</sub>]<sup>2+</sup> or the diamagnetic [Fe(phen)<sub>3</sub>]<sup>2+</sup> compound as the Mössbauer source; the only important consideration is the immediate ligand cage of <sup>57</sup>Co or <sup>57</sup>Fe, respectively, after decay. If the <sup>57</sup>Co ion decays in a somewhat weaker ligand field such as (phen)<sub>2</sub>(NCS)<sub>2</sub>, which is known to induce thermal spin crossover, LS ↔ HS, at the iron(II) centre, the nucleogenic <sup>57</sup>Fe(II) manifests itself in the HS state at all temperatures down to 4 K.<sup>53</sup> Similar results have been observed with other <sup>57</sup>Co-labelled iron(II) SC systems.

The essential information from these Mössbauer source experiments is that, at a given temperature, the probability of ‘trapping’ the HS state of the nucleogenic <sup>57</sup>Fe(II) within the <sup>57</sup>Fe Mössbauer time window is significantly greater in a SC compound with intermediate field strength than in strong field compounds. The discovery of the LIESST phenomenon (generating and trapping of metastable HS states by irradiation with an external light source) enables us to understand the mechanism of the ‘Nuclear Decay Induced Excited Spin State Trapping (NIESST)’, where the nuclear decay process <sup>57</sup>Co(EC)<sup>57</sup>Fe may be regarded as an ‘internal’ molecular excitation source.

The mechanism of NIESST is essentially the same as for LIESST (see Fig. 10), except for the initial excitation step. The electronic structure of the nucleogenic <sup>57</sup>Fe(II) is still highly excited within the Mössbauer time window (~10<sup>-7</sup>s after nuclear decay). There are fast (<< 10<sup>-7</sup> s), spin-allowed transitions to the <sup>1</sup>A<sub>1g</sub> ground state, as well as fast intersystem crossing processes (<< 10<sup>-7</sup>s), which are favoured by spin-orbit coupling as in the LIESST mechanism, feeding the metastable <sup>5</sup>T<sub>2g</sub> state. The branching ratio for the two relaxation paths (to either <sup>1</sup>A<sub>1g</sub> or <sup>5</sup>T<sub>2g</sub>) depends on the ligand field strength of the system, in analogy to the observed correlation of the lifetime of the metastable LIESST state and the energy difference ΔE<sup>o</sup><sub>HL</sub>, which also depends on the ligand field strength (‘reduced energy gap law’).

Measurements of the lifetimes of NIESST states by time-resolved Mössbauer emission spectroscopy<sup>56</sup> and of LIESST states by time-resolved optical spectroscopy<sup>57</sup> on the very same system (a single crystal of [Fe<sub>x</sub>Mn<sub>1-x</sub>(bpy)<sub>3</sub>]<sup>2+</sup>) gave similar results. This supports the suggestion that the mechanisms for

LIESST and NIESST relaxation are very similar, at least for the low energy regime.

## 8 Applications

The extreme sensitivity of the electronic properties of SC systems to relatively minor external perturbations renders them likely candidates for practical applications in various situations. Two aspects of the SC phenomenon are of particular interest in this regard. These are the occurrence in certain instances of thermal hysteresis in the HS → LS → HS cycle (Fig. 3c) and the ability of light irradiation to effect changes in spin state (LIESST and related effects). The existence of hysteresis is a prerequisite for molecular bistability, which in turn offers the potential for technical applications in memory and data storage devices. For exploitation in memory devices the bistability must be associated with a response function. In this respect ST systems offer considerable scope since they show two dramatic and readily detectable responses, change in colour and magnetism. The change in colour accompanying a ST is particularly suited to the development of display devices. Ideally, these applications require that room temperature should fall approximately in the middle of the hysteresis loop, *i.e.* 1/2(T<sub>1/2</sub> ↓ + T<sub>1/2</sub> ↑) ≅ 295 K. Systems meeting this criterion are known and can now be synthesised in a more or less controlled manner. Other criteria such as chemical stability and reproducibility of behaviour for new samples and after cycling through the hysteresis loop must also be met.<sup>19</sup>

The remarkable changes of ST behaviour under applied pressure may be exploited in pressure sensors for applications where remote sensing of pressure could be achieved by observation of a colour change in a SC material. The light-induced switching phenomena described above (LIESST and reverse-LIESST) offer much promise for application in optical data processing and information storage.<sup>7</sup> Data storage, although now limited to low temperature regions, may eventually play a role in holographic devices. Because of the large difference in the Fe–donor atom distances in the HS and LS states, the refractive index of an iron(II) SC system is expected to be substantially different in the two spin states, which gives rise to unusual photo-refractive properties which could be exploited to create phase holograms.<sup>34</sup>

## 9 Outlook

The academic interest in, and high pedagogical value of an understanding of the behaviour of ST systems ensure that activity in the field will remain high. After all, they provide one of the most striking models for illustrating many aspects of ligand field theory and, uniquely, in an essentially unchanging ligand environment for a metal ion. But the potential for practical applications of the kinds mentioned above, which has driven much of the recent research, will continue to stimulate the search for new systems and the discovery of new aspects of the crossover phenomenon.

Present research efforts are directed to the synthesis of new materials with specific properties and the application of powerful modern techniques to reveal new facets of spin transitions. The understanding of the features which lead to cooperativity in solid systems remains a major goal. Other specific aspects which are presently the focus of many research groups include the synergism (coupling) of magnetic exchange between metal centres and ST at the individual metal atoms. An example of this fascinating situation has already appeared for a cobalt(II) system.<sup>58</sup> A further area to be explored is the detailed structural characterisation of metastable states. Already im-



portant findings on the lattice parameters of a system in a LIESST-generated metastable state have emerged and detailed structural studies will allow greater understanding of light-induced phenomena in general.

## 10 Acknowledgements

Financial support from the TMR Research Network 'TOSS' under EU grant No. ERB-FMRX-CT98-0199, the Fonds der Chemischen Industrie, and the Materialwissenschaftliches Forschungszentrum of the University of Mainz is greatly appreciated. H. A. G. is grateful to the Alexander von Humboldt Stiftung for support.

## 11 References

- W. R. Scheidt and C. A. Reed, *Chem. Rev.*, 1981, **81**, 543.
- M. F. Perutz, G. Fermi, B. Luisi, B. Shaanan and R. C. Liddington, *Acc. Chem. Res.*, 1987, **20**, 309.
- M. Womes, J. C. Jumas, J. Olivier-Fourcade, F. Aubertin and U. Gonser, *Chem. Phys. Lett.*, 1993, **201**, 555.
- E. König, *Coord. Chem. Rev.*, 1968, **3**, 471.
- H. A. Goodwin, *Coord. Chem. Rev.*, 1976, **18**, 293.
- P. Gütllich, *Struct. Bonding (Berlin)*, 1981, **44**, 83.
- P. Gütllich, A. Hauser and H. Spiering, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 20.
- B. N. Figgis, *Introduction to Ligand Fields*, Interscience Publishers, New York, London, Sydney, 1964.
- E. König and K. Madeja, *Chem. Commun.*, 1966, 61.
- H. A. Goodwin, E. S. Kucharski and A. H. White, *Aust. J. Chem.*, 1983, **36**, 1115.
- R. J. Dosser, W. J. Eilbeck, A. E. Underhill, P. R. Edwards and C. E. Johnson, *J. Chem. Soc. A*, 1969, 810.
- H. Toftlund, *Coord. Chem. Rev.*, 1989, **94**, 67.
- H. R. Chang, J. K. McCusker, H. Toftlund, S. R. Wilson, A. X. Trautwein, H. Winkler and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1990, **112**, 6814.
- C. M. Harris, H. R. H. Patil and E. Sinn, *Inorg. Chem.*, 1969, **8**, 101.
- E. C. Constable, G. Baum, E. Bill, R. Dyson, R. van Eldik, D. Fenske, S. Kaderli, D. Morris, A. Neubrand, M. Neuburger, D. R. Smith, K. Wiegardt, M. Zehnder and A. D. Zuberbühler, *Chem. Eur. J.*, 1999, **5**, 498.
- B. J. Childs, D. C. Craig, M. L. Scudder and H. A. Goodwin, *Inorg. Chim. Acta*, 1998, **274**, 32.
- W. Linert, M. Konecny and F. Renz, *J. Chem. Soc., Dalton Trans.*, 1994, 1523; S. E. Livingstone and J. D. Nolan, *J. Chem. Soc., Dalton Trans.*, 1972, 218.
- K. H. Sugiyarto, D. C. Craig, A. D. Rae and H. A. Goodwin, *Aust. J. Chem.*, 1993, **46**, 1269.
- O. Kahn, E. Codjovi, Y. Garcia, P. J. van Koningsbruggen, R. Lapouyade and L. Sommier, *ACS Symp. Series*, 1996, **20**, 298.
- Y. Garcia, O. Kahn, L. Rabardel, B. Chansou, L. Salmon and J. P. Tuchagues, *Inorg. Chem.*, 1999, **38**, 4663.
- Y. Garcia, P. J. van Koningsbruggen, R. Lapouyade, L. Fournès, L. Rabardel, O. Kahn, V. Ksenofontov, G. Levchenko and P. Gütllich, *Chem. Mater.*, 1998, **10**, 2426.
- W. Vreugdenhil, J. H. van Diemen, R. A. G. de Graaff, J. G. Haasnoot, J. Reedijk, A. M. van der Kraan, O. Kahn and J. Zarembowitch, *Polyhedron*, 1990, **9**, 2971.
- J. A. Real, E. Andrés, M. C. Muñoz, M. Julve, T. Granier, A. Bousseksou and F. Varret, *Science*, 1995, **268**, 265.
- T. Kitazawa, Y. Gomi, M. Takahashi, M. Takeda, M. Enomoto, A. Miyazaki and T. Enoki, *J. Mater. Chem.*, 1996, **6**, 119.
- Y. Garcia, P. J. van Koningsbruggen, G. Bravic, P. Guionneau, D. Chasseau, G. L. Cascarano, J. Moscovici, K. Lambert, A. Michalowicz and O. Kahn, *Inorg. Chem.*, 1997, **36**, 6357.
- H. Spiering, E. Meissner, H. Köppen, E. W. Müller and P. Gütllich, *Chem. Phys.*, 1982, **68**, 65; N. Willenbacher and H. Spiering, *J. Phys. C: Solid State Phys.*, 1988, **21**, 1423; H. Spiering and N. Willenbacher, *J. Phys.: Condens. Matter*, 1989, **1**, 10089.
- M. Sorai, J. Ensling and P. Gütllich, *Chem. Phys.*, 1976, **18**, 199; I. Sanner, E. Meissner, H. Köppen, H. Spiering and P. Gütllich, *Chem. Phys.*, 1984, **86**, 227.
- R. Hinek, H. Spiering, D. Schollmeyer, P. Gütllich and A. Hauser, *Chem. Eur. J.*, 1996, **2**, 1127; R. Hinek, H. Spiering, P. Gütllich and A. Hauser, *Chem. Eur. J.*, 1996, **2**, 1435.
- A. Hauser, P. Gütllich and H. Spiering, *Inorg. Chem.*, 1986, **25**, 4245.
- Z. J. Zhong, J. Q. Tao, Z. Yu, C. Y. Dun, Y. J. Liu and X. Z. You, *J. Chem. Soc., Dalton Trans.*, 1998, 327.
- S. Decurtins, P. Gütllich, C. P. Köhler, H. Spiering and A. Hauser, *Chem. Phys. Lett.*, 1984, **105**, 1; S. Decurtins, P. Gütllich, K. M. Hasselbach, H. Spiering and A. Hauser, *Inorg. Chem.*, 1985, **24**, 2174.
- A. Hauser, *Chem. Phys. Lett.*, 1986, **124**, 543.
- P. Poganiuch, S. Decurtins and P. Gütllich, *J. Am. Chem. Soc.*, 1990, **112**, 3270.
- A. Hauser, *Coord. Chem. Rev.*, 1991, **111**, 275 and references therein.
- A. Desaix, O. Roubeau, J. Jetic, J. G. Haasnoot, K. Boukheddaden, E. Codjovi, J. Linares, M. Nogues and F. Varret, *Eur. Phys. B.*, 1998, **6**, 183.
- F. Renz, H. Spiering, H. A. Goodwin and P. Gütllich, *Hyperfine Interact.*, 2000, **126**, 155.
- C. Roux, J. Zarembowitch, B. Gallois, T. Granier and R. Claude, *Inorg. Chem.*, 1994, **33**, 2273.
- O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Science*, 1996, **272**, 704.
- D. Collison, C. D. Garner, C. M. McGrath, J. F. W. Mosselmann, M. D. Roper, J. M. W. Seddon, E. Sinn and N. A. Young, *J. Chem. Soc., Dalton Trans.*, 1997, 4371.
- A. H. Ewald, R. L. Martin, I. G. Ross and A. H. White, *Proc. R. Soc. London, Ser. A*, 1964, **280**, 235.
- H. G. Drickamer, *Angew. Chem.*, 1974, **86**, 61.
- S. Usha, R. Srinivasin and C. N. R. Rao, *Chem. Phys.*, 1985, **100**, 447.
- C. P. Köhler, R. Jakobi, E. Meissner, L. Wiehl, H. Spiering and P. Gütllich, *J. Phys. Chem. Solids*, 1990, **51**, 239.
- E. König, G. Ritter, H. Grünsteudel, J. Dengler and J. Nelson, *Inorg. Chem.*, 1994, **33**, 837.
- V. Ksenofontov, H. Spiering, A. Schreiner, G. Levchenko, H. A. Goodwin and P. Gütllich, *J. Phys. Chem. Solids*, 1999, **60**, 393.
- T. Granier, B. Gallois, J. Gaultier, J. A. Real and J. Zarembowitch, *Inorg. Chem.*, 1993, **32**, 5305.
- V. Ksenofontov, G. Levchenko, H. Spiering, P. Gütllich, J. F. Letard, Y. Bouhedja and O. Kahn, *Chem. Phys. Lett.*, 1998, **294**, 545.
- P. Gütllich, H. Spiering and A. Hauser, in *Inorganic Electronic Spectroscopy*, ed. E. I. Solomon and A. B. P. Lever, John Wiley and Sons, New York, 1999, II, 575.
- W. Wang, I. Y. Chan, S. Schenker and A. Hauser, *J. Chem. Phys.*, 1997, **106**, 3817.
- R. G. J. Strens, *J. Chem. Soc., Chem. Commun.*, 1966, 777.
- J. P. Rueff, C. C. Kao, V. V. Struzhkin, J. Badro, J. Shu, R. J. Hemley and H. K. Mao, *Phys. Rev. Lett.*, 1999, **82**, 3284.
- C. N. R. Rao, *Int. Rev. Phys. Chem.*, 1985, **4**, 19.
- T. Matsuura (ed.), in *Hot Atom Chemistry*, Kodansha Ltd, Tokyo, 1984.
- H. Sano and P. Gütllich, 'Hot Atom Chemistry in Relation to Mössbauer Emission Spectroscopy', in *Hot Atom Chemistry*, ed. T. Matsuura, Kodansha Ltd, Tokyo, 1984, and references therein.
- P. Gütllich, R. Link and A. Trautwein, in *Mössbauer Spectroscopy and Transition Metal Chemistry*, Springer (Berlin), New York, 1978.
- S. Deisenroth, H. Spiering, D. L. Nagy and P. Gütllich, *Hyperfine Interact.*, 1998, **113**, 351.
- A. Hauser, *Chem. Phys. Lett.*, 1990, **173**, 507.
- S. Brooker, P. G. Plieger, B. Moubaraki and K. S. Murray, *Angew. Chem., Int. Ed.*, 1999, **38**, 408.