# On the Nature of the Plateau in Two-Step Dinuclear Spin-Crossover Complexes

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**Abstract:** A remarkable feature of the spin-crossover process in several dinuclear iron(II) compounds is a plateau in the two-step transition curve. Up to now, it has not been possible to analyse the spin state of dinuclear pairs that constitute such a plateau, due to the relative high temperatures at which the transition takes place in complexes investigated so far. We solved this problem by experimentally studying a novel dinuclear spin-crossover compound [{Fe(phdia)(NCS)$_2$}$_2$(phdia)] (phdia: 4,7-phenanthroline-5,6-diamine). We report here on the synthesis and characterisation of this system, which exhibits a two-step spin transition at $T_{c1} = 108$ K and $T_{c2} = 80$ K, displaying 2 K and 7 K wide thermal hysteresis loops in the upper and the lower steps, respectively. A plateau of approximately 20 K width centred at about 90 K, which corresponds to the 50 % of the spin conversion, separates the two transitions. The composition of the plateau was identified in metastable state after quenching to 4.2 K by means of Mössbauer spectroscopy in an external magnetic field. Such experiments revealed that the plateau consists mainly of [HS–LS] pairs (HS = high spin, LS = low spin) and confirmed the hypothesis that the spin conversion in dinuclear entities proceeds through [LS–LS]↔[HS–LS]↔[HS–HS] pairs. The results are discussed in terms of a thermodynamic model based on the regular solution theory adapted for dinuclear spin-crossover compounds.

**Keywords:** iron · LIESST effect · Mössbauer spectroscopy · N ligands · spin crossover

## Introduction

Current developments in advanced electronic and photonic technologies require new functional materials exhibiting bistable behaviour at molecular scale.[1–2] In fact, the design and synthesis of molecules or molecular assemblies of molecules for information processing is one of the most appealing aims of modern molecular chemistry. Whatever the final goal, a fundamental underlying concept is that of bistability: the ability of the molecular system to be in two different electronic states at one and the same temperature. The reversible change between low-spin (LS) and high-spin (HS) states driven by variation of temperature and/or pressure or also by light irradiation, mainly observed in pseudo-octahedral iron(II) coordination complexes, is one of the best examples of molecular bistability.[3–5] At the molecular scale, spin crossover (SCO) in the Fe(II) compounds corresponds to an intra-ionic transfer of two electrons between the $t_{2g}$ and $e_g$ orbitals, $[(t_{2g})^4(e_g)^2] \leftrightarrow [(t_{2g})^6(e_g)^0]$, accompanied by a spin flip. The $^5T_{2g}((t_{2g})^4(e_g)^2)$ state is the ground state only up to the critical value of the ligand-field strength of 10 Dq, which is equal to the spin-pairing energy. Above this value the $^1A_{1g}((t_{2g})^6(e_g)^0)$ low-spin state is lower in the energy than the high-spin state and thus becomes the ground spin state.[3a] In the HS state, the antibonding $e_g$ orbitals are doubly occupied, and consequently the Fe–ligand bonds are larger than in the LS state by approximately 0.20 Å. This increase of the molecule size when passing from the LS to the HS state plays a crucial role in the cooperative mechanism of the SCO giving rise to abrupt transitions and hysteresis at macroscopic scale. For instance, the magnetic and optical properties may switch sharply in a very small range of temperature and/or pressure for cooperative transitions.[5–6] Due to this particularity the spin-crossover phenomenon has been considered one of the most interesting examples of molecular switching. The condition to accomplish in order

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to observe the phenomenon of spin transition is that the zero-point energy between the two states, $\Delta E^0_{\mathrm{HL}} = E^0_{\mathrm{HS}} - E^0_{\mathrm{LS}}$, has to be in the order of magnitude of the thermal energy, $k_{\mathrm{B}}T$. If this the case, all molecules will be in the low-spin state at very low temperatures or higher pressures whereas at elevated temperatures or lower pressures, an entropy-driven almost quantitative population of the high-spin state will occur. In general, spin transition is a well-established phenomenon and many examples of spin-crossover complexes exhibiting abrupt spin transitions at room temperature, with broad thermal hysteresis as well as an associated thermochromic effect (necessary conditions for display devices), have been reported. Among them the majority corresponds to mononuclear systems in which the structural characterisation has made possible to analyse qualitatively the cooperative mechanism from a microscopic point of view. Polymeric spin-crossover compounds represent a new approach to investigating new strong cooperative regimes. Currently, the reported examples concerning polymeric compounds are greatly limited to a small number and there are certain aspects regarding the conversion process of the spin states in such kind of complexes that remain unsolved. In this respect, an intriguing question is the nature of the plateau present in the two-step transition curve observed in bpym-bridged dinuclear iron(II) systems (bpym = 2,2′-bipyrimidine). Dinuclear iron(II) complexes of the type $[\{\mathrm{Fe(L)(NCX)_2}\}_2(\mathrm{bpym})]$ (L : 2,2′-bipyrimidine, 2,2′-bithiazoline (bt), X: S, Se) (see Figure 1) were first investigated by Real et al.,[7] but they have recently found revival after it was pointed out that different physical phenomena such as intramolecular exchange interaction and thermal SCO may coexist. One should mention external pressure or light irradiation effects in this type of molecular assembly as well.[8,9] The title compounds represent a first step in the research line aimed at combining magnetic exchange and SCO phenomena in a molecule or polymeric network, which could afford new switching materials with considerable amplification of the response signal.[10] However, it has not been possible to confirm through a microscopic physical method the nature of the species that constitute such a plateau, due to the relatively high temperatures at which the transition takes place in $[\{\mathrm{Fe(bt)(NCX)_2}\}_2(\mathrm{bpym})]$ (X: S, Se). In this article, we report the synthesis and physical characterisation of a new iron(II) SCO complex displaying a two-step transition with 108 and 80 K as characteristic critical temperatures $T_c(1)$ and $T_c(2)$, respectively. Due to these low temperatures at which the transitions take place, as will be discussed in the following, we were able to perform thermal trapping at liquid helium temperature of the species present in the plateau of the spin transition curve. Such experiments reveal that the [HS–LS] pairs are the main species in the region of the plateau and confirm the hypothesis formulated earlier[7b] that the spin conversion in dinuclear entities proceeds via [HS–HS]↔[HS–LS]↔[LS–LS] pairs.

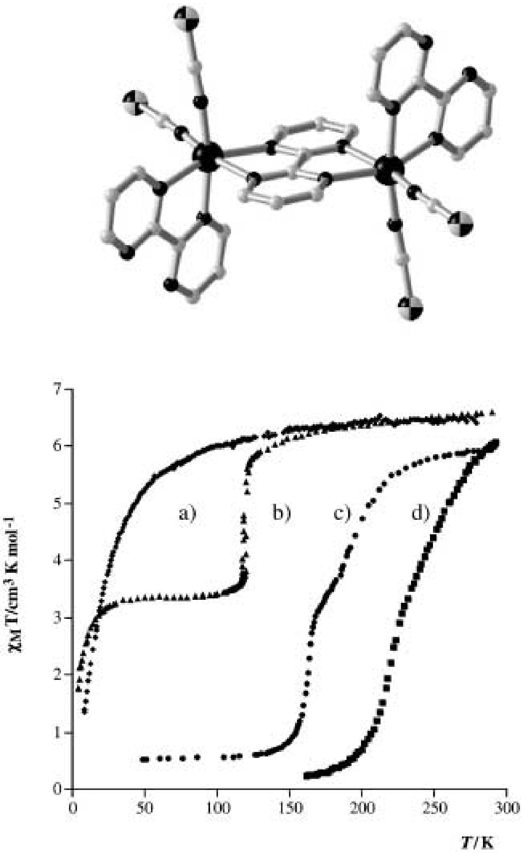

Figure 1. Top: Crystal structure of the molecule of $[\{\mathrm{Fe(bpym)(NCS)_2}\}_2(\mathrm{bpym})]$. Bottom: Temperature dependence of $\chi_M T$ for $[\{\mathrm{Fe(bpym)(NCS)_2}\}_2(\mathrm{bpym})]$ (a), $[\{\mathrm{Fe(bpym)(NCSe)_2}\}_2(\mathrm{bpym})]$ (b), $[\{\mathrm{Fe(bt)(NCS)_2}\}_2(\mathrm{bpym})]$ (c) and $[\{\mathrm{Fe(bt)(NCSe)_2}\}_2(\mathrm{bpym})]$ (d).

## Results and Discussion

**Proposed structure for $[\{\mathrm{Fe(phdia)_2(NCS)_2}\}_2(\mathrm{phdia})]$ (1)**: Complex **1** precipitates as a greenish-brown microcrystalline powder. All attempts to get single crystals suitable for X-ray experiments failed. Analytical data, variable-temperature magnetic susceptibility data and results from $^{57}$Fe Mössbauer spectroscopy in applied magnetic field (reported below) are consistent with the dinuclear nature of the compound. A perspective view of the molecule is shown in Figure 2. Complex **1** consists of centrosymmetric discrete dinuclear molecules, in which two iron(II) ions are bridged by a phdia ligand in a bis-bidentate fashion, the coordination sphere being completed by a peripheral phdia ligand and two NCS$^-$ groups in *cis* configuration.

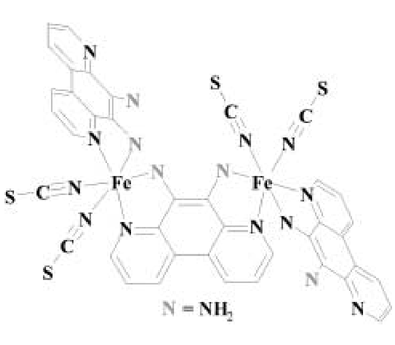

Figure 2. Proposed structure for $[\{\mathrm{Fe(phdia)(NCS)_2}\}_2(\mathrm{phdia})]$ (**1**).

**Magnetic properties**: The thermal dependence of the product $\chi_M T$ ($\chi_M$ being the molar susceptibility and $T$ the temperature) for **1** is displayed in Figure 3. The $\chi_M T$ value for **1** at room temperature is 6.40 $cm^3 K mol^{-1}$, which is in the range of values expected for a dinuclear $Fe^{II}$ complex mainly in the HS state. The amount of metal ions retained in the LS state was found to be approximately 16 % at 300 K from Mössbauer data (Figure 6a). It follows that the $\chi_M T$ value, extrapolated to the pure HS species can be estimated to be 7.6 $cm^3 K mol^{-1}$. In the temperature range between 300 and 160 K $\chi_M T$ is practically temperature independent, then below 130 K diminishes abruptly reaching a plateau centred at around 3.62 $cm^3 K mol^{-1}$ in the temperature range 100–80 K over which $\chi_M T$ varies smoothly. The $\chi_M T$ values in this flat region correspond to about 50 % of the complete spin transition (100 % HS ions at room temperature), around 36 % iron(II) ions are actually involved in this first step which has a characteristic temperature of $T_c(1)\downarrow = 108$ K. Below $T = 85$ K a steep drop of $\chi_M T$ centred at $T_c(2)\downarrow = 80$ K is observed; this corresponds to a second transition that is much more abrupt than the first one. Around 33 % of the molecules are involved in the spin transition of the second step. In the low-temperature region $\chi_M T = 1.07$ $cm^3 K mol^{-1}$ reflects that 15 % of the iron(II) ions remain in the HS configuration ($S = 2$) according to the Mössbauer spectra. The warming mode reveals the occurrence of 2 and 7 K wide thermal hysteresis loops for the first and the second steps, respectively. Despite the chemical differences of the bridging and peripheral ligands, **1** and the members of the bpym family share the same peculiarity, that is, the $S = 2 \leftrightarrow S = 0$ spin conversion occurs in two steps separated by an intermediate plateau. Further, it should be noted that the spin conversion in **1** takes place at temperatures unusually lower than those observed for the compounds $[\{Fe(bpym)(NCSe)_2\}_2(bpym)]$ and $[\{Fe(bt)(NCX)_2\}_2(bpym)]$ (X: S, Se; see Figure 1) and that the plateau located between the steps is much more pronounced in **1**. These differences can be explained considering the different interplay between inter- and intramolecular interactions with respect to the other members of the bpym family.

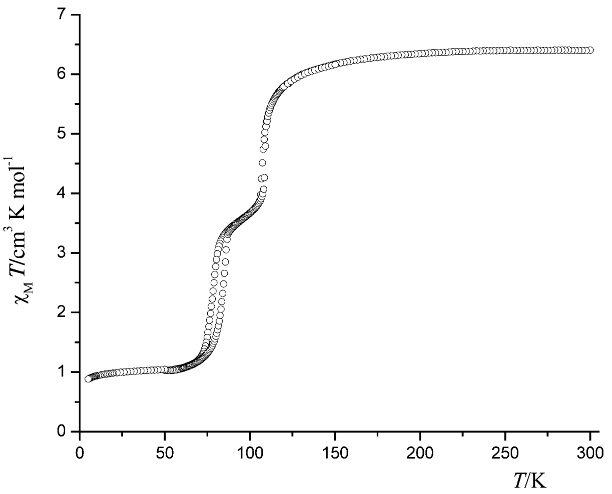

Figure 3. Thermal dependence of the magnetic susceptibility for **1**.

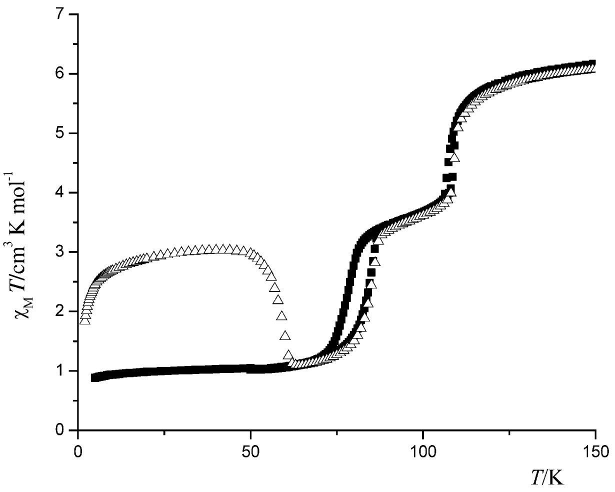

Figure 4. $\chi_M T$ versus $T$ plots for **1**. The sample was cooled from 300 to 2 K at 2 $K min^{-1}$ (■). Thermal quenching: the sample was cooled from 300 to 5 K at 100 $K min^{-1}$ and then warmed slowly (see text, △).

**Thermal quenching experiments—kinetics of the spin state conversion**: We have performed thermal quenching experiments by cooling the sample rapidly (≈100 $K min^{-1}$) from room temperature down to 5 K to study the kinetics of the spin state conversion in **1**. Figure 4 displays the magnetic behaviour of the quenched sample at increasing temperatures (filled triangles). At 5 K, $\chi_M T$ is equal to 2.4 $cm^3 K mol^{-1}$. This value represents apparently 30 % of trapped HS molecules. A progressive increase of $\chi_M T$ was observed as the sample was slowly warmed (0.5 $K min^{-1}$). $\chi_M T$ attains a maximum value of 2.6 $cm^3 K mol^{-1}$ in temperature range of 30–45 K. The thermal dependence of $\chi_M T$ in the temperature region of 5–45 K corresponds, most probably, to the occur-

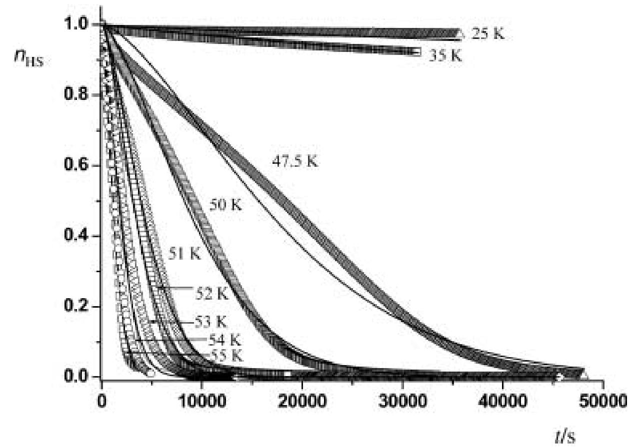

Figure 5. Time dependence at various temperatures of the normalised HS fraction ($n_{HS}$) generated by thermal quenching. Solid lines represents the best fit to the experimental HS→LS relaxation curves at different temperatures.

rence of zero-field splitting in the $S=2$ ground state of the trapped iron(II) ions; however, a small additional contribution arising from the expected weak intramolecular antiferromagnetic coupling between the iron(II) atoms quenched in the HS state cannot be ruled out. Hence, the effective thermal quenching at low temperature actually involves around 30% of molecules in the HS states. In the temperatures range of 52–60 K, $\chi_M T$ diminishes as a consequence of HS→LS relaxation. For temperatures higher than 52 K, the molecules absorb sufficient energy to overcome the energy barrier between the HS and LS potential wells. Consequently, the normal regime and thermal quenching experiments superimpose above 64 K. The kinetics of the HS→LS relaxation have been investigated in the temperature range of 25–50 K. The decays curves of the quenched HS molar fraction normalised to 1 at time zero ($n_{HS}$) versus time at various temperatures are presented in Figure 5. It should be pointed out that the following considerations have been taken into account for normalising the $n_{HS}$ values for **1**: 1) the $\chi_M T$ values measured after each trapping experiment remained in the range 3.0–2.6 $cm^3 K mol^{-1}$ between 25 and 55 K at time zero, and 2) under these conditions a maximum decay of the HS population took place to approximately 14% at temperatures as high as 55 K. In the temperature region between 10–45 K the relaxation is very slow. The rate constant $k_{HL}(T)$ follows simple exponential behaviour [Eq. (1)]:

$$n_{HS} = \exp(-k_{HL}(T)t) \qquad (1)$$

For $T > 45$ K, the decay shows a slight deviation from simple exponential behaviour. The expression that describes such a relaxation was extensively analysed by Avrami [Eq. (2)]:[11]

$$n_{HS} = \exp[(-k_{HL}(T)t)^{\alpha}] \qquad (2)$$

The Arrenhius plot, $\ln[k_{HL}(T)]$ versus $1/T$, for **1** according to Equation (3), in which $A_{HL}$ is the preexponential factor

$$k_{HL}(T) = A_{HL}\exp(-E_a/k_B T) \qquad (3)$$

and $E_a$ the thermal activation energy of the process, matches the theory of HS→LS relaxation proposed by Buhks et al.,[12] which predicts a temperature-independent rate (tunnelling region) at low temperature and thermal activated relaxation process at higher temperatures. However, the activation energy $E_a$ of $\approx 496$ $cm^{-1}$ and in particular the preexponential factor, $A_{HL}$ $\approx 345$ $s^{-1}$, obtained at temperatures higher than 50 K clearly indicate that in this temperature range tunnelling is still the dominant mechanism.

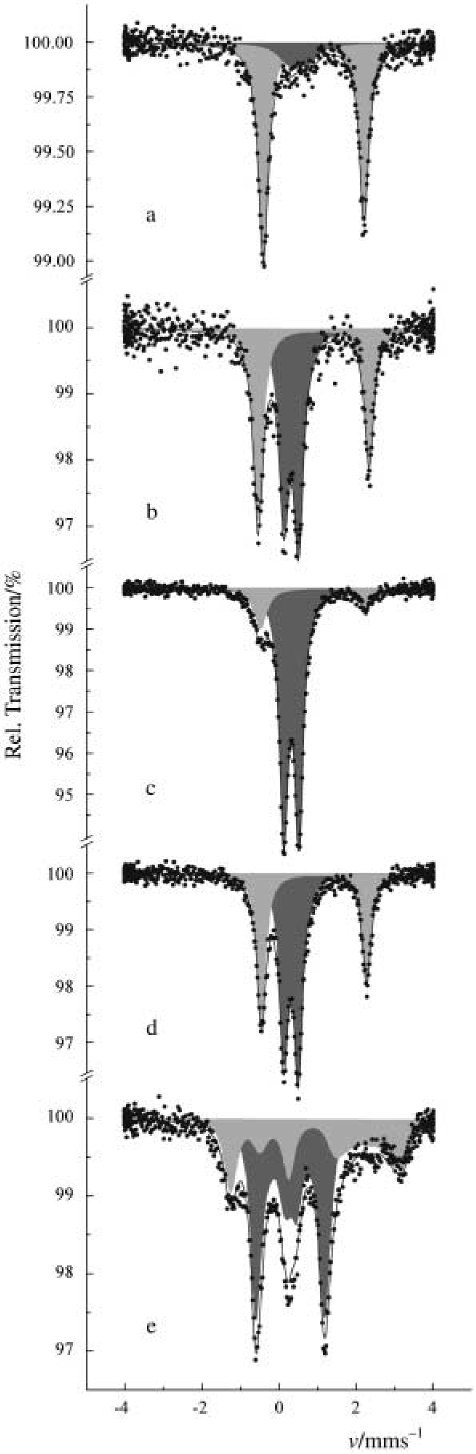

Figure 6. $^{57}$Fe Mössbauer spectra of **1** at a) room temperature, b) 100 K after subsequent slow cooling (< 1 $K min^{-1}$), c) 4.2 K after further slow cooling, d) 4.2 K after rapid cooling from the plateau with a rate 100 $K min^{-1}$ and e) 4.2 K in a magnetic field of 50 kOe after quenching from the plateau. LS in [HS–LS] and [LS–LS] pairs (grey), HS in [HS–LS] pairs (light grey).

**Quenching experiments and Mössbauer spectroscopy in a magnetic field—nature of the plateau in the two-step transition curve**: As discussed in a recent paper,[8] from the data analysis of pressure experiments on bpym-bridge dinuclear complexes it followed that the nature of the plateau is most probably determined by the formation of [HS–LS] pairs. The application of Mössbauer spectroscopy in an applied magnetic field directly within the plateau region is not possible, because of the relatively high temperature region in which the two-step transition takes place in the $[\{Fe(bt)(NCS)_2\}_2(bpym)]$ and $[\{Fe(bt)(NCSe)_2\}_2(bpym)]$ derivatives, $T_c(1) = 197$ K, $T_c(2) = 163$ K and $T_c(1) = 265$ K, $T_c(2) = 233$ K, respectively. The reason is that the non-negligible thermal population of the upper energetic levels $S=4$, 3, 2 and 1 in antiferromagnetically coupled [HS–HS] units yields a similar expectation value of $\langle S\rangle \cong 2$ for the antiferromagnetically coupled [HS–HS] pairs as well as for the [HS–LS] pairs; consequently very similar values for the effective local magnetic field $H_{eff}$ are obtained. Thermal trapping of the species from the plateau region by quenching down to temperature of liquid helium would be necessary in order to apply the direct monitoring method as has been performed in [{Fe(bpym)(NCSe)$_2$}$_2$(bpym)]. In this manner it has been demonstrated recently that an unambiguous distinction of different pairs at low temperatures is possible, if the Mössbauer measurements are carried out with the sample placed in an external magnetic field.[9] The effective hyperfine field $H_{eff}$ at iron nuclei of a paramagnetic non-conducting sample in an external field $H_{ext}$ may be estimated from Equation (4):

$$H_{eff} \approx H_{ext} - [220 - 600(g-2)]\langle S\rangle \qquad (4)$$

in which $\langle S\rangle$ is the expectation value of the atomic spin moment and $g$ the Landé splitting factor.[13–14] The difference between the expectation values of $S$ for the iron(II) atom in the LS and in the HS states in [HS–LS] and [HS–HS] pairs enables us to distinguish unambiguously between the dinuclear units consisting of two possible spin states in an external magnetic field. From the Equation (4) it follows that $H_{eff}$ becomes similar for both species in the high temperature region, and consequently the distinction between different pairs is suppressed. However, attempts to thermally quench from the relatively high temperatures at which the thermal spin transitions in the [{Fe(bt)(NCS)$_2$}$_2$(bpym)] and [{Fe(bt)(NCSe)$_2$}$_2$(bpym)] derivatives take place were unsuccessful. However, this was possible with compound **1**. The peculiar two-step spin transition occurring at relatively low temperatures has enabled us to elucidate the nature of the species present in the plateau centred at $T_p \cong 100$ K. The composition of the plateau could be identified in a metastable state after quenching from 100 K directly to the liquid helium temperature. The Mössbauer spectra recorded in the different experiments are displayed in Figure 6. The room-temperature Mössbauer spectrum is dominated by an HS doublet (outer two lines, light grey) with quadrupole splitting $\Delta E_Q(\text{HS}) = 2.62(1)\ \text{mm s}^{-1}$; however, an LS doublet (inner two lines, dark grey) with quadrupole splitting $\Delta E_Q(\text{LS}) = 0.5(1)\ \text{mm s}^{-1}$ and relative intensity of approximately 16 % is also present (Figure 6a). The spectrum recorded at 100 K after subsequent slow ($<1\ \text{K min}^{-1}$) cooling reveals 46.0 % of HS and 54.0 % of LS species (Figure 6b). The Mössbauer spectrum recorded at 4.2 K after further slow cooling indicates 84.0 % of LS and 16 % of HS iron(II) species (Figure 6c). Rapid cooling with a rate of $100\ \text{K min}^{-1}$ from 100 K to 4.2 K allowed the trapping of the species that exists in the plateau in the metastable state. The Mössbauer spectrum of the metastable state recorded at 4.2 K is very similar to that recorded at 100 K with a slight increase of the LS component up to 58 % (Figure 6d). The spectrum in Figure 6d proves that the thermal quenching was performed effectively. The application of a magnetic field of 50 kOe at 4.2 K revealed the nature of the metastable pairs that are present in the plateau of **1**. The Mössbauer spectrum consists of two subspectra (Figure 6e). One of them, with an effective value of the hyperfine magnetic field of 50.0 kOe, is the characteristic "fingerprint" of LS species in [HS–LS] and [LS–LS] pairs. The subspectrum with $H_{eff} = 62$ kOe corresponds to the Fe$^{II}$ HS species in the [HS–LS] pairs. It follows from the area fractions of the subspectra intensities that the "quenched plateau" consists of 84 % [HS–LS] and 16 % [LS–LS] pairs. This result proves experimentally the validity of the hypothesis formulated by Real et al.[7b] in which the [HS–LS] pair was proposed as an intermediate state in the spin-state transformation instead of a direct [HS–HS]↔[LS–LS] process. No [HS–HS] pairs have been found in the metastable state at low temperatures. It is therefore safe to conclude, that at $T = 100$ K the plateau in the transition curve of **1** involves mainly [HS–LS] species (92 %) with the remainder corresponding to [LS–LS] pairs arising from the residual LS fraction which is also detected at 300 K.

Important information about the intramolecular interaction in dinuclear units in **1** can be drawn from the study of the LIESST effect at low temperature. The Mössbauer spectrum recorded at 4.2 K after slow cooling reveals 16.0 % of HS and 84.0 % of LS species (Figure 7a). The spectrum recorded after irradiation of the sample for one hour at 4.2 K with $\lambda = 488$ nm shows an increase of the intensity of the HS doublet up to 25.0 % (Figure 7b). The spectrum recorded

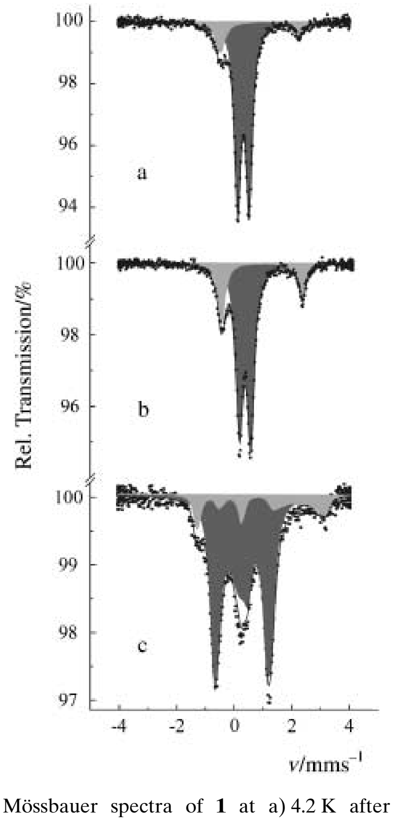

Figure 7. $^{57}$Fe Mössbauer spectra of **1** at a) 4.2 K after slow cooling ($<1\ \text{K min}^{-1}$) from room temperature, b) 4.2 K after irradiation, c) 4.2 K after irradiation in magnetic field of 50 kOe. LS in [HS–LS] and [LS–LS] pairs (grey), HS in [HS–LS] pairs (light grey).

subsequently with the sample placed in a magnetic field reveals no [HS–HS] pairs; it consists of 50.0% of [HS–LS] and 50% of [LS–LS] pairs (Figure 7c). This is further evidence of the inherent stability of mixed [HS–LS] pairs in **1**.

In the frame of the model mentioned above concerning the two-step character of the spin transition in [{Fe(bt)(NCS)$_2$}$_2$(bpym)], the enthalpy ($H$) of the [HS–HS] pair does not correspond exactly to the average enthalpy of the [HS–HS] and [LS–LS] pairs: $H_{\text{HS–LS}} \neq [(H_{\text{LS–LS}} + H_{\text{HS–HS}})/2]$. It is inferred from calculations, that the relation $H_{\text{HS–LS}} < [(H_{\text{LS–LS}} + H_{\text{HS–HS}})/2]$ is a necessary, but not a sufficient condition for the occurrence of a two-step transition. A further conclusion is that a certain degree of cooperativity stemming from the lattice is required as well. In other words, the two-step character of a transition arises from a synergy between the intramolecular interaction, which favours energetically the [HS–LS] spin state, and the intermolecular interactions, which favour the formation of domains constituted of dinuclear entities with identical spin state. The intramolecular interaction is characterised by the parameter $\rho = W/\Delta H$, in which $\Delta H$ is the enthalpy difference between [HS–HS] and [LS–LS] spin states and $W$ represents the energetic stabilisation of the [HS–LS] pair relative to the enthalpy average of the [HS–HS] and [LS–LS] states ($\Delta H/2$) (Figure 8). The stronger the intramolecular interaction (more negative $\rho$), the more probable is the formation of mixed pairs. In this model, a parameter $\Gamma$ accounts for the intermolecular interactions. At $\rho = 0$ a two-step transition appears when $\Gamma = 332$ cm$^{-1}$; for the plateau to exist at small intermolecular interactions relatively big negative values of $\rho$ are required. For [{Fe(bt)(NCS)$_2$}$_2$(bpym)], a good agreement between the experimental magnetic data and that calculated has been obtained at $\Gamma = 215$ cm$^{-1}$ and $\rho = -0.072$. An important result following from the magnetic susceptibility data fit is that the plateau in [{Fe(bt)(NCS)$_2$}$_2$(bpym)] is formed mainly by [HS–LS] pairs. The fraction of [HS–LS] pairs calculated in the middle of the plateau at $T_c \cong 180$ K is approximately 70%. From theoretical considerations it follows that the plateau between the steps will be more pronounced with more negative $\rho$. This conclusion can be experimentally proven by the analysis of the nature of metastable pairs excited by light irradiation from the [LS–LS] ground state. LIESST experiments with the [{Fe(bt)(NCS)$_2$}$_2$(bpym)] complex described in a recent papers,[10,15] revealed the appearance of [HS–HS] and [HS–LS] types of pairs after light excitation of ground [LS–LS] states. This leads to the conclusion that the parameter $\rho$ is close to zero. This result is in fair agreement with a value $\rho = -0.072$ obtained from magnetic experiments. On the other hand, LIESST experiments carried out with **1** demonstrated the inherent stability of [HS–LS] pairs, and, consequently, the definitive negative value of the parameter $\rho$. The fact that the intramolecular interaction responsible for the stabilisation of mixed spin pairs in **1** prevails over the interactions found in [{Fe(bt)(NCS)$_2$}$_2$(bpym)] explains qualitatively the more pronounced plateau width in the two-step transition curve in **1**.

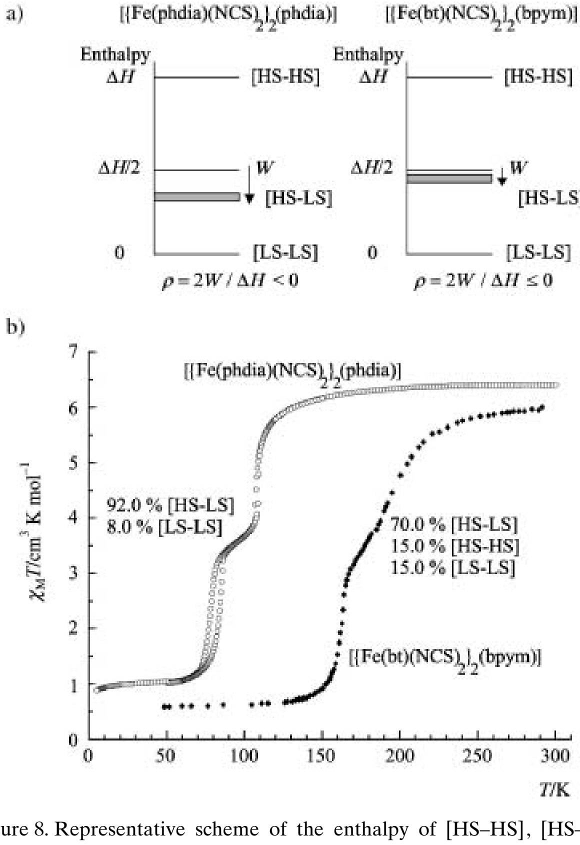

Figure 8. Representative scheme of the enthalpy of [HS–HS], [HS–LS] and [LS–LS] pairs (a) and comparative magnetic behaviour of [{Fe(bt)(NCS)$_2$}$_2$(bpym)] and **1** (b). The composition of the plateau region in pairs percentage is indicated.

It should be pointed out that the first stepwise thermal spin transition was observed in the mononuclear compound [Fe(2-pic)$_3$]Cl$_2$·EtOH (2-pic = 2-picolylamine).[16] The origin of the step in this system, as was later explained by Monte Carlo simulation, arises from a competition between short- and long-range interactions, favouring the formation of [HS–LS] species.[17] In the case of dinuclear compounds we have proved experimentally that the plateau of the two-step transition is due to the formation of [HS–LS] pairs. A combination of applied field Mössbauer spectroscopy with the LIESST effect confirmed the inherent stability of the mixed pairs. The synergistic effect between the intra- and intermolecular interactions confers the energetic stabilisation on this mixed spin state, gives rise to the plateau region of a two-step transition curve and determines its width.

## Conclusion

During the last twenty years after the realisation that spin-transition complexes could be used as data storage and display devices, chemists in the field have pursued the following challenge. This consists first in the design of bistable molecular compounds, then defining the physical property distinguishing the two states, and eventually optimising these compounds in such a way that the bistability range is easy accessible. In most cases, memory devices are expected to work at room temperature, so 293 K (20 °C) should fall within the bistablity range of the system.

Cooperativity is responsible for dramatic changes observed in the magnetic and optical properties of spin-crossover complexes. It strongly depends on the effectiveness of the intermolecular contacts in the crystal. The structural characterisation of an important number of complexes displaying different cooperative behaviours has been reported recently. This has made the analysis of the cooperative mechanism possible from a microscopic viewpoint and in some cases qualitatively also to rationalise the character of the ST through careful investigation of the intermolecular interactions.[18] It has been pointed out that strong intermolecular interactions result from the presence of an efficient hydrogen-bonding network or π–π stacking between the building blocks used to construct the spin-crossover entities. Another strategy developed for exploring cooperativity has been the approach of polymeric SCO system. The basic idea of this approach is to link together active sites (in this case $Fe^{II}$ ions) by chemical bridges that help to propagate intermolecular interactions between them. Such a strategy has led to the synthesis of one-, two- and three-dimensional SCO compounds with a rich variety of chemical bridges.[19] In contrast, examples of dinuclear SCO complexes are still scarce, which is understandable considering the number of bis-bichelating ligands available and the impossibility in many cases to avoid the polymerisation of the iron(II) cores. The synthesis and physical characterisation of tri-, tetra- and pentanuclear SCO based on triazole and substituted ligands can be found in the literature.[20] Similar characteristics of the spin transition are shown by the tetranuclear complexes synthesised by Lehn and coworkers, in which 4,6-bis(2′,2“-bipyrid-6′-yl)-2-phenyl-pyrimidine acts as bridging ligand.[21]

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

## Experimental Section

**Materials**: All chemicals except for 4,7-phenanthroline-5,6-dione were of reagent grade and obtained commercially without further purification. 4,7-Phenanthroline-5,6-dione was kindly supplied by Novartis laboratories.

**Synthesis of 4,7-phenanthroline-5,6-dioxime (phdiox)**: 4,7-Phenanthroline-5,6-dione (1 g, 4.762 mmol), $H_2NOH\cdot HCl$ (2 g, 0.028 mol) and ethanol (120 mL) were placed in a round-bottomed flask. The mixture was heated at 90 °C over 12 h; the resulting solution was concentrated and the solid was suspended in a solution of 0.2 N HCl (160 mL) for 1 h. The suspension was filtered and the solid washed with water, ethanol and diethyl ether and dried under vacuum. Yield: 61.25 %; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.4$ (s, $^3J$(H,H) = 8 Hz, 2H; OH), 8.76 (d, $^3J$(H,H) = 8 Hz, 2H; CH), 8 (d, $^3J$(H,H) = 8 Hz, 2H; $CH_3$), 6.66 (m, $^3J$(H,H) = 8 Hz, 2H; $CH_2$).

**Synthesis of 4,7-phenanthroline-5,6-diamine (phdia)**: 4,7-Phenanthroline-5,6-dioxime (700 mg, 2.916 mmol), Pd/C (10 % Pd, 690 mg, 0.648 mmol) and ethanol (120 mL) were placed in round-bottomed flask. An $N_2$ current was passed through the mixture for 30 min, followed immediately by heating at 90 °C over 12 h. During this time $H_2NNH_2$ (6.15 mL, 0.126 mol) dissolved in ethanol (15 mL) were added dropwise over a period of 1 h. The resulting mixture was filtered over Celite to eliminate the Pd/C, and then was washed several times with hot ethanol (4 × 40 mL). The solvent was evaporated and the solid obtained was suspended in 35 mL of water and stirred for 1 h. The suspension was kept at 4 °C for 12 h, after which the solid was filtered and dried under vacuum. Yield: 81.63 %; $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.4$ (d, $^3J$(H,H) = 8 Hz, 2H; CH), 8.8 (d, $^3J$(H,H) = 8 Hz, 2H; $CH_3$), 7.43 (m, $^3J$(H,H) = 8 Hz, 2H; $CH_2$), 4.84 (s, $^3J$(H,H) = 8 Hz, 4H; $NH_2$).

**Synthesis of [{Fe(phdia)$_2$(NCS)$_2$}$_2$(phdia)] (1)**: The synthesis was carried out under an argon atmosphere. A solution of KNCS (0.048 g, 0.5 mmol) in methanol (15 mL) was added to a solution of $FeSO_4\cdot 7H_2O$ (0.069 g, 0.25 mmol) in methanol (15 mL). The solution was stirred for 15 min and the resulting precipitate ($K_2SO_4$) was filtered off. This colourless solution, containing Fe/NCS$^-$ (1:2), was added to a solution of phdia (0.052 g, 0.25 mmol) in methanol (25 mL). After this addition, a brown-green precipitate appeared which corresponded to [{Fe(phdia)(NCS)$_2$}$_2$(phdia)]. Yield: 65 %; elemental analysis calcd (%) for $C_{40}H_{30}N_{16}S_4Fe_2$: C 49.28, H 3.10, N 23; found: C 50.02, H 3.5, N 22.80.

**Magnetic susceptibility measurements**: Variable-temperature magnetic susceptibility measurements were carried out on a microcrystalline sample by means of a Quantum Design MPMS2 SQUID susceptometer equipped with a 55 kG magnet and operating in the ranges 0.1–1 T and 1.8–300 K. The susceptometer was calibrated with $[Mn(NH_4)_2(SO_4)_2]-\cdot 12H_2O$. Experimental susceptibilities were corrected for diamagnetism of the constituent atoms by use of Pascal's constants.

**Mössbauer spectra**: $^{57}$Fe Mössbauer spectra were recorded by means of a constant-acceleration conventional spectrometer and a helium bath cryostat. A superconducting magnet was applied to create a magnetic field directed parallel to the wave vector of the $\gamma$-quanta. The sample and the Mössbauer source $^{57}$Co/Rh were immersed in liquid helium. About 40 mg of microcrystalline powder were placed in a 16 mm diameter absorber holder made of polished transparent acryl. The Recoil 1.03a Mössbauer Analysis Software was used to fit the experimental spectra. LIESST experiments were done by irradiating the sample immersed in liquid helium with a laser source of Ar$^+$ (514 nm, 25 mWcm$^{-2}$, Coherent Innova 70).

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