PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Iron(II)-1,2,4-Triazole Spin Transition Molecular Materials

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Iron(II)-1,2,4-triazole spin transition molecular materials

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The phenomenon of spin transition is probably one of the most spectacular examples of molecular bistability. Our main goal along this line concerns the design of molecular materials exhibiting abrupt spin transitions accompanied by thermochromic and large thermal hysteresis effects. The ideal situation, in terms of possible application of these compounds as active elements of memory devices, is realized when room temperature falls in the middle of the thermal hysteresis loop. In this context, we review our work concerning iron(II)-1,2,4-triazole compounds. We first introduce the idea that the cooperativity should be more pronounced in polymeric than in mononuclear compounds. Then we present some results concerning trinuclear iron(II)-1,2,4-triazole species. The heart of the paper is devoted to the polymeric compounds of formulae $[Fe(Htrz)_2(trz)](BF_4)$ and $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$. We report first on the magnetic, optical and calorimetric, then on the structural properties of these compounds. Afterwards, we introduce the concept of spin transition molecular alloy, and emphasize that it is possible to fine tune the spin transition regime of these alloys through their chemical composition. For some alloys, room temperature falls within the thermal hysteresis loop. In the conclusion, the mechanism of cooperativity in the spin transition polymeric compounds is briefly discussed.

1. Introduction

In some transition metal compounds, in particular in those containing $3d^4$–$3d^7$ metal ions in an octahedral environment, a transition between a low-spin (LS) state and a high-spin (HS) state may happen (Kahn 1993). Such a spin transition (or spin crossover) may be induced by a variation of temperature, of pressure, or by light irradiation. This crossover was observed for the first time by Cambi during the 1930s. However, the interest raised by this phenomenon remained limited until the beginning of the 1970s. During the last two decades a sort of 'renaissance' in the study of this phenomenon has occurred (Goodwin 1976; Gütlich 1981; Gütlich *et al.* 1990, 1994; Hauser 1991; König *et al.* 1985; König 1987, 1991; Zarembowitch 1992). One of the reasons of this interest lies in the fact that the spin transition phenomenon is probably the most spectacular example of molecular bistability (Zarembowitch & Kahn 1991)

At this stage, it is important to define the concept of molecular bistability in a clear fashion (Kahn & Launay 1988). A molecular system is said to be bistable when it may be observed in two different electronic states in a given external perturbation range. Usually, one of the two states is a stable state; the other is a metastable state. The concept of molecular bistability concerns the molecular system and the

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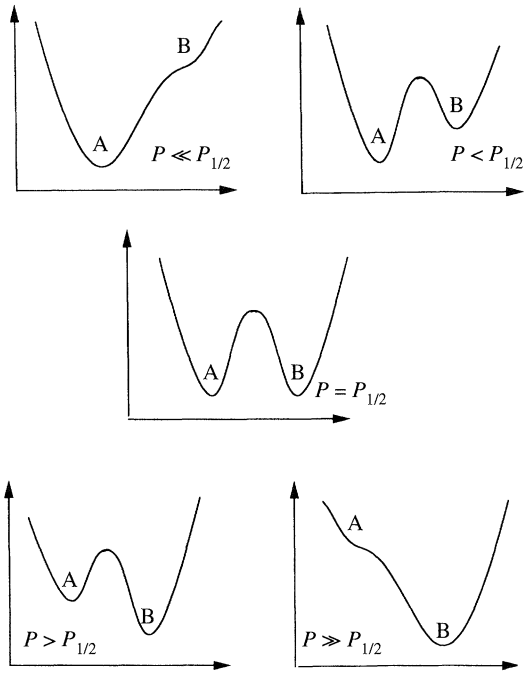

Figure 1. Double-well energy curves and hysteresis effect (see text).

perturbation in an indissociable way. It is meaningless to say that a given system is bistable. It is bistable with respect to a certain perturbation.

Molecular bistability is related to double-well energy curves as represented in figure 1. We consider a molecular system along with an external perturbation, denoted P. When P is weak enough, the A state is the ground state. When P increases, the energy gap between ground A and excited B states diminishes. These two states have the same energy for an inversion value of the perturbation, denoted $P_{1/2}$. Increasing P further results in a stabilization of B with respect to A. This double-well situation is a necessary but not sufficient condition for bistability. In addition, the system must be able to be trapped in a metastable state. If so, and referring again to the curves of figure 1, the system is in the A state as long as A is either the lowest or the secondary energy minimum for increasing P, and in the B state as long as B is either the lowest or the secondary energy minimum for decreasing P. It follows that the two routes when P increases and decreases are not identical. There is a hysteresis loop which confers a memory effect on the system.

We have not specified yet the exact meaning of the double-well energy curves of figure 1. If we consider an isolated molecule, or more probably an assembly of non-interacting molecules, the curves may represent the variation of the potential energy of one molecule, E, versus an internal coordinate, Q, such as a bond length. On the contrary, if we consider an assembly of interacting molecules, the curves usually represent the variation of the Gibbs free energy of the assembly, G, versus the molar fraction of molecules in the B state, x_{B}. Although the two kinds of curves $E = f(Q)$ and $G = f(x_{\mathrm{B}})$ may appear rather similar, they do not correspond to the same physical processes. Thus, in the $E = f(Q)$ diagram, there are at least three different ways to move from one well to another, namely: (i) either by climbing the activation barrier (the thermal process); (ii) by passing through the barrier (the tunnelling pro-

cess); or (iii), finally, by passing through an excited state in a Franck–Condon vertical process followed by vibrational relaxation (the optical process). On the contrary, in the $G = f(x_B)$ diagram, the system always evolves along the minimum energy path, and can be trapped in a secondary minimum, which leads to a hysteresis effect. One sees, therefore, that the bistability giving rise to a memory effect is much more probable for an assembly of interacting molecules than for a collection of non-interacting molecules. Actually, the possibility of hysteresis for non-interacting molecules is still a subject of debate (Bolvin & Kahn 1991). The intermolecular interactions, if they are strong enough, may give rise to cooperative behaviours. Our main objective in the field of spin-crossover compounds is to design and synthesize compounds exhibiting a large thermal hysteresis, and to explore to what extent these compounds could be used as active elements in memory devices.

This paper will briefly review our work carried out in the last few years in this area of molecular materials exhibiting cooperative spin transitions. It is organized as follows. First, we will introduce the idea that the cooperative character of spin transitions may be magnified in polymeric compounds, as regard to mononuclear compounds. Then, we will focus on the Fe(II)-1,2,4-triazole system. We will successively comment on trinuclear species and polymeric species. A section will be devoted to the concept of molecular alloys in the context of polymeric spin transition compounds. Finally, we will briefly discuss the perspectives in this area of research.

2. Cooperativity in polymeric spin transition compounds

As already mentioned, one of our objectives is to use spin transition compounds as active elements in memory devices. Our first step along this line deals with a display device. For that, some requirements must be fulfilled, which can be summarized as follows. (i) The transition must be abrupt both in the warming mode at $T_c\uparrow$ and in the cooling mode at $T_c\downarrow$. (ii) The transition must occur with a large thermal hysteresis effect (the bistability is achieved in the temperature range between $T_c\uparrow$ and $T_c\downarrow$. (iii) For an all-public application, the transition temperatures must be as close as possible to room temperature. The ideal situation is when the ambient temperature falls in the middle of the thermal hysteresis loop. (iv) The transition between LS and HS states must be accompanied by an easily detectable response, such as a change of colour (Kahn *et al.* 1992). The first two requirements are related to the cooperativity, i.e. to the magnitude of the interactions between active sites. In purely molecular crystals containing spin-crossover mononuclear entities, the intermolecular interactions are very weak, of the van der Waals type. Such mononuclear compounds seem not to be appropriate for our purpose. In many cases, the spin transition mononuclear entities are hydrogen bonded within the crystal lattice. These hydrogen bonds may lead to stronger intermolecular interactions. This situation is most often achieved when the crystal lattice contains some uncoordinated solvent molecules. Even larger interactions between active sites may be anticipated if these active sites are covalently linked by chemical bridges; in particular, if these bridges are conjugated. Our starting idea, illustrated in figure 2, is that in polymeric spin transition compounds the cooperativity should be magnified.

The first experimental result supporting this idea was provided by the compound $[Fe(btrz)_2(NCS)_2] \cdot H_2O$ with btrz = bis-1,2,4-triazole, the structure of which is depicted in figure 3 (Vreugdenhill *et al.* 1990). Each iron atom is surrounded by two NCS groups in a *trans* position and four btrz ligands coordinated through the

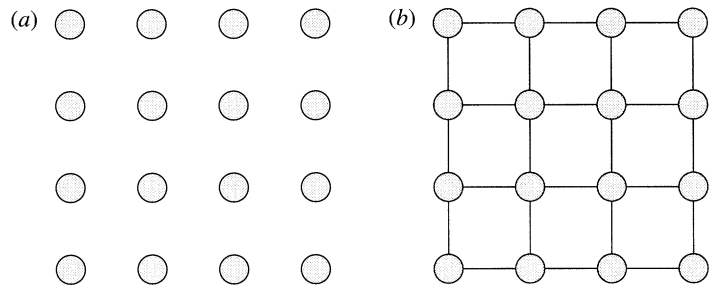

Figure 2. Cooperativity in spin transition mononuclear (*a*) and polymeric (*b*) species.

nitrogen 1- and 1′-positions. The btrz ligands bridge the iron atoms, which results in a two-dimensional structure. The non-coordinated water molecules are hydrogen bonded to the nitrogen atoms of btrz occupying the 2- and 2′-positions. This two-dimensional compounds shows extremely abrupt spin transitions at $T_c\uparrow = 144.5$ K and $T_c\downarrow = 123.5$ K (see figure 3). The thermal hysteresis width is 21 K. Between $T_c\uparrow$ and $T_c\downarrow$ the state of the system depends on its history.

A Fe(II)-triazole compound showing a spin transition above room temperature accompanied with a purple–white change of colour was mentioned in the literature for the first time by Haasnoot *et al.* (1977). Later, a Russian group reported on a series of iron(II)-1,2,4-triazole compounds, several of them exhibiting spin transitions around room temperature with thermal hysteresis and thermochromic effects (Larionova *et al.* 1986, 1991). More recently, Goodwin and co-workers also investigated these compounds (Sugiyarto & Goodwin 1994). A few years ago, it occurred to us that the compounds of this family could fulfill the criteria mentioned above, and we decided to investigate them in a thorough manner.

3. Trinuclear species

Some years ago, Reedijk and co-workers reported a trinuclear iron(II) compound arising from the reaction of 4-Et-1,2,4-triazole, abbreviated as Ettrz, with iron(II) triflate (Vos *et al.* 1984). The formula of the compound is $[Fe_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$. Within the trinuclear cation the iron(II) ions are aligned. The central iron atom is triply bridged to each of the two terminal iron atoms through the 1- and 2-positions of the triazole ligands. Each terminal iron atom completes an octahedral environment with three water molecules. As far as the physical properties of this compound are concerned, the most interesting feature lies in the fact that the central iron(II) ion undergoes a rather gradual spin conversion with $T_{1/2} = 210$ K, while the two external iron(II) ions are HS in the whole temperature range. The same kind of trinuclear species, with one out of three iron(II) ions exhibiting a spin crossover, may be obtained with many 4-substituted-1,2,4-triazole ligands. Actually, such compounds are usually obtained when the group attached to the 4-position is rather bulky. For instance, the reaction of 4-NMe_2-1,2,4-triazole (abbreviated as NMe_2trz) with $[Fe(H_2O)_6](ClO_4)_2$ affords a trinuclear compound of formula $[Fe_3(NMe_2trz)_6(H_2O)_6](ClO_4)_6$ in which only the central iron(II) ion undergoes a spin conversion, with $T_{1/2} = 175$ K. On the other hand, if NMe_2trz is replaced by NH_2trz (standing for 4-NH_2-1,2,4-triazole), the same reaction affords a polymeric compound of formula $[Fe(NH_2trz)_3](ClO_4)_2$.

A different situation has been found in the Fe(II)-*p*-MeOptrz system, where

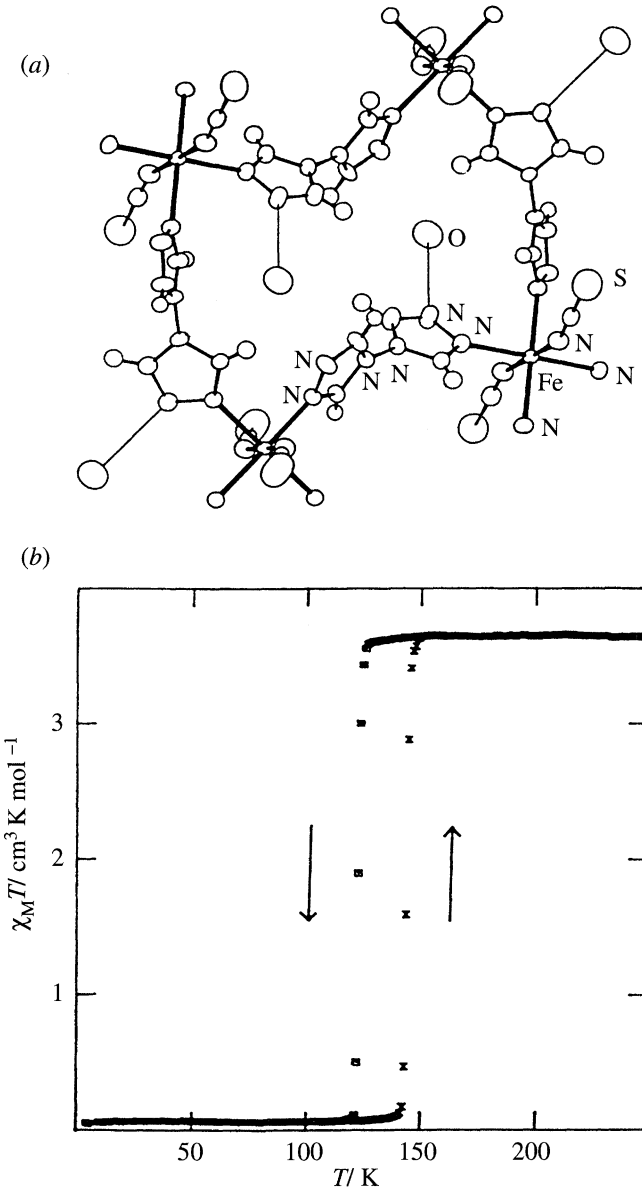

Figure 3. (*a*) Structure of $[Fe(btrz)_2(NCS)_2] \cdot H_2O$. (*b*) $\chi_M T$ versus T curves in the warming and cooling modes for this compound.

p-MeOptrz stands for 4-(p-methoxy)phenyl-1,2,4-triazole. Two compounds have been synthesized up to now, namely $[Fe_3(p\text{-MeOptrz})_8(H_2O)_4](BF_4)_6$ and $[Fe_3(p\text{-MeOptrz})_6(H_2O)_6](tos)_6$, with tos = tosylate (Thomann *et al.* 1994). Both structures consist of linear trinuclear cations with a +6 charge, and non-coordinated anions. The central iron atom lies on an inversion centre and is triply bridged to each of the external iron atoms through the *p*-MeOptrz ligands. Each external iron atom completes its octahedral surroundings with one *p*-MeOptrz ligand and two water molecules in the former compound, and with three water molecules in the

latter compound, as shown in figure 4. As for the two trinuclear compounds already mentioned, the central iron(II) ion in the tosylate derivative shows a spin conversion centered at $T_{1/2} = 245$ K. On the other hand, the three iron(II) ions of the tetrafluoroborate derivative are HS in the whole temperature range. These striking differences between the two compounds cannot be attributed to structural differences in the central FeN_6 cores. At room temperature, the bond lengths and angles around the central metal ion are almost identical. Actually, what seems to play a key role concerning the differences of magnetic properties are the values of the dihedral angle between triazole and phenyl rings of the bridging *p*-MeOptrz groups. The average value of these angles is 71.4° in the former compound, and only 33.2° in the latter. In other words, the triazole and phenyl rings are more coplanar, and therefore the conjugation between the two rings is significantly more pronounced in the tosylate derivative. The methoxy group on the phenyl ring is expected to exert an electron-donating effect which may be transmitted to the coordinating nitrogen atom through the conjugation between the two rings. This effect is transmitted more efficiently in the tosylate than in the tetrafluoroborate derivatives. The variation in dihedral angle creates a sort of switching effect high-spin and spin-crossover situation. Of course, in the present case we do not control this switching. The fact that the *p*-MeOptrz ligands are more coplanar in $[Fe_3(p\text{-MeOptrz})_6(H_2O)_6](tos)_6$ than in $[Fe_3(p\text{-MeOptrz})_8(H_2O)_4](BF_4)_6$ might be due to the shape of the anions. The small and rather spherical BF_4^- anions fit the space between the phenyl rings, while the tosylate anion forces the rings of *p*-MeOptrz to be coplanar.

The compound $[Fe_3(p\text{-MeOptrz})_8(H_2O)_4](BF_4)_6$, in which the three iron(II) ions are HS over the whole temperature range, allows us to determine the interaction parameter between two HS Fe(II) ions triply-bridged by triazole ligands. The $\chi_M T$ versus T curve for this compound is shown in figure 5. The decrease of $\chi_M T$ as T is lowered results from both an antiferromagnetic interaction between the adjacent magnetic centres and the local anisotropy of the Fe(II) ions. The curve of figure 5 has been quantitatively interpreted by full diagonalization of the spin Hamiltonian:

$$\mathcal{H} = -J\boldsymbol{S}_B \cdot (\boldsymbol{S}_A + \boldsymbol{S}_C) + D_A(\boldsymbol{S}_{A,z^2} + \boldsymbol{S}_{C,z^2}) + g\beta(\boldsymbol{S}_A + \boldsymbol{S}_B + \boldsymbol{S}_C) \cdot H,$$

where A and C denote the external metal ions (C being the central one). The first term on the right-hand side describes the isotropic interaction, the second term the local anisotropy of the terminal metal ions, and the third term the Zeeman perturbation. In the spin Hamiltonian, the local anisotropy of the central Fe(II) ion in an almost perfect octahedral environment has been assumed to be negligible with respect to the local anisotropies of the terminal Fe(II) ions. J has been found as $-5.7\,cm^{-1}$ and D_A and D_B as $7.21\,cm^{-1}$. One will note that antiferromagnetic interaction and local anisotropies are of the same order of magnitude.

4. Polymeric compounds

We have already mentioned that when the group attached to the nitrogen 4-position is small, compounds with the one metal–three ligands stoichiometry are obtained. In particular, this is the case for the unsubstituted 1,2,4-1H-triazole upon which we will focus.

The reaction of $[Fe(H_2O)_6](BF_4)_2$ with 1,2,4-1H-triazole affords two compounds depending on the experimental conditions. The former compound is $[Fe(Htrz)_2(trz)](BF_4)_2$; a spontaneous deprotonation of one out of three Hrtz ligands occurs.

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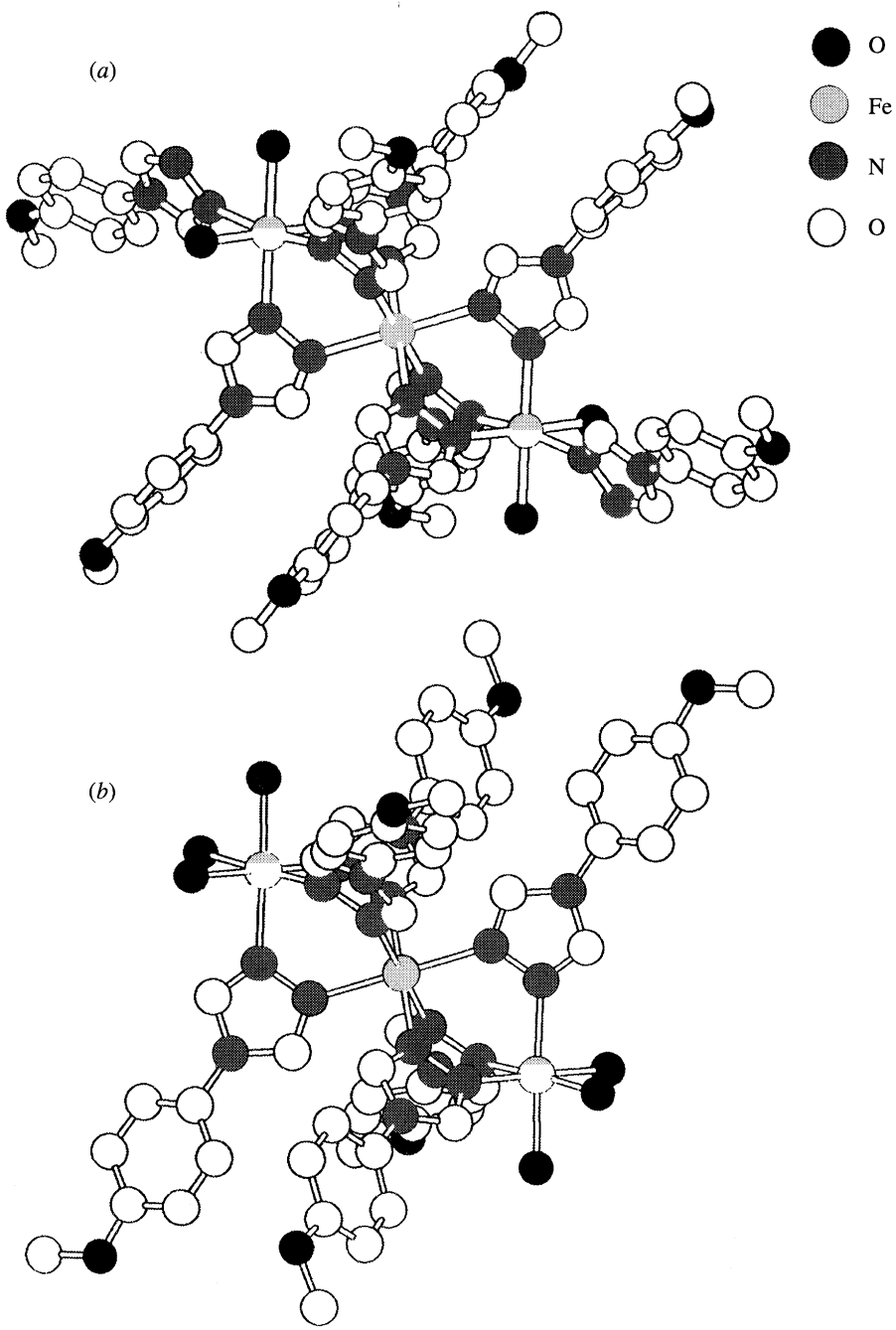

Figure 4. Structures of (*a*) $[Fe_3(p\text{-MeOptrz})_8(H_2O)_4](BF_4)_6$ and (*b*) $[Fe_3(p\text{-MeOptrz})_6(H_2O)_6](tos)_6$.

The latter compound is $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$ where no deprotonation has occured, and the three ligands are neutral. We will successively investigate the physical properties of both compounds.

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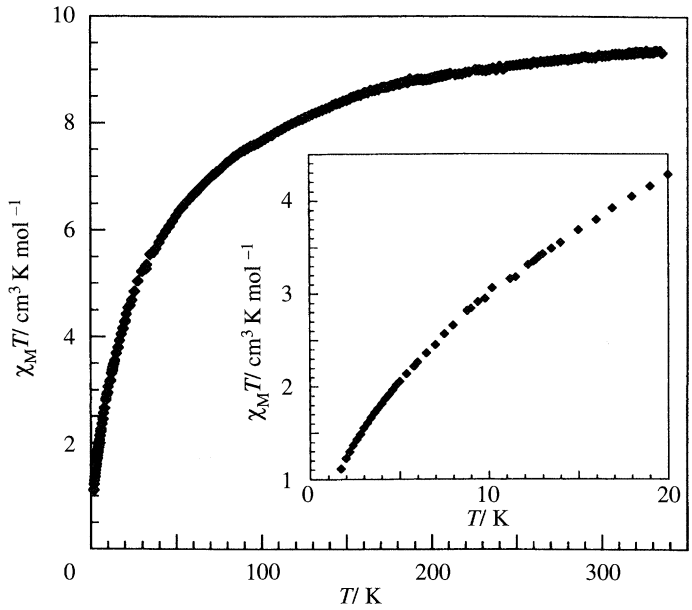

Figure 5. $\chi_M T$ versus T curve for $[Fe_3(p\text{-MeOptrz})_8(H_2O)_4](BF_4)_6$.

(*a*) $[Fe(Htrz)_2(trz)](BF_4)$

Actually, two modifications of this compound have already been obtained. Probably, other modifications could be synthesized. Adding a solution of 1,2,4-1H-trz dissolved in ethanol to a solution of the iron(II) salt dissolved in water results in a modification denoted ***a***. When the two reactants are dissolved in methanol, a modification ***b*** is obtained. The chemical formulae of these two modifications are strictly identical. They indicate that there is no solvent molecule in the lattice. However, as we will see later, ***a*** and ***b*** do not exhibit the same physical properties (Kröber *et al.* 1994).

Let us first consider ***a***. A large variety of physical techniques have been utilized to characterize the spin transition regime of this compound. The spin transition is exceptionally abrupt in both the warming and cooling modes. It is also accompanied by a well-pronounced thermochromism between the purple colour in the LS state and the white colour in the HS state. The purple colour in the LS state arises from the $^1A_{1g} \rightarrow {}^1T_{1g}d - d$ absorption at 520 nm. In the HS, the spin-allowed absorption of lowest energy appears at 800 nm, at the limit of the infrared range. The transition temperatures are found to be very slightly dependent on both the sample and of the technique used to detect the transition. They may be given as $T_c\uparrow = 383 \pm 3$ K and $T_c\downarrow = 345 \pm 2$ K. The thermal hysteresis width is then about 40 K.

Let us briefly comment on the physical data. The magnetic properties are shown in figure 6 in the form of the $\chi_M T$ versus T plot; χ_M being the molar magnetic susceptibility and T the temperature. Above $T_c\uparrow$ in the warming mode and $T_c\downarrow$ in the cooling mode, $\chi_M T$ is equal to 3.4(1) cm^3 K mol^{-1}, which corresponds to what is expected for an octahedral iron(II) compound in the HS state. Below the transition temperatures, $\chi_M T$ is equal to about 0.3 cm^3 K mol^{-1}, which indicates that there is a small residual fraction of HS molecules in the LS phase.

The Mössbauer spectroscopy is consistent with the magnetic data. Typical spectra are represented in figure 7. The spectrum is characteristic of a HS iron(II) compound

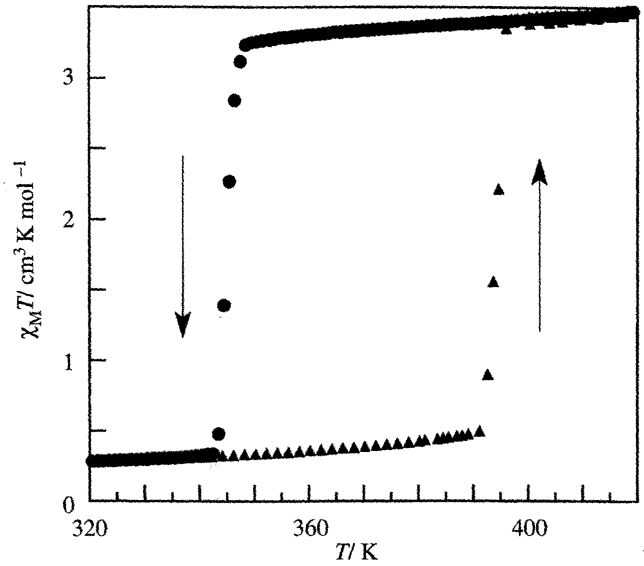

Figure 6. $\chi_M T$ versus T curve in the warming and cooling modes for the modification ***a*** of $[Fe(Htrz)_2(trz)](BF_4)$.

above 400 K and of a LS iron(II) compound below 340 K. The two spectra coexist within a few K in both the warming and cooling modes. The spectra do not show any dynamical broadening of the Mössbauer lines, thus indicating that the conversion rates remain lower than the Mössbauer hyperfine frequency (around 107 s^{-1}), despite the fact that the transitions take place above room temperature. The slowing down of the conversion rates, as compared to other iron(II) spin transition compounds, might be due to the polymeric nature of the compound.

The differential scanning calorimetry curves for ***a*** are represented in figure 8. They show an abrupt endothermic process at $T_c\uparrow$ in the warming mode, and an even more abrupt exothermic process at $T_c\downarrow$ in the cooling mode. The enthalpy variations associated with these processes are equal to 27.8 and 28.6 kJ mol^{-1}, respectively. These values are much higher than those found for the mononuclear iron(II) spin transition compounds, usually in the 5–15 kJ mol^{-1} range. For instance, the enthalpy variation for $Fe(phen)_2(NCS)_2$ with phen = *ortho*-phenantroline is equal to 8.59 kJ mol^{-1}.

As already pointed out, the spin transition in all the Fe(II)-1,2,4-trz compounds is accompanied by a dramatic change of colour, so that the transitions can be detected optically, using the setup schematized in figure 9. This setup records changes in optical properties of spin transition compounds in a remarkably simple and reliable way. The sample holder, containing about 50 mg of microcrystalline compound, is fitted to the common end of a double optical fibre and plugged into a cryogenic system. The temperature rises and decreases at the rate of 1 K min^{-1} without overshooting. A photomultiplier fitted with a 520 nm interferential filter converts the light reflected by the sample into an electric current, the intensity of which depends on the colour change. As the spin transition compound absorbs at 520 nm in the LS state and not in the HS state, the intensity recorded is null for the purple colour (LS state), and maximum for the white colour (HS state). A personal computer is used to control the process and record the data. One can then convert the arbitrary intensities into normalized HS molar fractions, identical to what is obtained with other techniques. The

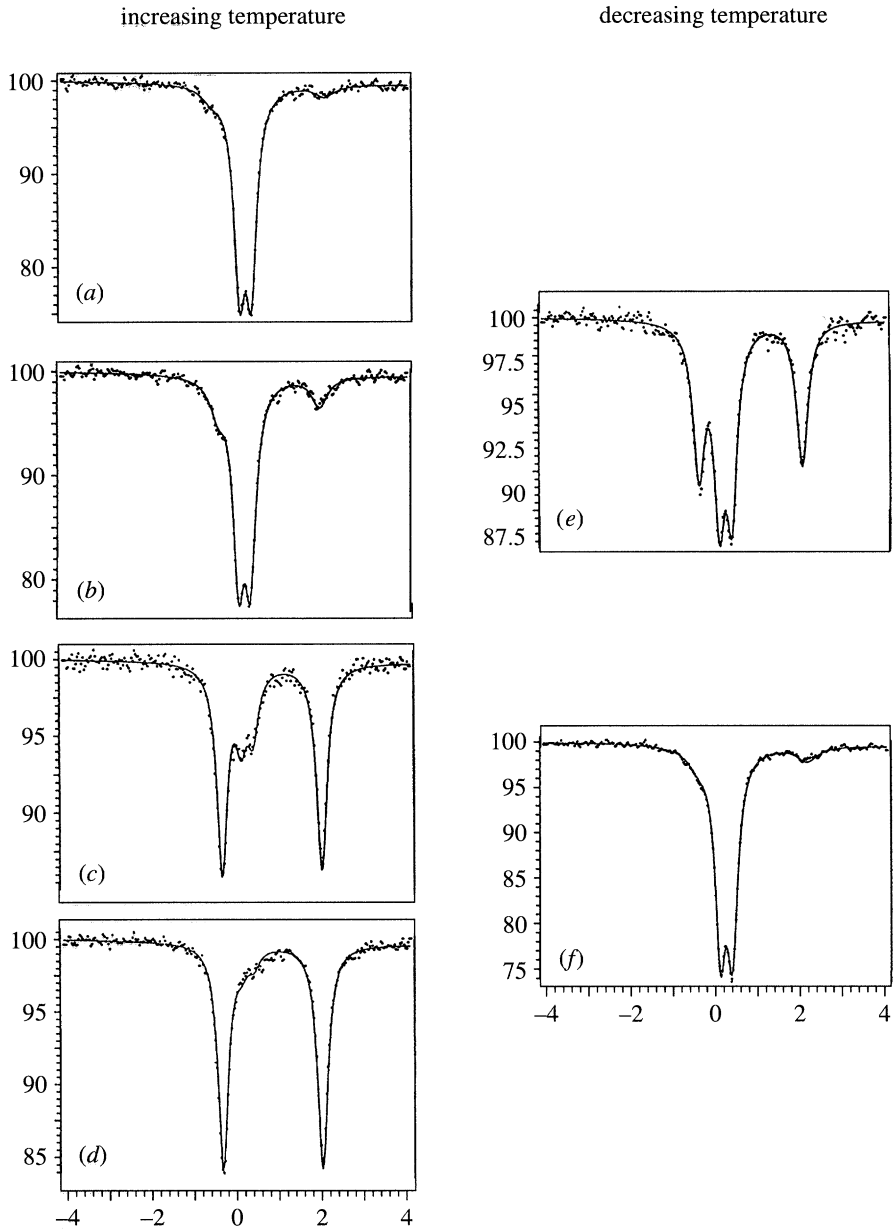

Figure 7. Mössbauer spectra at various temperatures for the modification ***a*** of $[Fe(Htrz)_2(trz)](BF_4)$.

optical response for ***a*** is shown in figure 10. Over many cycles the signal dynamics remains unchanged.

All the experimental techniques presented above were also used to characterize the spin conversion for ***b***. We mention the main differences between the modifications ***a*** and ***b*** as follows.

(i) The transitions for ***b*** are less abrupt in both the warming and cooling modes, so that the hysteresis loop is less square-shaped.

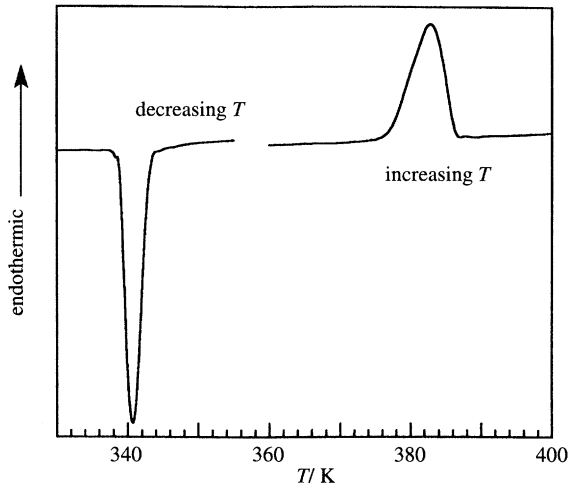

Figure 8. Differential scanning calorimetry curves for the modification ***a*** of $[Fe(Htrz)_2(trz)](BF_4)$.

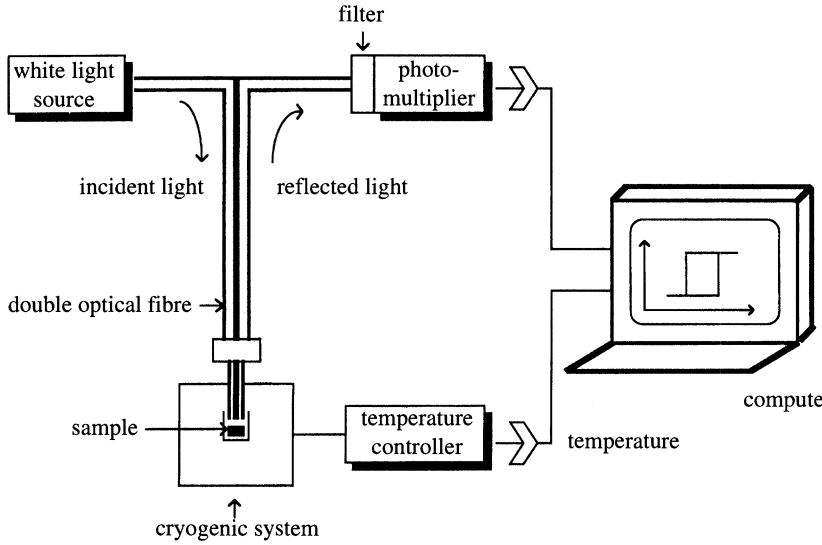

Figure 9. Device used for the optical detection of the spin transition in the Fe(II)-1,2,4-triazole compounds.

(ii) Successive thermal cycles do not modify $T_c\downarrow$, but displace $T_c\uparrow$ towards lower temperatures until it stabilizes after three or four cycles. These changes over cycles suggest a reconstruction of the material until it reaches a stable state. This effect was not observed for ***a***.

(iii) The enthalpy variations accompanying the transitions for ***b*** are around 21 kJ mol^{-1}, i.e. significantly lower than for ***a***.

(*b*) $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$

Let us first mention that the water molecule incorporated within the lattice of $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$ is progressively removed as the compound is warmed to *ca.* 370 K, so that it is not easy to investigate the physical properties of this monohy-

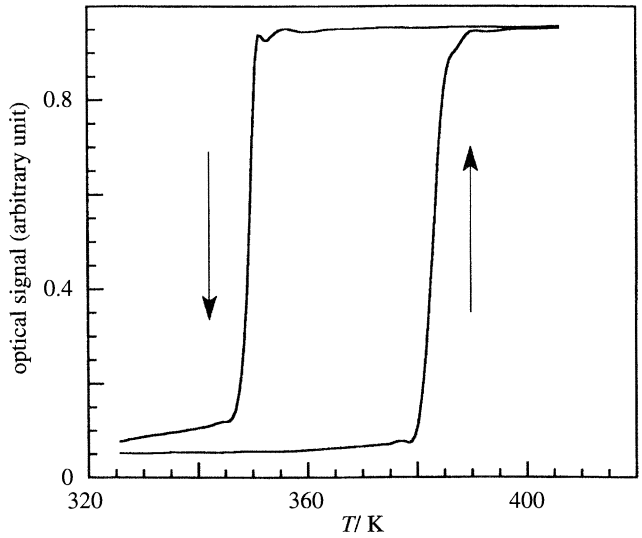

Figure 10. Optical detection of the spin transition for the modification ***a*** of $[Fe(Htrz)_2(trz)](BF_4)$.

drated form. On the other hand, the study of the dehydrated form does not present any difficulty. In a humid atmosphere $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$ shows rather abrupt spin transitions with $T_c\uparrow = 345 \pm 3$ K and $T_c\downarrow = 323 \pm 3$ K. For the dehydrated form, the transitions are rather less abrupt and the thermal hysteresis width is smaller.

The most interesting feature concerning $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$ is the crystallographic phase transition that occurs at around 430 K. Let us describe the thermodynamical process. $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$ is synthesized in the α phase. As the temperature is increased, a spin transition is observed in this α phase, and successive thermal cycles in a humid atmosphere (for instance in a tube sealed with a very small amount of humid cotton) do not significantly modify the hysteresis loop, provided that the temperature never goes beyond *ca.* 380 K. As T is increased further, the dehydration occurs (even in a humid atmosphere), then an $\alpha \rightarrow \beta$ phase transition takes place. This β phase remains HS down to room temperature, and shows a very abrupt spin transition loop just below room temperature with $T_c\uparrow = 282$ K and $T_c\downarrow = 276$ K. This β phase is metastable at room temperature; it spontaneously transforms back to the α phase within a few days or weeks. The $\beta \rightarrow \alpha$ back-transformation at room temperature is faster in the presence of a humid atmosphere. The magnetic and optical data accompanying this interplay between spin transitions and crystallographic phase transition are depicted in figures 11 and 12, respectively.

5. EXAFS and X-ray powder diffraction studies

In spite of many efforts, it has not yet been possible to grow single crystals of compounds $[Fe(Htrz)(trz)](BF_4)$ and $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$ suitable for X-ray diffraction. Extremely small crystals are sometimes obtained using the slow diffusion technique so that the problem is not hopeless, especially if a diffractometer of the imaging plate type can be utilized. So far, however, structural information has been obtained from alternative techniques such as EXAFS at the iron edge and X-ray powder diffraction.

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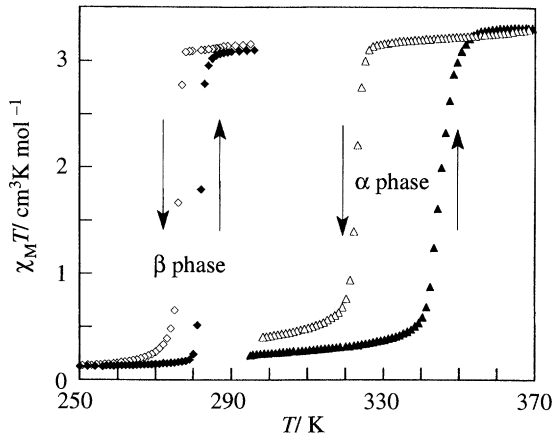


Figure 11. $\chi_M T$ versus T curve in the warming and cooling modes for the α and β phases of $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$. The curves for the α phase were recorded by raising and lowering the temperature between 293 and 380 K. Before recording the curves for the β phase, the sample was warmed up to 450 K and then cooled to room temperature. The curves were recorded during the lowering and raising of temperature between 293 and 250 K.

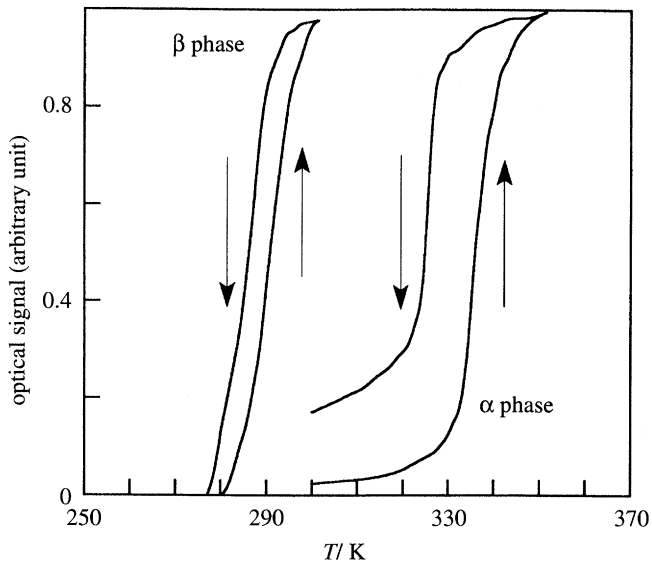


Figure 12. Optical detection of the spin transitions for the α and β phases of $[Fe(Htrz)_3](BF_4)_2$.

(*a*) *EXAFS spectra*

The EXAFS investigation has concerned the modifications ***a*** and ***b*** of $[Fe(Htrz)_2(trz)](BF_4)$ and $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$ together with the two trinuclear species $[Fe_3(p\text{-MeOptrz})_8(H_2O)_4](BF_4)_6$ and $[Fe_3(p\text{-MeOptrz})_6(H_2O)_4](tos)_6$, the crystal structures of which are known. The main findings of this EXAFS investigation may be summarized as follows.

(i) The EXAFS spectra of $[Fe(Htrz)_2(trz)](BF_4)$ (modifications ***a*** and ***b***) and $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$ are quite similar when the compounds are in the LS state.

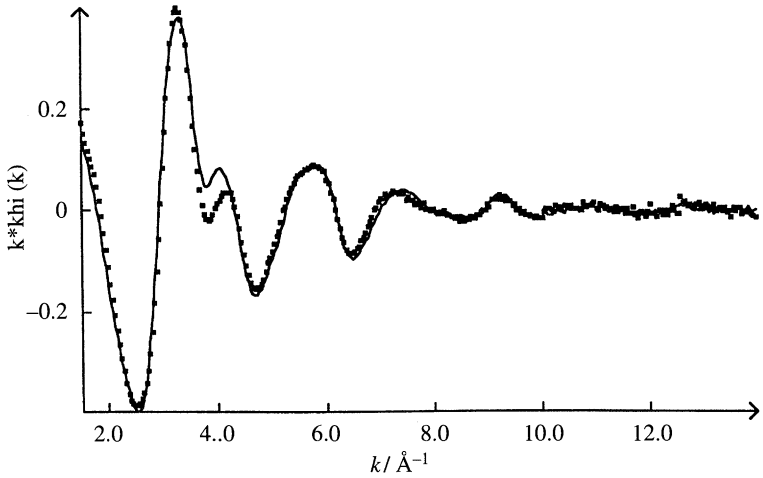


Figure 13. Comparison of the EXAFS data for $[Fe(Htrz)_2(trz)](BF_4)$ (***a***) at 403 K (■) and $[Fe_3(p\text{-MeOptrz})_8(H_2O)_4](BF_4)_6$ at room temperature (——).

They are also quite similar when they are in the HS state. It follows that the structures of these three compounds are very similar to each other.

(ii) The EXAFS spectrum of $[Fe(Htrz)_2(trz)](BF_4)$ (***a***) at 400 K, i.e. in the HS state, is much the same as that of $[Fe_3(p\text{-MeOptrz})_8(H_2O)_4](BF_4)_6$ at room temperature, with the three Fe(II) ions in the HS state, as shown in figure 13. This strongly suggests that the basis structure of $[Fe(Htrz)_2(trz)](BF_4)$ is that of a linear chain in which two adjacent iron atoms are triply bridged by triazole ligands through the nitrogen atoms occupying the 1- and 2-positions.

(iii) The spectra of the three compounds $[Fe(Htrz)_2(trz)](BF_4)$ (mofifications ***a*** and ***b***) and $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$ in the LS state show a characteristic peak at around 7 Å, which cannot be interpreted in the frame of the single-scattering approach of the standard EXAFS formula. This peak may be assigned to a three-atom path involving aligned iron atoms.

(iv) Finally, the EXAFS spectrum of $[Fe(Htrz)_2(trz)](BF_4)$ (***a***) is strongly modified when passing from the LS to the HS states, as emphasized in figure 14. These modifications correspond to a lengthening of 0.18 Å of the Fe—N bonds along with a distorsion of the FeN_6 octahedron. These findings concerning the Fe—N bond lengths and the symmetry of the FeN_6 core are not surprising. The same modifications have been found through single-crystal X-ray diffraction for mononuclear iron(II) spin transition compounds (König 1987; Gallois *et al.* 1990) and for the central iron(II) ion of $[Fe_3(Et\text{-}trz)_6(H_2O)_6](CF_3SO_3)_6$ (Vos *et al.* 1984).

From the EXAFS data, it has been possible to obtain a rather accurate description of the basic structure of the polymeric compounds. A model structure is represented in figure 15. The case of $[Fe(Htrz)_2(trz)](BF_4)$ raises a particular problem. One out of three triazole rings is deprotonated. The similarity of the EXAFS spectra of $[Fe(Htrz)_2(trz)](BF_4)$ and $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$ allows us to rule out the hypothesis that the deprotonated triazolato group would be triply bridging through its three nitrogen atoms, as observed in some Ru(II)-trz organometallic compounds (Oro *et al.* 1986) and Zn(trz)Cl (Kröber *et al.* 1995). Most likely, a proton hole in $[Fe(Htrz)_2(trz)](BF_4)$ is disordered over each $Fe(Htrz)_2(trz)Fe$ bridging network. If so, the three-fold symmetry of the chain compound depicted in figure 15 is retained.

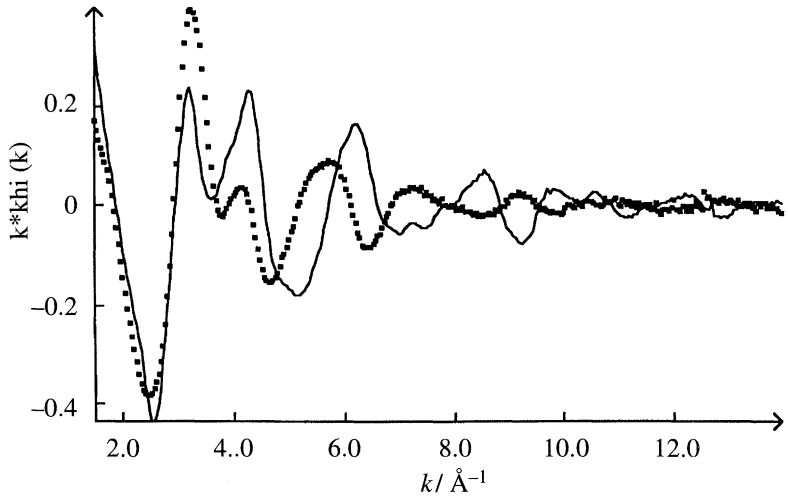


Figure 14. Comparison of the EXAFS spectra for $[Fe(Htrz)_2(trz)](BF_4)$ (***a***) at room temperature in the LS state (■) and at 403 K in the HS state (——).

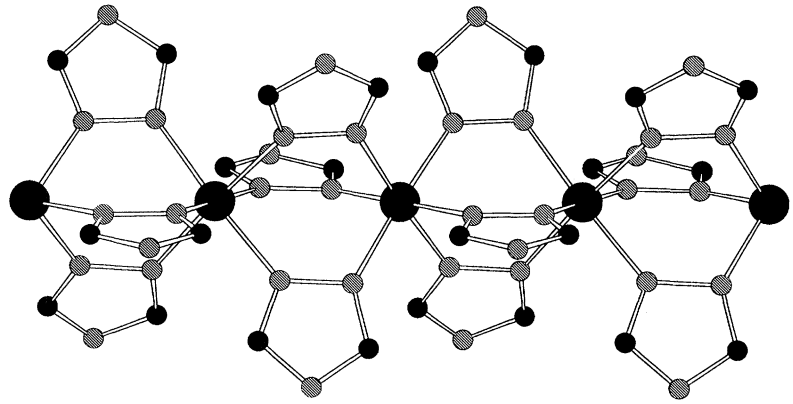


Figure 15. Structure of the polymeric Fe(II)-1,2,4-triazole compounds, as deduced from the EXAFS investigation.

(*b*) *X-ray powder diffraction*

X-ray powder diffraction brought additional structural information on the polymeric compounds. We restrict ourselves here to the two modifications ***a*** and ***b*** of $[Fe(Htrz)_2(trz)](BF_4)$, and we try to answer two questions, namely: (i) is there any crystallographic phase transition accompanying the spin transition? (ii) Is there any crystallographic difference between the modifications ***a*** and ***b***?

Concerning the former question (i), the X-ray diffractograms for ***a*** were recorded at various temperatures between room temperature and 430 K, both in the warming and cooling modes, as shown in figure 16. Abrupt modifications of the diffractograms were clearly observed at $T_c\uparrow$ and $T_c\downarrow$ with a thermal hysteresis of about 45 K. Several thermal cycles were successively carried out, and the transition temperature remained unchanged. The diffractograms recorded at room temperature after several thermal cycles were strictly identical to that recorded on a freshly prepared sample, which confirms the non-fatigability of the spin transition phenomenon. Let us now compare the diffractograms in the LS and HS states. These diffractograms are actually quite

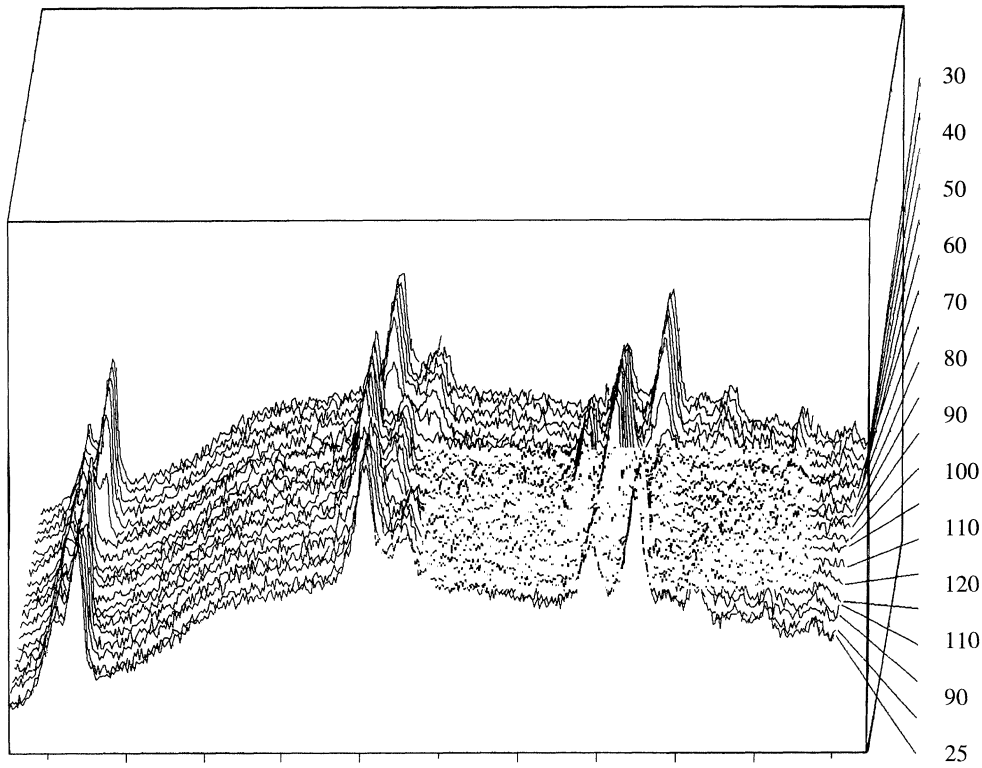


Figure 16. Diffractograms of $[Fe(Htrz)_2(trz)](BF_4)$ ($\boldsymbol{a}$) in the $4.5° < \theta < 15°$ range recorded every 10° between 90 °C (363 K) and 150 °C (423 K) in the warming mode, and between 150 °C (423 K) and 30 °C (303 K) in the cooling mode.

similar as far as both the number of peaks and their relative intensities are concerned. The LS → HS transition, however, is accompanied by an important dilatation of the crystal lattice. These results strongly suggest that the spin transition takes place without crystallographic phase transition. Of course, we cannot totally exclude that some very weak diffraction peaks are hidden by the background; some of these peaks could appear and disappear with the occurence of the transition. Therefore, although this is very probable, it is not possible to assert with an absolute certainty that the space group is retained.

Concerning the crystallographic differences between $\boldsymbol{a}$ and $\boldsymbol{b}$, the X-ray powder study brings a clear-cut answer. Actually, it reveals that in both the LS and HS states, the diffractograms of $\boldsymbol{a}$ and $\boldsymbol{b}$ are not identical, as shown in figure 17. More precisely, there are more diffraction peaks for $\boldsymbol{a}$. These additional peaks may be described as resulting from a doubling of the diffraction peaks for $\boldsymbol{b}$. Most likely, the two crystal lattices are close to each other with, however, a lower symmetry for $\boldsymbol{a}$. It is interesting to note that the nature of the solvents used for the synthesis influence the crystallographic characteristics of the compounds, though there is no solvent molecule in the crystal lattices. The presence of water during the synthesis process seems to be essential to obtain the modification $\boldsymbol{a}$ which shows the most abrupt spin transition. Interestingly, modification $\boldsymbol{b}$ can be transformed into modification $\boldsymbol{a}$; by stirring $\boldsymbol{b}$ with a small amount of water and then drying it under a vacuum.

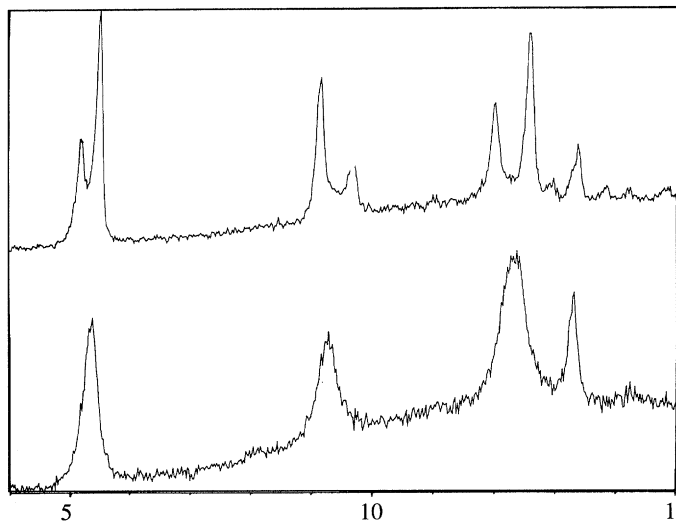
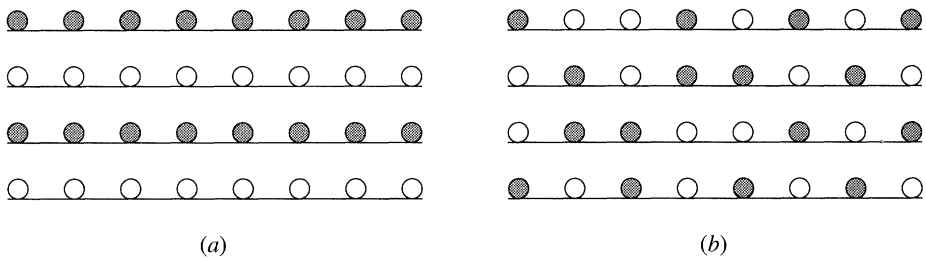


Figure 17. Comparison of the diffractograms of the modifications ***a*** (top) and ***b*** (bottom) of $[Fe(Htrz)_2(trz)](BF_4)$ in the $4.5^\circ < \theta < 15^\circ$ range at room temperature.

6. Molecular alloys

One of our main targets is to synthesize spin transition compounds for which room temperature exactly falls in the middle of the thermal hysteresis loop. Using the trial and error method, such compounds can be otained. We have synthesized, for instance $[Fe(NH_2trz)_2]Br_2 \cdot H_2O$, which shows a spin transition regime with $T_c\uparrow = 307$ K and $T_c\downarrow = 279$ K. The centre of the hysteresis loop is 293 K, i.e. exactly at room temperature. However, the transition in the cooling mode is rather gradual, so that this compound cannot be used in a display device (Kahn *et al.* 1992). We are presently exploring the iron(II)-triazole system as a whole. We will not enter into the details of our findings here. Rather, we would like to focus on another approach to obtain the ideal compound. This approach is based on the concept of spin transition molecular alloys.

Let us define explicitly what we mean by 'molecular alloy'. We know that the compounds with the stoichiometry $[Fe(Rtrz)_3]A_2$ or $[Fe(Rtrz)_2(trz)]A$, where A is a monovalent anion, have a one-dimensional polymeric structure. Let us assume now that we can synthesize two compounds of this sort, of formulae $[Fe(R_1trz)_3]A_2$ and $[Fe(R_2trz)_3]A_2$, respectively, where R_1trz and R_2trz are two different 4-substituted-1,2,4-triazole ligands. We assume further that both compounds exhibit a spin transition, the former around the temperature T_1 and the latter around T_2. T_1 and T_2 may be defined as the middles of the thermal hysteresis loops. If we mix 50% of $[Fe(R_1trz)_3]A_2$ and $[Fe(R_2trz)_3]A_2$ in the solid state, we obviously end up with a material containing 50% of chains $[Fe(R_1trz)_3]_\infty$ and 50% of chains $[Fe(R_2trz)_3]_\infty$. This material will display a two-step spin transition regime, one step occurring around T_1 and the other around T_2. On the other hand, if we react the $[Fe(H_2O_6]A_2$ salt with a mixture of 50% R_1trz and 50% R_2trz dissolved in a common solvent, we end up with another material in which all the chains now have a mixed composition with 50% of each of the two ligands, as emphasized in figure 18. Such a material is defined as a molecular alloy. The problem we are then faced with is to understand the behaviour of such an alloy. Within each chain, we most likely have a statistical distribution of



(a) (b)

Figure 18. Schematic representation of the structural difference between a 50:50 mixture (*a*) and a molecular alloy (*b*) with the same composition. The open and shaded circles symbolize the R_1trz and R_2trz ligands, respectively.

R_1trz and R_2trz ligands. Each iron(II) ion is then surrounded by six ligands with the relative ratios indicated as (in %)

$(R_1trz)_6$	1.56,
$(R_1trz)_5(R_2trz)_1$	9.38,
$(R_1trz)_4(R_2trz)_2$	23.44,
$(R_1trz)_3(R_2trz)_3$	31.25,
$(R_1trz)_2(R_2trz)_4$	23.44,
$(R_1trz)_1(R_2trz)_5$	9.38,
$(R_2trz)_6$	1.56.

If each type of chromophore $Fe(R_1trz)_{6-n}(R_2trz)_n$ (where n varies between 0 and 6) behaved independently of the others, then the spin transition regime would be the envelope of seven transitions. Therefore, the transition would appear as gradual, occurring over a large temperature range. Another situation might happen if, owing to the interactions between the Fe(II) ions along the chain, a mean effect was observed. In such a case, rather abrupt transitions around $T = \frac{1}{2}(T_1 + T_2)$ might be observed. In other words, the molecular alloy of formula $[Fe(R_1trz)_{1.5}(R_2trz)_{1.5}]A_2$ could exhibit a spin transition regime that no pure compound exhibits. More generally, the spin transition regime of the molecular alloys $[Fe(R_1trz)_{3-3x}(R_2trz)_{3x}]A_2$ might be fine tuned through the x value specifying the chemical composition of the alloy.

We are engaged in a thorough investigation of this completely new phenomenon, and we expect to report soon on numerous results dealing with this molecular alloy effect. Here, we restrict ourselves to one example, concerning the system $[Fe(Htrz)_{3-3x}(NH_2trz)_{3x}](ClO_4)_2 \cdot nH_2O$. Both $T_c\uparrow$ and $T_c\downarrow$ decreases almost linearly with x. For $x = 0$, $T_c\uparrow$ and $T_c\downarrow$ are equal to 321 and 296 K, respectively. For small x values, when x increases by 0.01, $T_c\uparrow$ decreases by 1.8 K and $T_c\downarrow$ by 1.6 K. For $x = 0.05$, the transition occurs on either side of room temperature, with $T_c\uparrow = 304$ K and $T_c\downarrow = 288$ K, as shown in figure 19. At 295 K, one may observe a purple compound in its $S = 0$ state or a white compound in its $S = 2$ state, depending on the history of the sample (Kröber *et al.* 1993). Both states are stable at room temperature. A gentle cooling (for instance by dipping the tube containing the alloy in acetone and evaporating the acetone) or a gentle warming of the sample is sufficient to induce the transition.

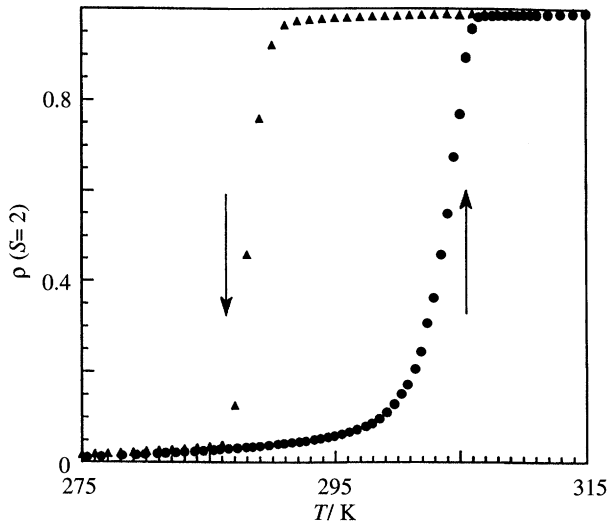


Figure 19. Thermal hysteresis loop at room temperature for $[Fe(Htrz)_{2.85}(NH_2trz)_{0.15}](CLO_4)_2 \cdot H_2O$.

7. Conclusion

In this last section, we would like to approach briefly two questions, namely: (i) what are the perspectives concerning the spin transition molecular materials with large thermal hystereses around room temperature? (ii) What are the factors controlling the abruptness of the transitions and the width of the thermal hystereses?

Concerning the former question (i), we would like to emphasize that the concept of molecular alloy seems to be of the utmost importance for fine-tuning the spin transition regime of a material. What is very striking is to compare the behaviour of a mixture of two spin transition compounds with that of an alloy with the same composition. This alloy is definitely a new material, with a new spin transition regime. The physics which is behind this phenomenon is far from being completely understood yet, although it is clear that this alloy behaviour is intimately related to the polymeric structure of the materials. We intend to invest the time necessary to obtain a clear picture of what happens. For the moment, we have found several alloys for which room temperature exactly falls within the thermal hysteresis loop. For one of them, the width of the loop is about 30 K

Not only is the theoretical basis of the molecular alloy behaviour not yet perfectly understood, but the mechanism of the cooperativity in polymeric materials is also rather obscure. Let us try to sum up some ideas. The abruptness of a spin transition and the occurrence of a thermal hysteresis are related to the cooperativity of the material of interest, i.e. to the intermolecular interactions. Everybody agrees on this point. The difficulties start when we attempt to specify the microscopic mechanism of the cooperativity. Some authors such as Spiering & Gütlich have suggested that the cooperativity is entirely governed by the elasticity of the medium (Spiering *et al.* 1982). The spin transition molecules are treated as rigid spheres, the volume and shape of which depend on the spin state inserted in an elastic medium. The spin change of a molecule induces some constraints within the lattice, and forces the nearest-neighbour molecules to undergo the spin transition as well. Quite a few experimental results, in particular those concerning the metal dilution effects, seem

to validate such a model. One may wonder, however, if this model is still valid for polymeric compounds in which the metal ions are bridged by conjugated chemical groups. In such compounds, the intersite interactions are probably essentially mediated through the bridges, and, in addition to the elasticity of the medium, electronic factors could also play a role. One may remember that the magnetic interaction between two HS iron(II) ions triply bridged by triazole ligands is not negligible ($J = -5.7\ \mathrm{cm}^{-1}$ in $[Fe_3(p\text{-MeOptrz})_8(H_2O)_4](BF_4)_6$). It is well known that this magnetic interaction is of orbital nature. The key question may be formulated as follows: what is the relation (if any) between the abruptness of the spin transitions and the presence of wide hysteresis effect in compounds such as $[Fe(Htrz)_2(trz)](BF_4)$ on the one hand, and the polymeric nature of the compounds on the other? We hope to be able to answer some elements of this question in the near future.

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