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Spin Transitions and Thermal Hystereses in the Molecular-Based Materials $[Fe(Htrz)_2(trz)](BF_4)$ and $[Fe(Htrz)_3](BF_4)_2{\cdot}H_2O$ (Htrz = 1,2,4-4*H*-triazole; trz = 1,2,4-triazolato)

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One of our main interests in the field of spin transition compounds concerns the use of spin transition materials as active elements of devices for display and data recording. Along this line we have investigated the compounds afforded by the reaction of $Fe(BF_4)_2{\cdot}6H_2O$ with 1,2,4-1*H*-triazole (hereafter abbreviated as Htrz). Two compounds have been obtained, namely, $[Fe(Htrz)_2(trz)](BF_4)$ (**1**) and $[Fe(Htrz)_3](BF_4)_2{\cdot}H_2O$ (**2**$\cdot H_2O$). Actually, two modifications of **1** have been synthesized, noted **1a** and **1b**. These compounds have been studied through magnetic susceptibility measurements, Mössbauer spectroscopy, differential thermal analysis, differential scanning calorimetry, optical techniques, and powder X-ray diffraction. **1a** exhibits a very abrupt spin transition centered around 360 K with a thermal hysteresis which may reach 50 K after a few thermal cycles. The hysteresis width for **1b** is smaller, and decreases through successive thermal cycles. **2**$\cdot H_2O$ was found to undergo a $\alpha \rightleftarrows \beta$ phase transition around 440 K. The α phase shows a rather abrupt spin transition centered around 335 K with a thermal hysteresis of about 20 K. The β phase is metastable at room temperature and shows a very abrupt spin transition centered at 279 K with a hysteresis width of 6 K. The enthalpy variations associated with all these processes have been determined, and the findings have been discussed and analyzed in the perspective of the design of memory devices.

Introduction

In some transition metal compounds, in particular those containing $3d^4$–$3d^7$ metal ions in octahedral surroundings, a transition between a low-spin (LS) and a high-spin (HS) state may occur. This spin transition (ST) may be induced by a variation of temperature or of pressure or by an irradiation with light. LS $\rightleftarrows$ HS conversions were observed for the first time more than 50 years ago.[1] However, the interest raised by this phenomenon has known a new impetus in the past two decades.[2-9] New aspects of the phenomenon were discovered. Among them, we can mention the light-induced excited spin state trapping,[10-12] the occurrence of multistep transitions,[13-15] or ST driven by ligand photoisomerization.[16] Quite recently, a ST-like

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behavior resulting from a valence-tautomeric conversion in Co(II) semiquinonate compounds was observed.[17]

The ST has many fascinating facets, some of them not fully understood yet despite numerous theoretical studies.[9] One of our main interests in this area concerns the bistability exhibited by some ST compounds. Bistability is defined here as the possibility for a compound to show two stable or metastable states in a given external perturbation range. This bistability confers a memory effect on the system.[18,19]

Three years ago, we initiated a new research project, whose goal was to design devices for display or recording incorporating ST compounds as active elements.[20-22] Till now we focused on the variation of temperature as external perturbation. Along this line, we defined five key requirements that a ST compound must fulfill for this purpose. These requirements may be summed up as follows: (i) The ST must occur with a thermal hysteresis. In other words the transition temperature in the warming mode, $T_c\uparrow$, must be higher than the transition temperature in the cooling mode, $T_c\downarrow$. There is bistability, thus memory effect, in the $T_c\uparrow - T_c\downarrow$ temperature range. (ii) The transitions must be abrupt, in both the warming and cooling regimes, in order for the system to provide a clear information. (iii) The thermal hysteresis loop must be as close as possible to room temperature. The ideal situation is that where room temperature exactly falls in the middle of the hysteresis loop.[22] When it is not so, the device needs to be equipped with an auxiliary warming (or cooling) source. (iv) The nature of the spin state, LS or HS, must be easily detected. For a display device the human eye is the most obvious detector. It follows that the ST must be accompanied by a pronounced thermochromic effect. (v) Finally, the ST compound must be stable in the normal conditions of utilization and conversely must not pollute the environment.

The first two requirements are related to the cooperativity within the crystal lattice, i.e., to the magnitude (and the sign) of the interactions between the active metal ions.[9,23] This cooperativity may be expected to be large when the ions undergoing the transition are linked to each other by bridging ligands. The fourth requirement is obviously related to the optical properties. It is well-known that the d–d bands for a transition metal complex are totally different in LS and HS states;[24] this difference provokes a thermochromic effect in ST compounds, provided that the d–d bands are not hidden by more intense charge-transfer bands. The third requirement dealing with the temperature range in which the system is bistable is the most difficult to control in a rational manner. To a large extend, the trial-and-error method is still the best.

All the requirements recalled above led us to investigate the iron(II)–1,2,4-1*H*-triazole system in a thorough fashion. In the following the neutral ligand will be abbreviated as Htrz (note that the acidic hydrogen atom of Htrz may be linked to the 1-position as well as to the 4-position), and the deprotonated ligand 1,2,4-triazolato(–) as trz$^-$. To the best of our knowledge, one of us reported for the first time on a compound of this family showing a ST around 350 K, with a rather large thermal hysteresis, and a pink (in the LS state)–white (in the HS state) color change accompanying the transition.[25] The formula of this compound is [Fe(Htrz)$_2$(trz)](BF$_4$). Later on, Lavrenova et al. reported on a series of iron(II)–1,2,4-triazole compounds, several of them exhibiting a ST around room temperature with thermal hysteresis, and thermochromic effects.[26,27] In particular, these authors described a compound to which they attributed the formula [Fe(Htrz)$_3$](BF$_4$)$_2$. We repeated several times the synthesis they proposed for this compound, and invariably obtained the compound [Fe(Htrz)$_2$(trz)](BF$_4$) we already mentioned. This compound containing both Htrz and trz$^-$ seems to be the most stable one afforded by the reaction of Fe(BF$_4$)$_2$·6H$_2$O with Htrz. We found, however, a method to prepare [Fe(Htrz)$_3$](BF$_4$)$_2$·H$_2$O which also exhibits extremely interesting physical properties. This work is devoted to the study of these two compounds, [Fe(Htrz)$_2$(trz)](BF$_4$) (**1**) and [Fe(Htrz)$_3$](BF$_4$)$_2$·H$_2$O (**2**·H$_2$O). Actually, **1** exists in the form of two modifications, noted **1a** and **1b**, whose properties are significantly different. As for **2**, it undergoes a $\alpha \rightleftarrows \beta$ phase transition around 440 K, the two phases showing very different thermal properties. The paper is organized as follows: first, we describe the syntheses of the compounds and then we analyze the ST behaviors of each compound, using magnetic susceptibility, Mössbauer, calorimetric (DTA and DSC), optical, and powder X-ray diffraction techniques. Finally, we discuss our findings in the perspective of designing memory devices.

Experimental Section

Syntheses. We have seen that we can obtain two modifications of the compound [Fe(Htrz)$_2$(trz)](BF$_4$), noted **Ia** and **Ib**, whose physical properties are different. **Ia** was obtained as follows: a solution of 2.080 g (3×10^{-2} mol) of 1,2,4,-1*H*-triazole in 10 mL of ethanol was added to a solution of 3.374 g (10^{-2} mol) of Fe(BF$_4$)$_2$·6H$_2$O in 20 mL of water. A precipitate appeared after a short while; its color was first white and then turned pink. It was allowed to stand for 24 h, then was filtered off, washed with ethanol, and dried under primary vacuum in a desiccator containing silica gel. Anal. Calcd for C$_6$H$_8$N$_9$BF$_4$Fe (**1a**): C, 20.66; H, 2.31; N, 36.14, B, 3.10; Fe, 16.01. Found: C, 20.33; H, 2.33; N, 35.74; B, 3.17; Fe, 15.64. The modification **Ib** is synthesized in much the same way, except that both 1,2,4-1*H*-triazole and Fe(BF$_4$)$_2$·6H$_2$O are dissolved in pure methanol. Anal. Calcd for C$_6$H$_8$N$_9$BF$_4$Fe (**1b**): C, 20.66; H, 2.31; N, 36.14, B, 3.10; Fe, 16.01.

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Found: C, 20.17; H, 2.16; N, 35.86; B, 3.09; Fe, 15.83. The chemical analyses of **1a** and **1b** are identical within the experimental uncertainties. Modification **Ib** could be transformed into modification **Ia**; for that, **1a** was stirred with a small amount of water for 2 h and then dried again under vacuum.

$[Fe(Htrz)_3](BF_4)_2\cdot H_2O$ (**2·H₂O**) was synthesized as follows: A solution of 207 mg (3×10^{-3} mol) of 1,2,4-1*H*-triazole in 100 mL of methanol was added into a solution of 337.5 mg (10^{-3} mol) of $Fe(BF_4)_2\cdot 6H_2O$ in 60 mL of methanol. The mixture remained limpid; it was concentrated rapidly at 70 °C with a rotavapor, and a white precipitate appeared on the walls of the flask used for the evaporation. On cooling the precipitate turned red-violet; the solution was eliminated, and the precipitate was scratched from the wall with a glass spatula and isolated without being washed. Indeed, in the presence of pure methanol, the compound tends to transform into compound 1. Anal. Calcd for $C_6H_{11}N_9OB_2F_8Fe$ (**2·H₂O**): C, 15.85; H, 2.44; N, 27.73; O, 3.52; B, 4.75; F, 33.43; Fe, 12.28. Found: C, 16.22; H, 2.50; N, 28.01; B, 4.69; Fe, 12.02. All the compounds studied in this paper are stable in the air.

Magnetic Measurements. These were carried out with a Faraday-type magnetometer equipped with a new temperature-controlled device working in the 4.2–450 K temperature range. This device allows us to record the thermal hysteresis loops, even when they occur around room temperature. The temperature was varied at a rate of 0.5 K min^{-1} in both the cooling and warming modes. All the magnetic data are represented in the form of the $\chi_M T$ versus T plots, χ_M being the molar magnetic susceptibility corrected of the diamagnetism of the closed-shell core, and T the temperature.

Mössbauer Spectra. These were obtained on a constant-acceleration spectrometer with a 25-mCi source of ^{57}Co in rhodium matrix. The calibration was made with a metallic iron foil at room temperature. The absorber was a sample of about 120 mg of compound **1a** spread over a 3 cm^2 area in a home-designed sample holder maintained in a primary vacuum. The typical counting time was ca. 6 h. A least-squares computer program was used to fit the Mössbauer parameters and to determine their standard deviations of statistical origin.

Differential Thermal Analyses. These were performed under argon on samples weighting a few milligrams using an apparatus equipped with semimicroprobes. The heating rate was around 7 K min^{-1}. For the enthalpy variations the apparatus was calibrated with the phase transitions of ammonium nitrate and the melting of indium. The accuracy was estimated to be of the order of 10%, except in the 320–380 K temperature range where it is possible to use the two phase transitions of ammonium nitrate and to reach an accuracy of 5%.

Differential Scanning Calorimetry Measurements. These were performed on a Perkin-Elmer DSC-2 instrument. Sealed sample pans were used. Both warming and cooling curves were recorded and analyzed with a TADS-3600 Perkin-Elmer system. Temperature and enthalpy were calibrated by using the melting point of indium. The experimental uncertainty in temperature is ±0.5 K, and in enthalpy values is 3% for a scan rate of 2.5 K min^{-1}.

Optical Measurements. These were carried out with a setup consisting of a common white lamp source, a multimodal optical fiber, a cooling and warming device, and a photomultiplier working at 520 nm. This wavelength corresponds to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition in the LS state. The feedback signal is a direct reflection signal detection, transmitted by the optical fiber.

X-ray Patterns. The X-ray patterns were recorded on powder samples, using a diffractometer (Cu Kα radiation, λ = 1.541 78 Å) equipped with a Laboratory-made heating device working beween room temperature and 490 K.

Compounds 1a and 1b

Magnetic Properties. The magnetic properties of $[Fe(Htrz)_2(trz)](BF_4)$ (**1a**) have already been briefly presented.[20] We recall here the main features and provide additional information. The $\chi_M T$ versus T curves reveal very abrupt and almost complete transitions occurring around $T_c\uparrow$ = 385 K in the warming mode, and $T_c\downarrow$ = 345 K in the cooling mode. We define the abruptness of the transition by the temperature range, $\Delta T_{80}\uparrow$ (or $\Delta T_{80}\downarrow$), in which 80% of the iron(II) ions undergo the transition. In the present case both $\Delta T_{80}\uparrow$ and $\Delta T_{80}\downarrow$ are equal to 4.2 ± 0.2 K.

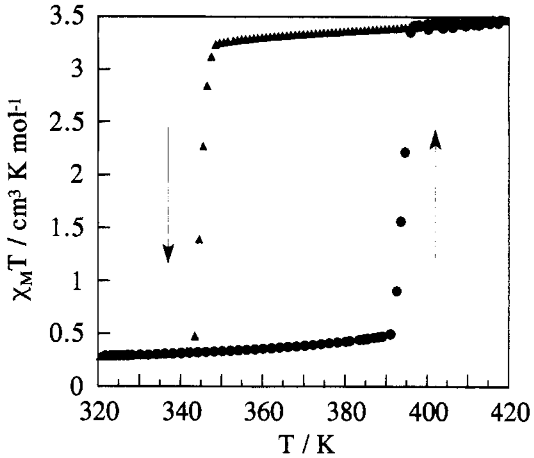

Figure 1. $\chi_M T$ versus T plots in the warming and cooling modes for $[Fe(Htrz)_2(trz)](BF_4)$ (**1a**).

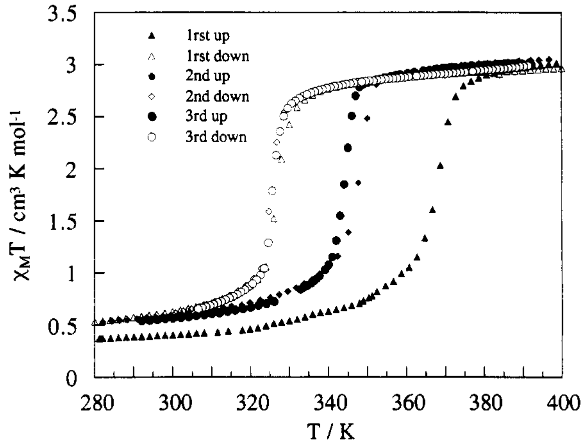

Figure 2. $\chi_M T$ versus T plots over three successive thermal cycles for $[Fe(Htrz)_2(trz)](BF_4)$ (**1b**).

The $T_c\uparrow$, $T_c\downarrow$, $\Delta T_{80}\uparrow$, and $\Delta T_{80}\downarrow$ values indicated above correspond to the first thermal cycle. During the following three or four cycles $T_c\downarrow$ as well as the abruptness of the transitions remain unchanged, but $T_c\uparrow$ is progressively shifted a few degrees toward higher temperatures, so that the width of the thermal hysteresis loop may reach 50 K. This behavior may be viewed as a sort of "running in" of the material. Additional cycles do not modify further the hysteresis loop. A typical hysteresis loop after a few thermal cycles is shown in Figure 1.

It is worth noting that the magnetic behavior of compound **1a** is weakly sample dependent. For instance, $T_c\uparrow$ and $T_c\downarrow$ may be displaced a few degrees, and $\Delta T_{80}\uparrow$, and $\Delta T_{80}\downarrow$ may vary by ±0.5 K for different samples undergoing the same number of thermal cycles. The synthesis of **1a** described in the Experimental Section seems to lead to an optimized form of the compound. The magnetic behavior of compound **1b**, on the other hand, is a bit more sample dependent. However, in all the cases, the following differences as compared to **1a** are observed: (i) the transitions are less abrupt in both the warming and cooling modes, so that the hysteresis loop is less square shaped. $\Delta T_{80}\uparrow$ and $\Delta T_{80}\downarrow$ are always larger than 20 K; (ii) successive thermal cycles do not modify $T_c\downarrow$, but displace

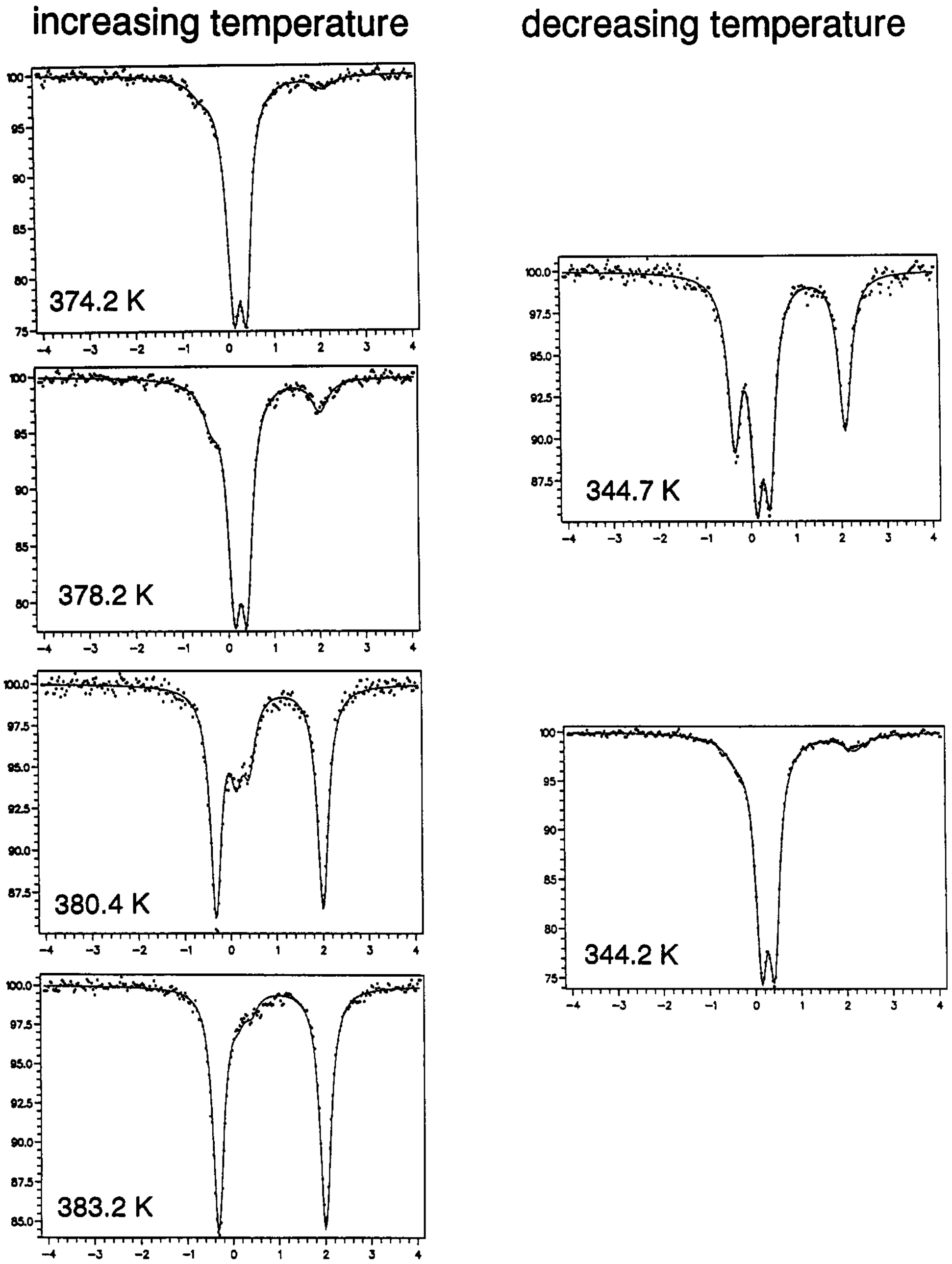

Figure 3. Some typical Mössbauer spectra around the transition temperatures for [Fe(Htrz)$_2$(trz)](BF$_4$) (**1a**).

Table 1. Selected Mössbauer Data: Fitted Parameters of the Main Component with Mean-Squares Deviations of Statistical Origin Given in Brackets[a]

T (K)	I.S. (mm s^{-1})	Γ (mm s^{-1})	Q.S. (mm s^{-1})	rel area (%)	main component
77	0.481(1)	0.312(2)	0.271(1)	87(1)	LS
300	0.430(1)	0.294(1)	0.284(1)	89(1)	LS
342.7↑	0.406(1)	0.316(2)	0.286(1)	89(1)	LS
347.2↓	0.996(1)	0.304(4)	2.428(3)	97(1)	HS
376.7↑	0.392(1)	0.312(2)	0.277(1)	91(1)	LS
383.2	0.971(1)	0.292(4)	2.323(2)	92(1)	HS
426.2	0.940(1)	0.282(2)	2.143(2)	97(1)	HS

[a] Isomer shifts are referred to metallic iron at room temperature.

T_c↑ toward lower temperatures. After three or four cycles, the width of the thermal hysteresis loop may be reduced of more than 50%, as exemplified in Figure 2.

Mössbauer Spectra. The Mössbauer study was limited to compound **1a**. The spectrum at room temperature is characteristic of a LS iron(II) compound with narrow lines. Additional broad lines are attributed to a residual HS fraction which remains constant over the whole temperature range. Above 400 K, the spectrum is characteristic of a HS iron(II) compound. All the iron(II) ions seem to occupy the same site, in both the LS and HS states. Typical spectra are shown in Figure 3, and least-squares fitted data are reported in Table 1. The measured hyperfine parameters are in good agreement with literature data.[32] The resulting temperature dependence of the high-spin molar fraction, $x_{HS} = f(T)$, is shown in Figure 4. This

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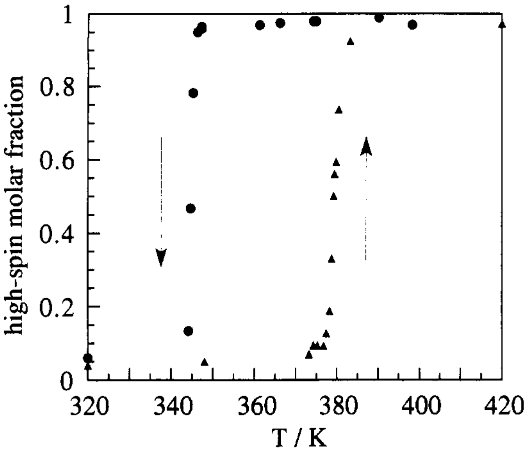

Figure 4. High-spin molar fraction versus temperature curves for [Fe(Htrz)$_2$(trz)](BF$_4$) (**1a**), deduced from the Mössbauer data.

curve confirms the abruptness of the transitions, in both the warming and cooling mode. The critical temperatures are found as $T_c\uparrow$ = 380 K and $T_c\downarrow$ = 344 K.

Two unusual features deserve to be pointed out, namely, (i) the relatively large value of the recoil-free fraction, leading to the Debye temperatures θ_D(LS) = 247(7) K, and θ_D(HS) = 200(7) K. Those values have been measured from the experimental total areas, using a thickness correction, within the usual Debye model;[32] they are significantly larger than those obtained so far for ST compounds, which are in the 140–160 K range. This difference certainly reflects the polymeric character of compound **1a**; (ii) the absence of any dynamical broadening of the Mössbauer lines, thus indicating that the conversion rates remain lower than the Mössbauer hyperfine frequency (around 10^7 s^{-1}), despite the fact that the transitions occur above room temperature. The slowing down of the conversion rates with respect to the expectations based on literature data[33,34] might be attributed to the unusual strength of the intermolecular interactions in this material.

DTA and DSC Measurements. The ST in compounds **1a** and **1b** were also investigated by DTA and DSC techniques. The DTA curve for **1a** (see Figure 5) shows an intense endothermic peak when the temperature is risen, and an intense exothermic peak when the temperature is lowered. The critical temperatures are estimated as $T_c\uparrow$ = 383 K and $T_c\downarrow$ = 343 K. The enthalpy variations are estimated as 25.5 ± 1.5 kJ mol^{-1} in the warming mode, and 26.7 ± 1.5 in the cooling mode. The DSC curve for **1a** (see Figure 5) reveals an abrupt endothermic process at 379 K in the warming mode and an even more abrupt exothermic process at 342 K in the cooling mode. The enthalpy variations associated with those processes were found to be equal to 27.8 and 28.6 kJ mol^{-1}, respectively.

The DTA and DSC data for **1b** confirm the magnetic data. Moreover, they reveal that the enthalpy variation associated with the ST is weaker than for **1a**. ΔH is found as 19 ± 1 kJ mol^{-1} from DTA and 22.5 kJ mol^{-1} from DSC.

Optical Data. Due to the drastic change of color accompanying the ST, it was of obvious interest to study the optical behavior of the compounds in the visible range using the technique described in the Experimental Section. **1a** and **1b** were investigated that way. **1a** displays the very well shaped hysteresis shown in Figure 6, with $T_c\uparrow$ = 381 K and $T_c\downarrow$ = 347 K. Over many cycles the signal dynamics remains unchanged.

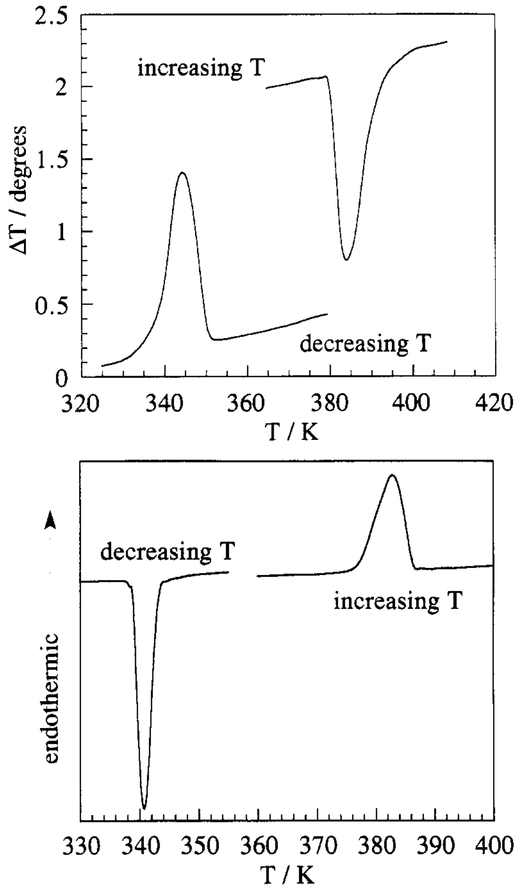

Figure 5. DTA (top) and DSC (bottom) curves for [Fe(Htrz)$_2$(trz)](BF$_4$) (**1a**).

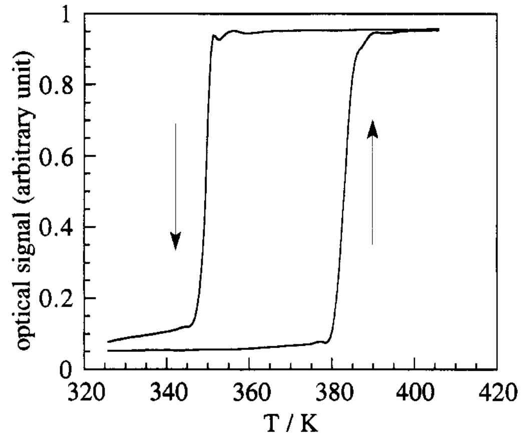

Figure 6. Optical signal versus temperature at 520 nm for [Fe(Htrz)$_2$(trz)](BF$_4$) (**1a**).

Compound **1b** exhibits the same change of optical response concerning the hysteresis width versus successive thermal cycles as what has been magnetically evidenced. On the other hand, there is a gain in intensity of the HS state. One can also notice that the optical signal varies until the third writing erasing cycle, then stabilizes. These changes over cycles let us think of a reconstruction of the material until it reaches a stable state.

X-ray Diffraction Data. The powder X-ray diffraction patterns of both **1a** and **1b** at room temperature, i.e., in the LS state, show only weak and broad diffraction peaks. The compounds are poorly crystallized. When

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the samples are warmed up to the LS → HS transition temperature, a giant enhancement of one of the peaks, at $\theta = 10.5°$ ($d = 8.6$ Å), is observed. This behavior suggests that in the HS state there is a long-range organization of the structure along one of the directions. This process is essentially reversible for **1a**; when the sample is cooled below $T_c\downarrow$, this peak at $\theta = 10.5°$ disappears almost entirely. In contrast, when **1b** is cooled below $T_c\downarrow$, the intensity of this peak is reduced but remains higher than it was before performing this thermal cycle. This striking difference between **1a** and **1b** is in line with the fact that successive thermal cycles substantially modify the shape of the hysteresis loop for **1b**, as emphasized in Figure 2.

Compound 2

Magnetic Properties. The chemical analysis of compound **2**·H_2O indicates the presence of one water molecule per molecular unit. This water molecule is progressively removed as the sample is warmed to ca. 370 K. Therefore, if the magnetic measurements are carried out as usual, with an open sample holder, the material may evolve as the temperature is increased. The compound is then not exactly the same in the warming and cooling regimes, and the hysteresis loop becomes meaningless. That is why we decided to work with a sealed sample holder.

The first experiment we performed consisted in warming the sample in its sealed holder to ca. 380 K and then cooling it to room temperature. Rather abrupt transitions were then observed with $T_c\uparrow = 345$ K and $T_c\downarrow = 323$ K. $\Delta T_{80}\uparrow$ and $\Delta T_{80}\downarrow$ were found as 13 and 9 K, respectively. Additional thermal cycles within the 293–380 K temperature range do not modify significantly the hysteresis loop, which indicates that the compound remain unchanged.

In a second experiment, the sample was warmed up to ca. 450 K, then cooled to room temperature. The LS → HS transition was observed during the heating at $T_c\uparrow = 345$ K. On the other hand, the HS → LS reverse transition totally disappeared. As T is lowered to room temperature, the iron(II) ions remain in the HS state. This behavior is attributed to a phase transition noted $\alpha \rightarrow \beta$ taking place around 440 K (vide infra). The α phase exhibits the spin transition described above ($T_c\uparrow = 345$ K and $T_c\downarrow = 323$ K), and the β phase is HS down to room temperature. This β phase, however, exhibits also a spin transition, but below room temperature, with $T_c\downarrow = 276$ K and $T_c\uparrow = 282$ K. While the thermal hysteresis width for the β phase is only of 6 K, the transitions are even more abrupt than for the α phase, with $\Delta T_{80}\downarrow = 7$ K and $\Delta T_{80}\uparrow = 4$ K. The β phase is metastable at room temperature; it spontaneously transforms back to the α phase within a few days or weeks. These very peculiar magnetic properties are represented in Figure 7.

We also investigated the magnetic properties of the dehydrated form, $[Fe(Htrz)_3](BF_4)_2$, in the 293–380 K temperature range. This form presents a behavior similar to that of the hydrated one. The ST, however, is a bit less abrupt, and the hysteresis width is smaller.

DTA and DSC Measurements. The spin and phase transitions for compound **2** were also investigated using calorimetry techniques. Because it was technically not possible to work in another way, the DTA measurements were carried out with an open sample holder so that the results take into account the loss of water during the first warming and then deals with the dehydrated form.

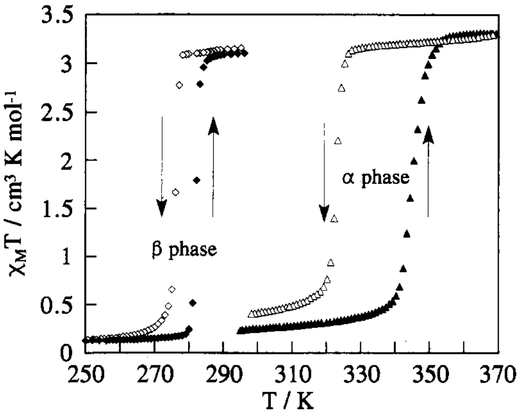


Figure 7. $\chi_M T$ versus T plots in the warming and cooling modes for the α and β phases of $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$ (**2**·H_2O). The curves for the α phase are recorded in rising and lowering the temperature between 293 and 380 K. Before recording the curves for the β phase the sample was warmed to 450 K and then cooled to room temperature. The curves are recorded in lowering and warming the sample between 293 and 250 K.

The first experiment consisted in raising the temperature to 360 K and then lowering it to 293 K. The DTA curve at increasing temperature shows an endothermic feature at 344 K, corresponding to both the LS → HS transition and the removal of one water molecule per repeat unit. The enthalpy variation associated with these two phenomena is estimated as 13.3 ± 1 kJ mol^{-1}. As the temperature is lowered, the exothermic peak at 325 K corresponds to only the HS → LS transition in the dehydrated form, with an enthalpy variation of 8 ± 1 kJ mol^{-1}.

The second experiment consisted in warming the same sample (which has now lost its water molecule) to 460 K and then cooling it to room temperature. The endothermic peak corresponding to the LS → HS transition now appears at 330 K with an enthalpy variation of 8.6 ± 1 kJ mol^{-1}. As the temperature is risen further, another endothermic feature, apparently in two steps, happens around 440 K. The enthalpy variation attributed to the $\alpha \rightarrow \beta$ phase transition is estimated as 5.7 ± 0.8 kJ mol^{-1}. When the temperature is lowered from 460 K to room temperature, no other thermal feature is observed. In particular the HS → LS transition does not occur. On the other hand, the features corresponding to the ST in the β phase are observed below room temperature with a weaker enthalpy variation, of the order of 3 kJ mol^{-1}. These DTA data are shown in Figure 8.

The DSC measurements were performed on the α phase of $[Fe(Htrz)_3](BF_4)_2 \cdot H_2O$ and confirm all the features we already spoke about. ΔH for this α phase is found as 9.5 kJ mol^{-1} in the warming mode and 8.9 kJ mol^{-1} in the cooling mode.

It is clear that the magnetic susceptibility and calorimetry experiments agree with each other. However, we must keep in mind that the magnetic data of Figure 7 were obtained with a sealed sample holder, and the DTA data of Figure 8 with an open sample holder. Even when working in a sealed sample holder, water could be removed from the lattice. If this was so, however, the hysteresis loop over the second thermal cycle would be less wide and square shaped than over the first thermal cycle. Indeed, we checked that for the dehydrated form (**2**) the transitions are less abrupt and the hysteresis width smaller than for the hydrated form (**2**·H_2O). Such a decreasing of the

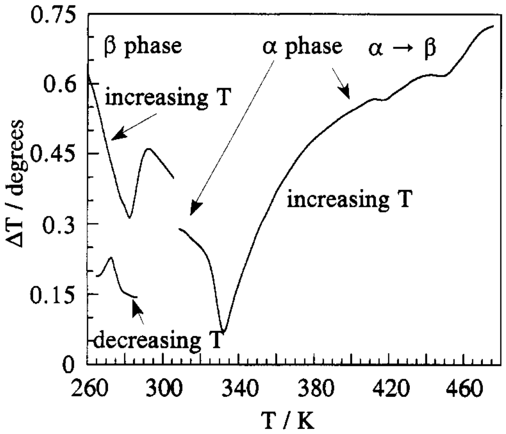


Figure 8. Differential thermal analysis curves for the α and β phases of $[Fe(Htrz)_3](BF_4)_2$ (**2**). The successive steps of this study are the following: (i) the temperature is raised from 293 to 370 K and then decreased to room temperature. The curves are not shown (ii) the temperature is raised again, now to 460 K. Both the LS → HS transition in the α phase and the $\alpha \rightarrow \beta$ transformation are observed. (iii) The temperature is decreased to room temperature, and no thermal feature is detected. (iv) The temperature is decreased further to 260 K and then raised to room temperature, and the transitions in the β phase are observed. Note that the microprobes utilized above and below room temperaturer are not the same and have not the same sensitivity.

hysteresis width after a first cycle is not observed, which seems to confirm that the compound investigated in magnetism was $[Fe(Htrz)_3](BF_4)\cdot H_2O$, at least up to 350 K. This compound in its α phase exhibits a rather abrupt spin transition centered at 334 K with a thermal hysteresis width of 22 K. As T increases further, the noncoordinated water molecule might be removed, even in the sealed tube. Above 400 K the α phase transforms into the β phase which is HS at any temperature down to room temperature. The compound investigated in DTA was first $[Fe(Htrz)_3](BF_4)\cdot H_2O$. The water molecule goes away in the temperature range where the LS → HS transition in the α phase takes place. This dehydrated form also undergoes a $\alpha \rightarrow \beta$ phase transition around 440 K, and the β phase of $[Fe(Htrz)_3](BF_4)$ is HS at any temperature down to room temperature. To sum up, we can say that the spin transition in the α phase is more abrupt with the hydrated compound. The role of noncoordinated water molecules in spin-transition compounds is now well documented. Most probably, these water molecules create a network of hydrogen bonds which increases further the cooperativity.

Optical Data. Compound **2** was investigated in its dehydrated form. The thermochromism of the two crystalline phases are observed, as shown in Figure 9. The transitions for the α phase are observed at $T_c\uparrow = 336$ K and $T_c\downarrow = 323$ K. The transitions for the β phase are observed at $T_c\uparrow = 291$ K and $T_c\downarrow = 286$ K.

Discussion

We will successively discuss about the possible structures of the compounds, the origin of the different physical behaviors of modifications **1a** and **1b**, the interplay between spin transitions and $\alpha \rightarrow \beta$ transformation in compound **2**, and finally the magnitude of the enthalpy and entropy variations associated with the spin transitions.

Structures of Compounds 1 and 2. The compounds studied in this work are all rather poorly crystallized, and obtaining single crystals suitable for X-ray diffraction seems to be very difficult, if not hopeless. Therefore, at best, we can suggest some hypotheses concerning the structures of the compounds.

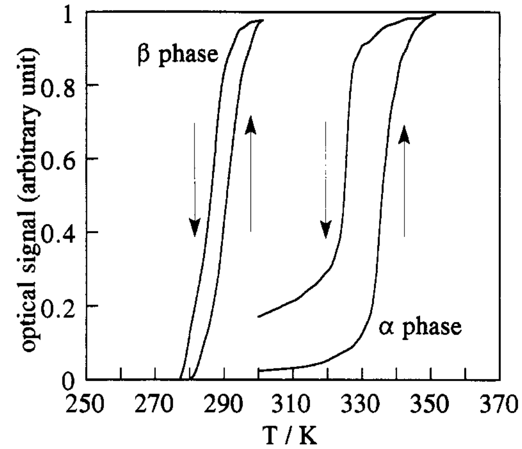
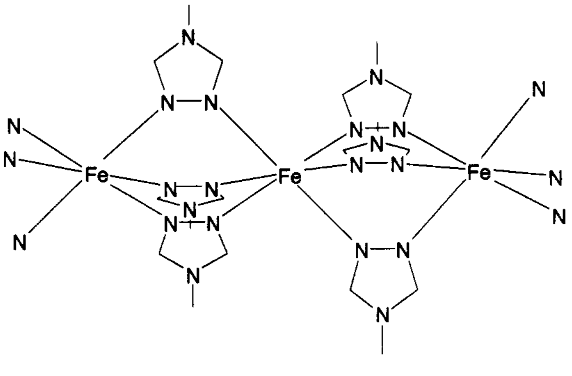


Figure 9. Optical signal versus temperature at 520 nm for compound $[Fe(Htrz)_3](BF_4)_2$ (**2**) in the α and β phases.

The simplest case seems to be that of compound **2**. The Htrz ligand may bind a transition metal ion either in a terminal or in a bridging fashion.[35] In the former case it binds through the 4-position;[36-38] in the latter case, it may bind through either the 1,2-positions[39-41] or the 2,4-positions.[42,43] The rather strong cooperativity exhibited by compound **2** strongly suggests that the structure is polymeric with bridging triazole ligands. The 1,2-coordination seems to us to be the most likely; indeed, this coordination was found in binuclear, trinuclear, and chain compounds, whereas the 2,4-coordination so far was exclusively found in layered compounds containing also the thiocyanato ligand. Moreover, the infrared data indicate that Htrz retains a C_{2v} symmetry.[25,35] Finally, a ST is observed for the central iron(II) ion of several iron(II) trinuclear species. In all the cases, this iron(II) ion is surrounded by six triazole ligands bridging this central ion to the terminal ones through the 1,2-positions.[44,45] In compound **2** all the iron(II) ions should have the same surroundings as the central ion of these trinuclear species. If this was so, the probable structure would be that of a chain compound with octahedral $Fe(Htrz)_6$ chromophores linked to each other through the 1,2-positions of the ligands, as schematized below:



Perhaps, the acidic hydrogen atom of Htrz in the 4-position participates together with the labile water molecule to a network of hydrogen bonds connecting the chains to each

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other, and increasing further the cooperativity. Perhaps also, the mean chain length depends somewhat on the synthesis, which would account for slight sample dependence of the physical properties.

The situation for compound 1 is more complicated. The first idea coming to mind is that this compound retains a linear structure, each bridging network consisting of two Htrz and one trz$^-$ ligands instead of three Htrz ligands in 2. Such a situation would be fulfilled if a proton hole was disordered over a Fe[(Htrz)$_2$(trz)]Fe bridging network. Such a H$^+$ disorder has been found in a trinuclear Co(II)–triazole compound.[48]

Another hypothesis may be put forward; the triazolato ligand, trz$^-$, would be triply bridging trough its three nitrogen atoms. Several crystal structures of compounds containing trz$^-$ are known. In all the cases trz$^-$ is actually triply bridging.[46,47] This is in particular the case for Zn(trz)Cl which possesses a layered structure.[47] The triply bridging character of trz$^-$ in 1 might lead to a polymeric structure of higher dimensionality than in 2, which would account for the extremely high cooperativity. This hypothesis, however, would require that half of the Htrz ligands be terminal and not bridging. These terminal Htrz groups would loose their C_{2v} symmetry, which is not in line with the IR data. The former hypothesis dealing with a chain structure and a H$^+$ disorder seems to us to be the most likely. The increased cooperativity in 1 as compared to 2 might be due to the electrostatic interactions between positive iron(II) ions and negative [(Htrz)$_2$(trz)] triple bridges.

Comparison between 1a and 1b. The chemical analyses of compounds **1a** and **1b** give the same results within the experimental errors. They do not indicate the presence of water, even for **1a** which is synthesized in a methanol/water mixture. Nevertheless, the physical behaviors of those compounds are clearly different. The hysteresis loop is broader and much more square shaped for **1a**. Moreover, successive thermal cycles seem to increase slightly the hysteresis width for **1a** and clearly decreases this width for **1b**. The problem we are faced with concerns the chemical and/or structural differences between the two modifications. Two hypotheses may be put forward, namely, (i) **1a** contains a very small amount of water, so that its formula would be [Fe(Htrz)$_3$(trz)](BF$_4$)·ϵH$_2$O. ϵ would be too small to be determined by chemical analysis; however, this amount of water would play a crucial role in the ST behavior, probably through hydrogen bonds. If it was so, this water would be very efficiently linked to the network. Indeed, warming a sample of **1a** up to 400 K through reduced pressure does not alter the ST behavior; (ii) the presence of a sufficent amount of water during the synthesis modifies the crystal structure and/or the crystallinity of the material. It may be worth mentioning that the compound is water soluble (of course with decomposition), so that working in a water/alcool mixture results in a much slower precipitation. Although we do not have any experimental evidence, we incline toward the second hypothesis.

The role of successive thermal cycles is most likely related to an annealing process. Why is the hysteresis loop slightly improved for **1a**, and considerably deteriorated for **1b** is not understood yet, even if the X-ray data suggest some ideas (see above).

α and β Phases of Compound 2. The discovery of the transformation taking place around 440 K in compound 2 was quite unexpected. As it often happens, this discovery is due to serendipity. Once, we fortuitously heated a sample of 2 to 450 K, and noticed that, after cooling to room temperature, the sample was still white, the color of the HS state. After a few weeks, however, it turned back to violet. The high-temperature phase of 2, the β phase, can be trapped at room temperature; this phase shows an abrupt ST just below room temperature. We have not investigated yet the kinetics of the $\beta \rightarrow \alpha$ transformation around 300 K that currently occurs spontaneously. In any case, the interplay between $\alpha \rightleftarrows \beta$ tranformation and spin transitions above and below room temperature opens quite interesting perspectives we intend to explore further. What we can already point out is that, if we consider the $T_c\uparrow$(α phase)–$T_c\downarrow$(β phase) process, we have a thermal hysteresis width of more than 70 K, with abrupt transitions in both the warming and cooling regimes, and room temperature falling within the hysteresis loop.

Enthalpy and Entropy Variations. One of the most striking features of the ST in compound **1a** is the magnitude of the enthalpy variation, ΔH, accompanying the LS $\rightleftarrows$ HS reaction. ΔH is found to be equal to about 27 kJ mol^{-1}. This ΔH value is by far the largest enthalpy variation reported for ST compounds. The entropy variation may be estimated as 75 J K^{-1} mol^{-1}. Let us recall that for the prototype ST compound Fe(NCS)$_2$(phen)$_2$ (phen = *o*-phenantroline),[49] ΔH is equal to 8.59 kJ mol^{-1}, and ΔS to 48.8 J K^{-1} mol^{-1}. We will come back to these thermodynamical characteristics in a subsequent paper. We limit ourselves here to stress that these very large ΔH and ΔS values are obviously related to the polymeric nature of the compound and take into account a strong modification of the lattice accompanying the ST. For **1b**, ΔH is smaller than for **1a**, 22.5 and 27 kJ mol^{-1}, respectively. The modification of the lattice might be less pronounced. Concerning 2, the ΔH and ΔS values are close to those found in other ST compounds for the α phase and surprisingly weak for the β phase.

Conclusion

Most ST compounds investigated so far are molecular crystals with ST units well separated from each other in the crystal lattice. One noticeable exception is *trans*-bis(thiocyanato)bis(4,4′-di-1,2,4-triazole)iron(II) hydrate which possesses a two-dimensional structure.[30] Very important results concerning the mechanism of the ST phenomenon have arisen from the investigation of those systems. None

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of them, however, may be considered as a genuine material. The ST compounds with a polymeric structure, on the other hand, seem to offer new perspectives as molecular materials. Owing to their structure, the cooperative effects are magnified, and the perturbation range in which a bistable behavior is observed may be large.

ST compounds exhibiting abrupt transitions associated with a change of color have already been reported for being potential candidates as information display and storage medium, and prototypes have also been described.[20,21] Their ease of implementation and their compatibility with flexible substrates are the practical arguments that make them appealing in comparison with liquid-crystal-based techniques.

Fundamentally, those compounds have to fulfill key requirements for being completely adapted to a real display (storage) application, among which two are particularly important and difficult to control, namely, a working temperature (center of the hysteresis loop) close to room temperature, and a bistability as less sensitive to temperature as possible. Ideally, we look for a ST system with a hysteresis width of at least 50 K and abrupt transitions occurring on either side of room temperature.

Among all the ST compounds reported so far, those described in this paper seem to exhibit the physical behaviors the closest ones to this ideal situation. Considering the modification **1a** of $[Fe(Htrz)_2(trz)](BF_4)$, the criterion of an extended bistability region is well fulfilled with a hysteresis width of 50 K. However, the requirement dealing with a compound working at room temperature is not reached yet. Compound **2** offers us a new alternative for solving this problem. In associating two phenomena, a phase transition (not associated with ST) on the one hand, and a ST on the other hand, one has obtained a system where room temperature falls within the hysteresis loop. The last default to focus on is the control of the way back from the β phase to the α phase.

Our work suggests that the ideal compound might not be far from being found, and that it makes sense working in that direction. As a matter of fact a more generic application of those compounds is their use as storage medium, the display being a particular case. Their main advantage in that field is the small size requested for storing one bit of information, 20 × 20 × 20 molecules from recent theoretical studies.[50] In optical data storage processes the minimum size is limited by the writing light spot (usually 1–2 μm in diameter). Actually, the last reported performance in that field is 0.4 mm, obtained by IBM,[51] with a frequency doubler. With such a resolution, there is only 1 order of magnitude between the material feature and the writing tool performance.

Important Remark. During the reviewing process of this paper, a paper from Sugiyarto and Goodwin appeared, concerning $[Fe(Htrz)_2(trz)](BF_4)$. The results of these authors are perfectly in line with our results.[52]

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