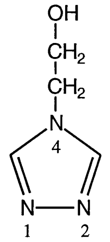
Non-classical Fe^{II} spin-crossover behaviour leading to an unprecedented extremely large apparent thermal hysteresis of 270 K: application for displays

Yann Garcia, Petra J. van Koningsbruggen, Epiphane Codjovi, René Lapouyade, Olivier Kahn* and Louis Rabardel

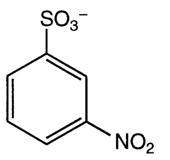
Laboratoire des Sciences Moléculaires, Institut de Chimie de la Matière Condensée de Bordeaux, UPR CNRS no. 9048, 33608 Pessac, France

$[Fe(hyetrz)_3](anion)_2{\cdot}3H_2O$ [hyetrz = 4-(2′-hydroxyethyl)-1,2,4-triazole, anion = 3-nitrophenylsulfonate] is a novel linear polynuclear Fe^{II} spin-crossover compound. The low-spin to high-spin transition accompanied by a pronounced thermochromic effect occurs at 370 K in a very abrupt way. Just before this temperature, the three non-coordinated water molecules are removed. The dehydrated high-spin form remains stable down to *ca.* 100 K, where it transforms into a new low-spin form, implying that this material shows an apparent thermal hysteresis width of 270 K. Applications of this material are discussed.

Iron(II) spin-crossover materials have acquired increasing interest during the last decade. Evidently, the fast developments in advanced electronic technology may require compounds showing bistability behaviour on the molecular scale.[1] A fascinating example of molecular bistability is represented by Fe^{II} spin-crossover compounds, which show a transition from the high-spin state (HS, $S=2$) to the low-spin state (LS, $S=0$) on cooling, upon increasing pressure, or by light irradiation.[2–9] The use of such materials as molecular-based memory devices and displays has been investigated.[10,11] This type of application requires abrupt spin transitions involving a large thermal hysteresis as well as an associated thermochromic effect.[3,7,9,10,12,13] The occurrence of abrupt transitions involving hysteresis is related to cooperativity. Although the mechanism of this cooperativity is not yet fully understood, it is commonly accepted that these interactions may become extremely important when the active spin-crossover sites are covalently linked by conjugated ligands. The cooperativity may even be enhanced by hydrogen bonding interactions within the crystal lattice.[7,9] Indeed, in the linear polynuclear Fe^{II} spin-crossover compounds of general formula $[Fe(NH_2trz)_3](anion)_2{\cdot}xH_2O$ (NH_2trz = 4-amino-1,2,4-triazole; anion = NO_3^-,[9,14,15] ClO_4^-,[16] BF_4^-,[10,16] I^-,[17] Br^-,[10,16] $CH_3SO_3^-$[18]), in which the Fe^{II} ions are linked by triple N^1,N^2-1,2,4-triazole bridges,[19] relatively large thermal hysteresis (up to about 35 K) was observed. Within this family of compounds, the derivatives containing tosylate[20] and related aromatic sulfonate anions show an exceptionally large apparent hysteresis loop up to 80 K, owing to the synergy between Fe^{II} spin-crossover behaviour and a dehydration–rehydration process. Modifying the 1,2,4-triazole ligand yielded a novel polynuclear Fe^{II} spin-crossover compound showing unprecedented behaviour, and offering a new opportunity to use such compounds in display devices.



hyetrz



3-nitrophenylsulfonate

$[Fe(hyetrz)_3](anion)_2{\cdot}3H_2O$ [hyetrz = 4-(2′-hydroxyethyl)-1,2,4-triazole, anion = 3-nitrophenylsulfonate] was synthesized as follows. A methanolic solution (20 ml) containing 3 mmol (1.72 g) of $[Fe(H_2O)_6](3\text{-nitrophenylsulfonate})_2$ and a small amount of ascorbic acid was heated and added under stirring to a methanolic solution (10 ml) containing 9.1 mmol (1.03 g) of hyetrz prepared from monoformyl hydrazine, triethylorthoformate and 2-ethanolamine according to the method described by Bayer *et al.*[21] A white precipitate was formed immediately which was filtered, washed with methanol and dried in air. The compound changes from white to pink during the drying process, due to the $^1A_{1g}\rightarrow{}^1T_{1g}$ d–d transition at 520 nm of the compound in the LS state. The compound changes to white upon heating to *ca.* 370 K, because the spin-allowed d–d transition of lowest energy of the compound in the HS state, $^5T_{2g}\rightarrow{}^5E_g$, occurs at the limit of the visible and IR regions. Surprisingly, subsequent cooling to room temperature leaves the white colour of the compound unaffected. Since this compound shows a thermochromic effect, the Fe^{II} spin transition has been studied optically using a device described previously.[7,21] This device records the change in intensity of the absorption band at 520 nm, and therefore allows one to follow the spin crossover in a remarkably simple and reliable way. The results of the optical measurements displayed in Fig. 1 reveal a very abrupt LS→HS transition taking place at 370 K, after which the compound is further heated to 400 K. Subsequent cooling shows the HS→LS transition to occur at 100 K, yielding an extremely wide apparent hysteresis of 270 K.

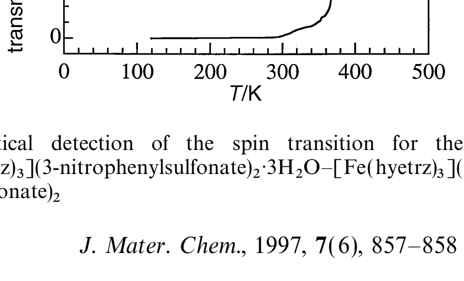


Fig. 1 Optical detection of the spin transition for the couple $[Fe(hyetrz)_3](3\text{-nitrophenylsulfonate})_2{\cdot}3H_2O$–$[Fe(hyetrz)_3](3\text{-nitrophenylsulfonate})_2$

A second heating experiment reveals a LS→HS transition with $T_C\uparrow = 115$ K. Additional heating and cooling cycles show that this hysteresis of 15 K is maintained.

Thermogravimetry (see Fig. 2) carried out with the same velocity of heating (1 K min^{-1}) as for the optical measurements reveals a continuous loss of mass starting at room temperature. This decrease in mass proceeds rapidly in the temperature range 325–340 K, after which it continues in a much smoother fashion. At 370 K the percentage mass lost is in exact agreement with the removal of all three lattice water molecules from $[\mathrm{Fe(hyetrz)_3}]$(3-nitrophenylsulfonate)$_2\cdot 3H_2O$. Consequently, when the spin transition occurs, no lattice water molecules are present in the compound. Upon cooling no change in the mass of the sample is observed, which indicates that the compound is not rehydrated.

The magnetic properties have also been investigated. The results are in good agreement with the optical data of Fig. 1. In addition, the magnetic data indicate that the LS→HS transition at 370 K for the starting material is essentially complete, while the HS→LS transition for the dehydrated compound at 100 K is incomplete; about 15% of the $\mathrm{Fe^{II}}$ ions remain in the HS state below 100 K.

These results can be interpreted as follows. At room temperature the thermodynamical stable state for the hydrated compound $[\mathrm{Fe(hyetrz)_3}]$(3-nitrophenylsulfonate)$_2\cdot 3H_2O$ is the LS state. Evidently, this LS state is stabilized by the hydrated nature of this modification. Indeed, studies on mononuclear $\mathrm{Fe^{II}}$ spin-crossover compounds have already revealed that the low-spin state may be stabilized by interactions with lattice water molecules.[22–25] Upon heating, the compound loses all its lattice water molecules, yielding just below 370 K the dehydrated $[\mathrm{Fe(hyetrz)_3}]$(3-nitrophenylsulfonate)$_2$ analogue in a LS state. However, at this temperature this LS state is a metastable state, and transforms in an exceptionally abrupt fashion to the HS state. Further cooling of $[\mathrm{Fe(hyetrz)_3}]$(3-nitrophenylsulfonate)$_2$ reveals the HS→LS transition for the dehydrated compound taking place at 100 K. Subsequent heating shows the LS→HS transition with $T_C\uparrow = 115$ K. This hysteresis of 15 K is now stable and can be considered as a genuine hysteresis, whose origin is governed by cooperative interactions. Evidently, the crucial feature allowing the occurrence of the apparent hysteresis of 270 K results from the stabilization of the LS state by water molecules, which ceases only when the water molecules are removed leading to the formation of the metastable low-spin state of $[\mathrm{Fe(hyetrz)_3}]$(3-nitrophenylsulfonate)$_2$. The LS $[\mathrm{Fe(hyetrz)_3}]$(3-nitrophenylsulfonate)$_2\cdot 3H_2O$ compound, after being cycled once, can be reconstructed at room temperature from the HS $[\mathrm{Fe(hyetrz)_3}]$(3-nitrophenylsulfonate)$_2$ compound by placing the latter in a very humid (*i.e.* a water saturated) atmosphere. The reverse process requires the removal of lattice water molecules either by heating the sample as described above, or by secondary pumping at a pressure of 10^{-6} mbar.

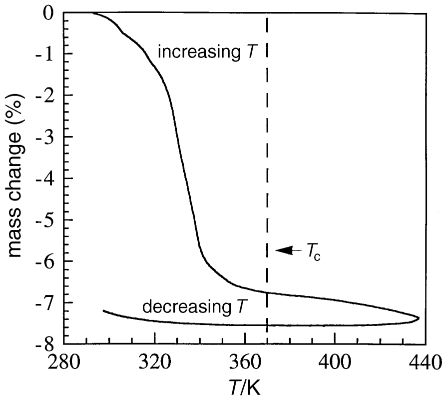


Fig. 2 Thermogravimetric analysis for $[\mathrm{Fe(hyetrz)_3}]$(3-nitrophenylsulfonate)$_2\cdot xH_2O$

The unprecedented wide apparent hysteresis loop of 270 K for $[\mathrm{Fe(hyetrz)_3}]$(3-nitrophenylsulfonate)$_2\cdot xH_2O$ implies that we are dealing with a compound using its memory effect only once; after it has been addressed by increasing temperature to the value of $T_C\uparrow$, leading to an abrupt LS→HS transition involving a colour change from pink to white, it remains in this white HS state in the absence of extreme humidity, provided it is not cooled to very low temperature. At room temperature $[\mathrm{Fe(hyetrz)_3}]$(3-nitrophenylsulfonate)$_2$ in the HS state and under normal atmospheric conditions does not rehydrate, in contrast to $[\mathrm{Fe(NH_2trz)_3}]$(tosylate)$_2$.[20] The information induced by the abrupt spin transition is retained. Therefore, this material may be of use in applications in which detection of a specific temperature is required in a very simple and accurate way. The spin-crossover material then acts as a thermal sensor giving an optical response only when $T_C\uparrow$ is reached, for instance as an alert when the temperature exceeds an upper limit. More interestingly, this thermal addressing accompanied by an abrupt and stable optical response may also be used in single-use (or one-shot) displays. Further physical studies along with detailed exploration of implementation in devices of $[\mathrm{Fe(hyetrz)_3}]$(3-nitrophenylsulfonate)$_2\cdot xH_2O$ and related materials are in progress.

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