Spin Transition Regime in New One-Dimensional Polymeric Iron(II) Compounds. Importance of the Water Content for the Thermal and Optical Properties

Olivier Roubeau,[†] Jaap G. Haasnoot,[*,†] Epiphane Codjovi,[‡] François Varret,[‡] and Jan Reedijk[†]

Gorlaeus Laboratories, Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands, and Laboratoire de Magnétisme et d'Optique, CNRS, Université de Versailles, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France

A new series of polymeric chainlike materials exhibiting the spin crossover phenomenon has been synthesized in aqueous conditions using different iron(II) salts and 4-(formylamino)-1,2,4-triazole (fatrz). The magnetic and thermogravimetric behaviors of the compounds of general formula $[Fe(fatrz)_3](A)_2 \cdot xH_2O$ are presented for **1** (A = trifluoromethanesulfonate and $x = 3$), **2** (A = tetrafluoroborate and $x = 2$), **3** (A = *p*-tolylsulfonate and $x = 3$), and **4** (A = nitrate and $x = 1$). In **1**, the high ($S = 2$) ↔ low ($S = 0$) spin transition of the iron(II) ions occurs sharply in the close vicinity of 0 °C. Reflectivity measurements show that this transition can be cycled and used as a temperature sensor. However, **1** loses water when warmed above 320 K, whereby its transitions become more gradual and shift to lower temperatures. Calorimetric parameters for the spin transition of **1** have been obtained and indicate a strongly cooperative phenomenon, with $\Delta H = 17.19$ kJ mol^{-1} and $\Delta S = 64.26$ J K^{-1} mol^{-1} in the warming mode. **2** has a more gradual transition in the range 265−285 K. **3** and **4** are low spin at room temperature and possess large apparent hysteresis due to a loss of water upon the first L → H spin change. The reabsorption of water in **3** makes it a possible reusable temperature threshold sensor. The prominent role of water molecules in the whole family of chainlike spin crossover materials is discussed.

Introduction

A whole family of d^4-d^7 first-row transition-metal complexes bearing octahedral symmetry (or distorted octahedral) is known to exhibit a thermally induced crossover between a low-spin (LS) and a high-spin (HS) state.[1,2] Although first discovered in iron(III) bisdithio-carbamates,[3] the growing research activities in this field in the past 3 decades have focused on Fe(II) systems,[4] mainly because the two spin states involved are then dia- and paramagnetic. Moreover, the spin change is then usually accompanied by a strong thermochromism, which provides additional possibilities of applications for these systems.[5] Although the physical phenomenon of spin crossover or spin transition is fundamentally molecular, intermolecular interactions were shown to induce very abrupt crossovers,[6] exhibiting in some cases a hysteresis effect.[7−9] These properties confer a bistable character to the system and allow their use in informa-

tion storage or optical displays,[10] provided that the inversion temperatures $T_{1/2}{}^{\uparrow}$ and $^{\downarrow}$, for which the population is 50% LS and 50% HS, are relatively close to room temperature (RT). Strong intermolecular interactions can originate from strong hydrogen-bonding networks,[11] from aromatic rings $\pi-\pi$ stacking,[12] or more simply from direct chemical bonds that act as bridges between the metal centers.[8,13] These bridges need then to have a limited flexibility so as to propagate the average 0.2 Å change in the Fe−L bond length occurring upon the spin transition. This particular point is well shown by the gradual transition observed in $[Fe(btzp)_3](ClO_4)_2$ [btzp = 1,2-bis(tetrazol-1-yl)propane],[14] the first Fe(II) linear spin-transition chain of which the crystal structure has been solved. The bridging ligand btzp has a

* Corresponding author. E-mail: haasnoot@chem.leidenuniv.nl.
† Leiden Institute of Chemistry.
‡ Laboratoire de Magnétisme et d'Optique.
(1) Goodwin, H. A. *Coord. Chem. Rev.* **1976**, *18*, 293.
(2) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.
(3) Cambi, L.; Szegö, L. *Ber. Dtsch. Chem. Ges.* **1931**, *10*, 2591−2598.
(4) Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2024.
(5) Kahn, O.; Kröber, J.; Jay, C. *Adv. Mater.* **1992**, *4*, 718.
(6) Sorai, M.; Seki, S. *J. Phys. Chem. Solids* **1974**, *35*, 555−570.
(7) König, E.; Ritter, G. *Solid State Commun.* **1976**, *18*, 279−282.

(8) Vreugdenhil, W.; Van Diemen, J. H.; De Graaff, R. A. G.; Haasnoot, J. G.; Reedijk, J.; Van der Kraan, A.; Kahn, O.; Zarembowitch, J. *Polyhedron* **1990**, *9*, 2971−2979.
(9) Létard, J. F.; Guionneau, P.; Rabardel, L.; Howard, J. A. K.; Goeta, A. E.; Chasseau, D.; Kahn, O. *Inorg. Chem.* **1998**, *37*, 4432−4441.
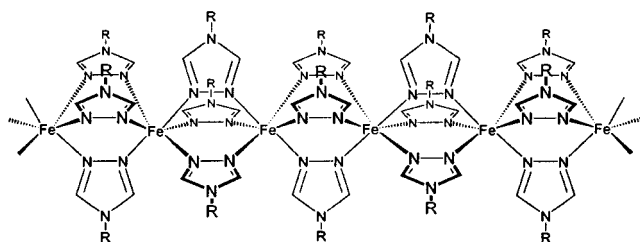(10) Kahn, O.; Martinez, J. C. *Science* **1998**, *279*, 44.
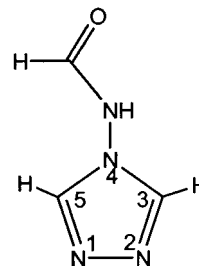(11) Sorai, M.; Ensling, J.; Hasselbach, K. M.; Gütlich, P. *Chem. Phys.* **1977**, *20*, 197.
(12) Létard, J. F.; Guionneau, P.; Codjovi, E.; Lavastre, O.; Bravic, G.; Chasseau, D.; Kahn, O. *J. Am. Chem. Soc.* **1997**, *119*, 10861.
(13) Haasnoot, J. G. In *Magnetism: A Supramolecular Function*; Kahn, O., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1996; p 299.
(14) van Koningsbruggen, P. J.; Garcia, Y.; Kahn, O.; Fournès, L.; Kooijman, H.; Spek, A. L.; Haasnoot, J. G.; Moscovici, J.; Provost, K.; Michalowicz, A.; Renz, F.; Gütlich, P. *Inorg. Chem.* **1999**, *39*, 1891−1900.

Chart 1. Schematic Representation of the Linear Chains [Fe(Rtrz)$_3^{2+}$]$_n$

saturated ethyl chain between its two tetrazole rings and is, therefore, flexible enough to soften the propagation of the structural change and lower the cooperativity. This is not the case for the compounds of formula [Fe(Rtrz)$_3$]A$_2 \cdot n$H$_2$O (Rtrz = 4-R-1,2,4-triazole; see Chart 1), which fulfill the presence of a weakly flexible direct chemical bridge. As opposed to monomeric complexes, which hardly present a hysteresis effect without a crystallographic phase change, these polymeric materials very often possess hysteresis loops together with sharp transitions. An additional difference with many monomeric systems is their stability with respect to oxidation of the iron(II). They all present a pronounced thermochromism upon the spin transition, with an absorption band around 520 nm in the purple LS state and an absorption of lower energy in the near infrared in the uncolored HS state. Moreover, changing the anion A and/or the substituent R on the 4 position of the triazole permits the tuning of the inversion temperatures[15-17] and the sharpness of the transitions.[17] The feasibility of "alloys" of two differently substituted triazoles was also shown to allow a further control on the spin-transition temperatures.[18] These properties make these classes of polymeric compounds the best spin-transition candidates for possible applications. So far, no crystal structure of these types of compounds has been reported. However, rather precise structural information was deduced from EXAFS at the iron edge[19,20] and LAXS spectroscopy,[21] showing the structure to consist most probably of linear chains in which neighboring iron ions are triply bridged by the Rtrz ligands through their N1 and N2 donor atoms. The only detailed crystal structure of a copper(II) analogue [Cu(hyetrz)$_3$]-(ClO$_4$)$_2 \cdot 3$H$_2$O also shows this linear structure,[22] as an additional proof. Several groups have investigated this family of compounds,[17,23-26] showing the direct relation-

Chart 2. Schematic Representation of 4-(Formylamino)-1,2,4-triazole (fatrz) Including the Ring Numbering

ship between $T_{1/2}$ and the diameter of spherical anions A and the influence of the R substituent. One of the basic requirements for the physical properties lies in the size of the chains. Anions based on a tosylate group yield transitions at temperatures close to or above RT in all cases, with usually a loss of water inducing the first L → H spin change.[27-29] Another series of compounds with transitions in the region of RT is that of triazoles bearing an amino group as the 4-substituent.[30] The present study deals with a related series, with the substituent being a formylamino group.

Experimental Section

Synthesis. The ligand fatrz [fatrz = 4-(formylamino)-1,2,4-triazole; see Chart 2] was first obtained as a side product of btr [btr = 4,4′-bis(1,2,4-triazole)] in its synthesis from hydrazine monohydrate and formic acid. It was then prepared on a larger scale following Salazar et al.[31] by reacting 4-amino-1,2,4-triazole (obtained from hydrazine monohydrate and formic acid[32]) and formic acid in equimolar amounts in diisopropyl ether with a Dean−Stark apparatus. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta_{\text{C−H}_{\text{trz}}}$ 8.63 and 8.80, δ_{CHO} 8.36 and 8.33, $\delta_{\text{N−H}}$ 11.59 ppm. The two different values for the triazole and the amide protons correspond to the equilibrium found in solution between the two isomers Z and E, respectively.[31] IR (neat): $\nu_{\text{C=O}}$ 1683, $\nu_{\text{N−H}}$ 1548, $\gamma_{\text{C−H}}$ (ring torsion) 641 cm^{-1}. Anal. Calcd (found) for C$_3$H$_4$N$_4$O: C, 32.1 (31.6); H, 3.6 (3.3); N, 50.0 (49.9).

The iron(II) salts [Fe(H$_2$O)$_6$](triflate)$_2$ (triflate = trifluoromethanesulfonate) and [Fe(H$_2$O)$_6$](p-tol)$_2$ (p-tol = p-tolylsulfonate) were obtained as follows: an aqueous solution of trifluoromethanesulfonic acid/p-toluenesulfonic acid was kept warm while suspending iron powder by vigorous stirring. A white crystalline material for the triflate and large platelike crystals for the tosylate deposited upon cooling.

[Fe(fatrz)$_3$](A)$_2 \cdot x$H$_2$O compounds (**1**, A = triflate, x = 3; **2**, A = BF$_4^-$, x = 2; **3**, A = p-tol, x = 3; **4**, A = NO$_3^-$, x = 1) were synthesized by adding an aqueous hot solution of fatrz (3 mmol, 10 mL) to a hot aqueous solution of the iron(II) salt (1 mmol, 10 mL), plus a little ascorbic acid to prevent oxidation of the iron(II). The solutions were reduced to ca. 2−3 mL and left in air at RT. White solids formed only when the volume of

(15) Varnek, V. A.; Lavrenova, L. G. *J. Struct. Chem.* **1995**, *36*, 104−111.

(16) Garcia, Y. Ph.D. Thesis, University of Bordeaux, Bordeaux, France, 1999.

(17) Roubeau, O.; Gomez, J. M. A.; Balskus, E.; Kolnaar, J. J. A.; Haasnoot, J. G.; Reedijk, J. *New J. Chem.* **2001**, *25*, 144−150.

(18) Kröber, J.; Codjovi, E.; Kahn, O.; Grolière, F.; Jay, C. *J. Am. Chem. Soc.* **1993**, *115*, 9810.

(19) Michalowicz, A.; Moscovici, J.; Ducourant, B.; Cracco, D.; Kahn, O. *Chem. Mater.* **1995**, *7*, 1833.

(20) Michalowicz, A.; Moscovici, J.; Kahn, O. *J. Phys. IV* **1997**, *7*, 633.

(21) Verelst, M.; Sommier, L.; Lecante, P.; Mosset, A.; Kahn, O. *Chem. Mater.* **1998**, *10*, 980−985.

(22) Garcia, Y.; van Koningsbruggen, P. J.; Bravic, G.; Guionneau, P.; Chasseau, D.; Cascarano, G. L.; Moscovici, J.; Lambert, K.; Michalowicz, A.; Kahn, O. *Inorg. Chem.* **1997**, *36*, 6357.

(23) Sugiyarto, K. H.; Goodwin, H. A. *Aust. J. Chem.* **1994**, *47*, 263.

(24) Bausk, N. V.; Erenburg, S. B.; Lavrenova, L. G.; Mazalov, L. N. *J. Struct. Chem.* **1995**, *36*, 925−931.

(25) Bronisz, R.; Ciunik, Z.; Drabent, K.; Rudolf, M. F. *Conf. Proc., ICAME-95* **1996**, *50*, 15.

(26) Kolnaar, J. J. A. Ph.D. Thesis, Leiden University, Leiden, The Netherlands, 1998.

(27) Codjovi, E.; Sommier, L.; Kahn, O.; Jay, C. *New J. Chem.* **1996**, *20*, 503.

(28) van Koningsbruggen, P. J.; Garcia, Y.; Codjovi, E.; Lapouyade, R.; Kahn, O.; Fournès, L.; Rabardel, L. *J. Mater. Chem.* **1997**, *7*, 2069−2075.

(29) Garcia, Y.; van Koningsbruggen, P. J.; Lapouyade, R.; Fournès, L.; Rabardel, L.; Kahn, O.; Ksenofontov, V.; Levchenko, G.; Gütlich, P. *Chem. Mater.* **1998**, *10*, 2426.

(30) Lavrenova, L. G.; Ikorskii, V. N.; Varnek, V. A.; Oglezneva, I. M.; Larionov, S. V. *Russ. J. Coord. Chim.* **1986**, *12*, 119.

(31) Salazar, L.; Espada, M.; Sanz, D.; Claramunt, R. M.; Elguero, J.; Garcia-Granda, S.; Diaz, M. R.; Gómez-Beltrán, F. *J. Chem. Soc., Perkin Trans.* **1993**, *2*, 377.

(32) Herbst, R. M.; Garrison, J. A. *J. Org. Chem.* **1953**, *18*, 872.

the solution was reduced to ca. 1 mL. These precipitates were allowed to stand for 24 h and then were filtered off and thoroughly washed with absolute ethanol and diethyl ether. **3** and **4** turned purple during the drying process. Anal. Calcd (found) for $C_{11}H_{18}N_{12}O_{12}F_6S_2Fe$ (**1**): C, 17.7 (18.0); H, 2.4 (2.1); N, 22.6 (24.0); S, 8.6 (8.5). Anal. Calcd (found) for $C_9H_{16}N_{12}O_5$-B_2F_8Fe (**2**): C, 17.9 (17.6); H, 2.7 (2.5); N, 27.9 (28.9). Anal. Calcd (found) for $C_{23}H_{32}N_{12}O_{12}S_2Fe$ (**3**): C, 35.0 (35.3); H, 4.1 (3.9); N, 21.3 (21.2); S, 8.1 (7.9). Anal. Calcd (found) for $C_9H_{14}N_{14}O_8Fe$ (**4**): C, 20.2 (19.8); H, 2.6 (2.7); N, 36.7 (36.0). It is noteworthy to say that the water content is difficult to determine solely by elemental analysis. The *x* values given here were confirmed by thermogravimetric analysis. IR (neat): **1**, $\nu_{C=O}$ 1706, ν_{N-H} 1622 cm^{-1}; **2**, $\nu_{C=O}$ 1634, ν_{N-H} 1550 cm^{-1}; **3**, $\nu_{C=O}$ 1705, ν_{N-H} 1620 cm^{-1}; **4**, $\nu_{C=O}$ 1700, ν_{N-H} 1622 cm^{-1}.

We also synthesized [Fe(Htrz)$_2$trz]BF$_4$ following a literature method[33] for comparison.

When methanol or ethanol were used as the solvent, immediate precipitates formed, which appeared to have properties different than the ones obtained from aqueous solutions. Their full characterization will not be included in this study. The solids obtained from aqueous solutions were not soluble in alcohols. No improvement in crystallinity was obtained by redissolving in water mixtures. All compounds described in this paper are stable in air.

Analysis. *Elemental analyses* (C, H, N, and S) were performed on a Perkin-Elmer 2400 series II analyzer. *UV−visible−near-IR (NIR) spectra* were obtained on a Perkin-Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. *Fourier transform infrared (FTIR) spectra* were obtained on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate attenuated total reflection device, using the reflectance technique (4000−300 cm^{-1}; resolution 4 cm^{-1}).

Magnetic Measurements. Magnetization of powder samples was measured using a Quantum Design MPMS-5S SQUID magnetometer operating at 0.5 or 1 T. Calibration was achieved with samples of palladium and [HgCo(NCS)$_4$]. The measured values were corrected for diamagnetism of the samples as estimated from Pascal tables and for the magnetic contribution of the sample holder. All magnetic data are represented in the form of $\chi_M T$ vs *T* plots. Warming and cooling rates were approximately 0.5 and 0.3 K min^{-1}.

Thermogravimetric Measurements. These were carried out with a Setaram TAG 24 apparatus coupled to a Setaram universal controller G11, in the 300−450 K temperature range under ambient atmosphere. The scanning rate was 0.5 K min^{-1}, and the experimental uncertainty in temperature was ±0.5 K.

Heat Capacity Measurements. The series of measurements were performed by use of a Perkin-Elmer DSC-7 apparatus with warming and cooling rates ranging from 20 to 2 K min^{-1}. Calibration was achieved with cyclohexane and sapphire. The 13.70 mg powder sample was sealed in the alumina sample holder.

Powder X-ray Diffraction. X-ray powder patterns were recorded at RT using a Philips PW 1730 X-ray generator working with Cu Kα radiation coupled with a laboratory-made counter diffractometer.

Optical Measurements. Optical detection of the spin transition was achieved through the diffuse reflectance of the sample at various wavelengths in the visible using a setup described elsewhere,[34,35] based on a multiwire Y-shaped optical fiber. The temperature scan speed was 0.3 K min^{-1}.

(33) Kröber, J.; Audière, J. P.; Claude, R.; Codjovi, E.; Kahn, O.; Haasnoot, J. G.; Grolière, F.; Jay, C.; Bousseksou, A.; Linarès, J.; Varret, F.; Gonthier-Vassal, A. *Chem. Mater.* **1994**, *6*, 1404.

(34) Morscheidt, W.; Jeftic, J.; Codjovi, E.; Linarès, J.; Bousseksou, A.; Constant-Machado, H.; Varret, F. *Meas. Sci. Technol.* **1998**, *9*, 1311−1315.

(35) Codjovi, E.; Morscheidt, W.; Jeftic, J.; Linarès, J.; Nogues, M.; Goujon, A.; Roubeau, O.; Constant Machado, H.; Desaix, A.; Bousseksou, A.; Verdaguer, M.; Varret, F. *Mol. Cryst. Liq. Cryst.* **1999**, *2*, 1295−1304.
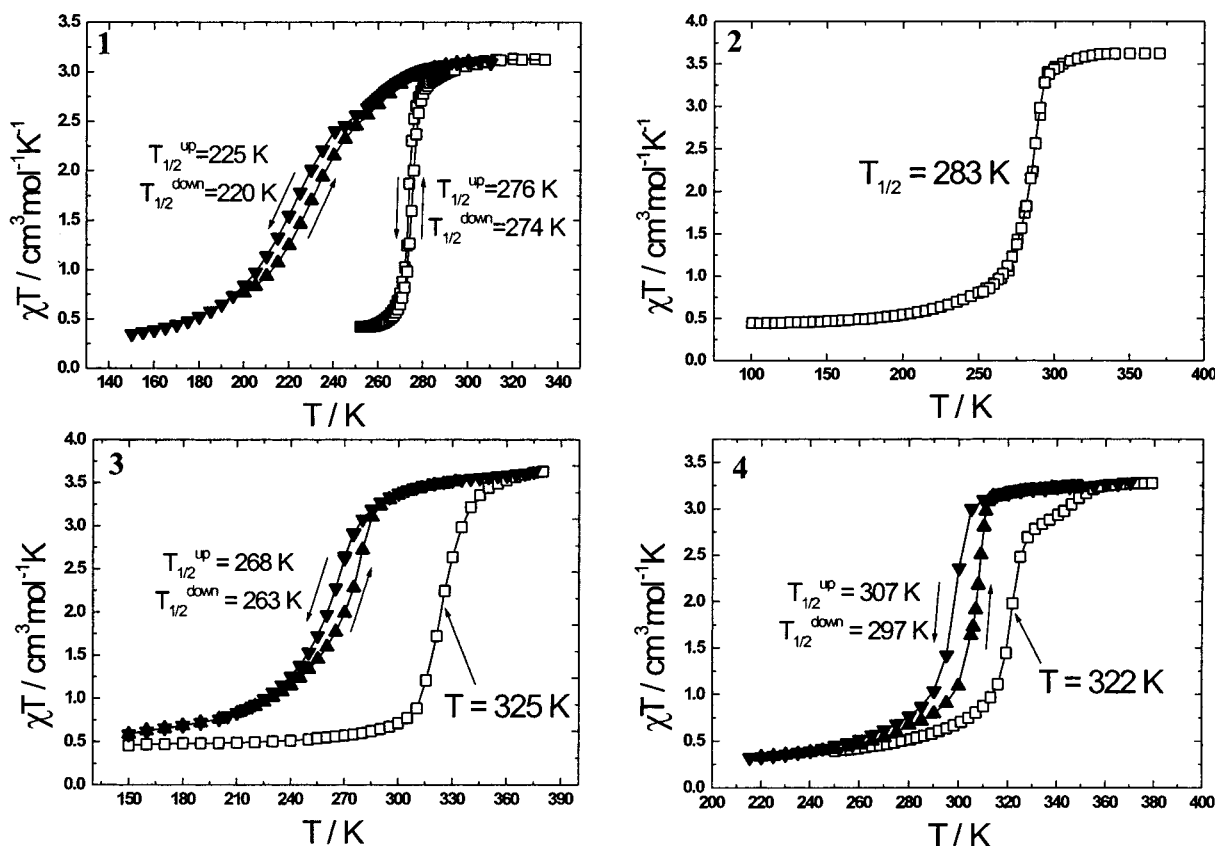
Physical Studies

Magnetism. The temperature dependence of the product $\chi_M T$ for compounds **1−4** is shown in Figure 1. At RT, $\chi_M T$ of **1** is equal to 3.2 cm^3 mol^{-1} K^1, which is close to what would be expected for a HS iron(II) compound (the spin-only value is 3.0 cm^3 mol^{-1} K^1). As the temperature is lowered, $\chi_M T$ starts to decrease, first smoothly and then sharply until 0.4 cm^3 mol^{-1} K^1 at 255 K. As *T* is increased again, the same is observed with a small hysteresis of about 2 K centered on 275 K. The abruptness of the transitions can be defined by the temperature range ΔT_{80}, in which 80% of the iron(II) ions undergo the transition. In **1** this value is identical on cooling and warming and amounts to 8 K, which is sufficiently small for the transition to be considered abrupt. If the temperature is then raised above 340 K, this behavior is no longer reproducible, with then much smoother HS ↔ LS transformations ($\Delta T_{80} \sim 70$ K), still showing hysteresis with inversion temperatures $T_{1/2}^{\downarrow} = 220$ K and $T_{1/2}^{\uparrow} = 225$ K. Compound **2** presents the same kind of transition, centered at 283 K with $\Delta T_{80} = 25$ K, only without hysteresis nor any change of behavior after warming up to 380 K.

Compounds **3** and **4** are LS at RT with $\chi_M T$ of 0.5 and 0.3 cm^3 mol^{-1} K^1, respectively. They turn white on heating, with $\chi_M T$ reaching 3.3 and 3.5 cm^3 mol^{-1} K^1, respectively, above 350 K. Upon cooling, **3** remains HS down to 290 K and turns LS at $T_{1/2}^{\downarrow} = 263$ K and **4** down to 305 K with $T_{1/2}^{\downarrow} = 297$ K. However, on warming the samples again, the LS → HS transitions occur then at 268 and 307 K, respectively. The large hysteresis widths of 60 and 25 K, respectively, detected in the first cycle are thus only apparent. The first L → H spin change is indeed dictated by the kinetics of warming and occurs for **3** at 325 and 331 K, respectively, with warming rates equal to 0.5 and 1 K min^{-1}. This behavior, ascribed to a loss of water, has already been observed in a few compounds of the same type,[27−29] all including anions of the tosylate type. In **4**, a change of steepness occurs in the last stages of the first L → H spin change, indicating a more complex mechanism.

In all four compounds a small residual paramagnetism is still present even well below $T_{1/2}^{\downarrow}$. This is indeed characteristic of these chainlike materials in which the terminal iron(II) ions have water or monodentate triazole ligands coordinated and therefore do not show the spin-transition phenomenon and do remain HS over the whole temperature range. The amount of residual paramagnetism is thus related to the average length of the chains. TIP associated with iron(II) LS may also participate in a residual paramagnetism at low temperature, although reports of Mössbauer spectra of such polymeric compounds have pointed at chain ends remaining HS.[15,24,30,33] The broadness and weak intensity of the $^5T_2 \rightarrow {}^5E$ absorption band makes the detection of small quantities of HS species difficult. When all of the residual paramagnetism is ascribed to chain ends, it results in an average length of more than 20 Fe(II) ions. Considering the average Fe−Fe distance found by EXAFS[19] of 3.65 Å, the chains would be at least 7 nm long. It has to be emphasized that this is only an indication of the average chain size.

It is worth noting that the magnetic behavior of the compounds under study is only weakly sample depend-

Figure 1. Thermal dependence of $\chi_M T$ of compounds **1**–**4**. The triangles (▲) represent the behavior of the dehydrated sample (see text) and the squares (□) that of the hydrated samples.

ent. For instance, displacements of 1 deg in $T_{1/2}$ and ΔT_{80} can be observed for different samples prepared identically. Considering the polymeric form of these materials, the synthesis described indeed leads to reproducible properties.

Optical Detection. One can use the thermochromic effect present in the materials under study to follow the spin state of a thin sample, by irradiating the sample with a chosen wavelength, and simply monitor the reflected intensity when scanning temperature. The thermal behavior in the range 260–300 K of **1** is shown on Figure 2 with wavelengths 550 ± 50 nm, which is in the LS $^1A_1 \rightarrow ^1T_1$ absorption band, and 800 ± 50 nm, which is in the $^5T_2 \rightarrow ^5E$ absorption band of the HS. The presence of a hysteresis of 2 K width is confirmed, with inversion temperatures identical to those obtained by magnetic measurements with $T_{1/2}^{\downarrow} = 274$ K and $T_{1/2}^{\uparrow} = 276$ K. This method also permitted testing of the reproducibility of the transitions. In total the cycle was repeated 12 times without any change of its properties. Provided that the temperature is not raised above 320 K, **1** may therefore be used as an optical sensor of temperature, close to the freezing temperature of water. The form of the curve at high temperature with 550 ± 50 nm has been observed in other samples of this type[36] and is likely to be due to some specificities of the surface properties of the samples. The distortion of the 550 nm hysteresis loop is attributed to the low penetration depth
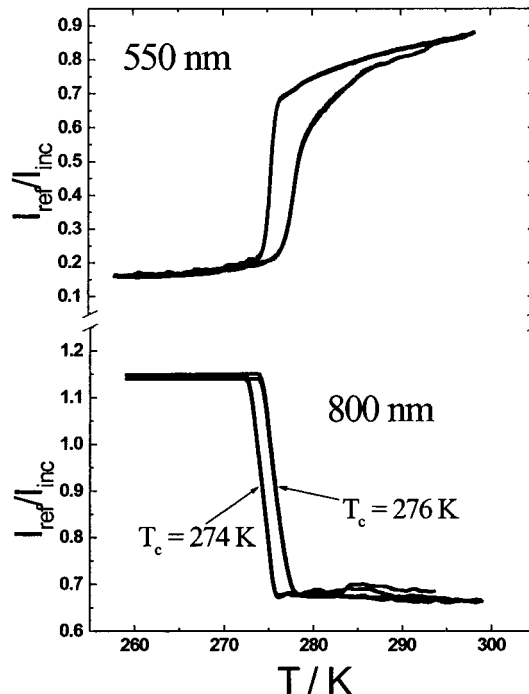
(36) Roubeau, O.; Stassen, A. F.; Gramage, I. F.; Codjovi, E.; Linarès, J.; Varret, F.; Haasnoot, J. G.; Reedijk, J. *Polyhedron* **2001**, *20*, 1709.
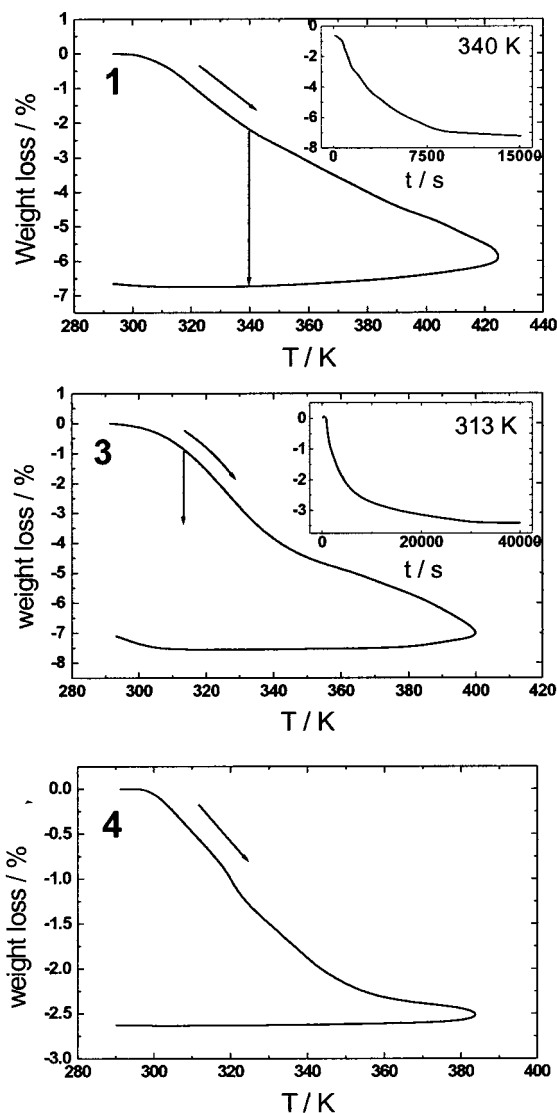

Figure 2. Thermal dependence of the optical response of **1** measured when applying white light with 550 and 800 nm filters (100 nm width). The data plotted are the ratios of reflected intensity over incident intensity.

of light, which only probes the surface layers of the sample.

Thermogravimetric Analysis (TGA) Studies. Considering that the change in behavior of **1**, **3**, and **4** when

Figure 3. Thermogravimetric properties of **1**, **3**, and **4**. Insets depict the time dependence of the weight at a fixed temperature. Corresponding data are shown as vertical arrows on the main figures. The temperature scanning rate was 0.5 K min^{-1}.

warmed above 340 K could be due to loss of water, as previously shown in tosylate-type compounds,[27−29] different TGA experiments were performed. TGA curves for the three compounds are shown in Figure 3 at 0.5 K min^{-1}. In **1**, a continuous loss of mass is observed from 310 to 400 K, without reaching any minimum in mass. The loss reached at that speed is of ca. 6%, which corresponds to ca. 80% of the water molecules. Upon cooling no increase in mass is detected. The kinetics of dehydration were followed at 313 and 340 K, showing an exponential behavior with a final total loss of mass corresponding to about half of the water content (ca. 3.5%) and all of the water molecules (ca. 7.2%), respectively. The peak due to water was no longer observed in the IR spectrum in the latter case, confirming total dehydration. Both samples, partially and totally dehydrated, remained white in an ice/water/NaCl bath, showing that the change in behavior is due to loss of water and that even a partial dehydration can affect drastically the transition properties of that compound, as a difference to previously observed behavior.[29]
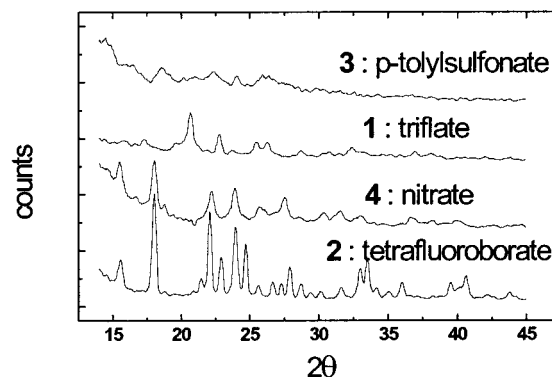

Figure 4. X-ray powder patterns for **1**−**4** at RT.

The weight of **2** is stable up to 380 K, meaning that in that sample the water is quite strongly bound in the material. The magnetic properties shown in Figure 1 are, therefore, reproducible in that case.

Compound **3** exhibits much the same behavior as the triflate **1**, with a continuous loss of mass starting already from 310 K and a slowing down above 345 K. Total dehydration is almost reached with a loss of 7% at 400 K. The main difference is a slow and partial reabsorption of water upon cooling. The sample indeed is again purple and identical with that before thermal treatment after a few minutes in air at RT. The apparent large hysteresis is present again after reabsorption of water. Obviously, in the magnetic measurements which are performed in a He atmosphere, no reabsorption occurred. If the dehydrated sample is put in a water-saturated atmosphere, it immediately turns back to purple/LS, and these properties have been reproduced in up to 10 cycles. The kinetics of weight loss were followed at 313 K, showing an exponential behavior. A stable weight is reached after about 10 h (3.4%).

The nitrate **4** starts losing weight already at 305 K. A total loss of 2.65% is reached at 380 K, and total dehydration (ca. 3.3% weight loss) is attained when keeping the sample at temperatures above 350 K. Compound **4** differs from the tosylate compound **3** in that it does not reabsorb water in normal conditions within months. The change in steepness in the magnetic transition curve of **4** corresponds to the last stages of dehydration. This unexpected slowing down of the dehydration effect might be explained, as in the literature,[29] as being due to a rearrangement of the chains occurring after complete dehydration and therefore a change of the spin-transition regime. Only if put in water-saturated atmosphere does the dehydrated **4** reabsorb water and show again its original properties.

Powder X-ray Diffraction. X-ray powder patterns of compounds **1**−**4** were recorded at RT. None of the compounds is isostructural, with the as yet only published structure[22] of such chains formed by triple triazole bridges (cf. Figure 4). No common intense peak with [Fe(Htrz)$_2$trz]BF$_4$ is found, which shows, together with the fact that only the nitrate and the tetrafluoroborate have comparable patterns, that although the chain structure is likely to be very similar in all of these compounds, different packing and lattice arrangements may yield completely different crystallographic patterns. Samples of **1** and **4** were completely dehydrated using
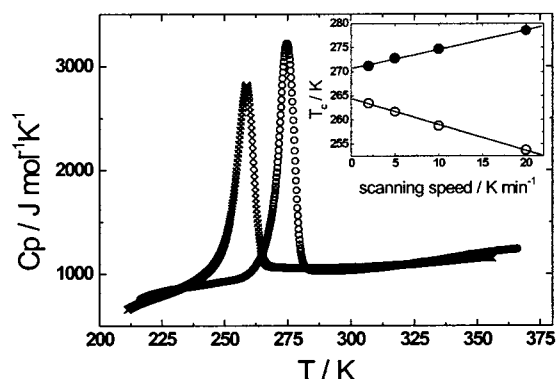
Figure 5. Calorimetric data for **1**: molar heat capacity curves in the cooling (×) and warming (○) modes. The inset depicts the dependence of the peak maxima with respect to the kinetics of the measurements.

the TGA apparatus and then measured at RT. No marked differences in the powder patterns were observed between the hydrated and dehydrated forms for both compounds. This observation differs from the previous report[29] of a change from a crystalline to a noncrystalline material upon water loss in [Fe(hyetrz)$_3$]-(3-nitrophenylsulfonate)$_2$·3H$_2$O. This suggests that the water molecules in **1** and **4** are distributed without any order in the lattice and, moreover, that their interaction with the metallic chains is likely to be very weak.

Calorimetric Study. Results from differencial scanning calorimetry (DSC) measurements performed on **1** are presented on Figure 5. A heat capacity anomaly appears in warming (260–285 K) and cooling (240–265 K) which corresponds to the transitions observed in the magnetic measurements. The heat capacity humps, therefore, obviously arise from the spin crossover phenomenon. DSC measurements are dynamic in nature, and static figures for the temperature of the maximum of the peaks are deduced by extrapolating for zero speed the dependence of this maximum in scanning speeds (see the inset in Figure 5). A hysteresis width of 6 K and transition temperatures of 271 and 265 K respectively in warming and cooling are thus obtained. The shift to a lower temperature side of about 4 K and the larger hysteresis width with respect to magnetic measurements may be due to the use of a different sample together with the different conditions of measurement.

The excess heat capacity due the spin crossover phenomenon is obtained by estimating a normal heat capacity curve with the high- and low-temperature data and subtracting it from the total heat capacity. Excess enthalpies ΔH of 17.2 and 14.8 kJ mol^{-1} and entropies ΔS of 64.3 and 59.0 J mol^{-1} K^{-1} are deduced respectively for the warming and cooling modes. The entropy gains are much larger than the value expected for the change in the spin manifold of a ferrous complex, $R \ln 5$ (13.4 J mol^{-1} K^{-1}). The differences between the warming and cooling are probably arising from the tail observed at low temperatures in the cooling curve, which makes the determination of a normal heat capacity curve more difficult.

Discussion

Structure and Cooperativeness. The first point that should be discussed is why the compounds under study can be considered as chainlike linear polymeric materials. The linear structure of compounds of the general formula [Fe(Rtrz)$_3$]A$_2$·xS (S = solvent) has been established unambiguously on the basis of EXAFS data,[19,20] with a comparison to structures of linear trimeric units including the same triazole triple bridges. Moreover, the crystal structures of three copper(II) analogues[16,22,38] confirm the structural features found by EXAFS, which are (i) linearity of the metal centers with a coordination sphere very symmetric (almost perfect octahedron), (ii) alternating triple triazole bridges with C_{2v} symmetry, and (iii) importance of hydrogen bonding.

Other techniques indicated earlier this chainlike arrangement and were used to confirm the linear structures of **1**–**4**. First of all, IR shows that the Rtrz retains a C_{2v} symmetry, pointing at a 1,2-bridging coordination mode of the triazole ring. The amide bond peak of fatrz remains present in all IR spectra of **1**–**4** with only a very small shift to higher wavenumbers with respect to the free ligand, showing that the amide function does not coordinate. The small amounts of remaining paramagnetism at low temperatures indicate that most iron(II) cores undergo the thermal spin transition, which in turn points at 6-bridging triazole surroundings[39–41] for most of the iron(II). Indeed, **1** and **2** do not have a measurable HS absorption in UV spectroscopy at ∼100 K nor do **3** and **4** at RT, which is due to the broadness and weakness of that absorption together with the low amount of HS species. As in the trimeric compounds in which only the central iron(II) shows a spin transition, the outer iron(II) remaining HS, only the terminal iron(II) ions of polymeric chains, coordinated by water molecules and/or monodentate triazoles, would remain HS. Therefore, the lower the residual HS fraction is, the longer the chains are. Only the average chain length might be sample dependent, but the used synthesis resulted in reproducible physical properties (vide supra). The average chain length of at least 7 nm found in compounds **1**–**4** is comparable to other cooperative compounds of this type[17] but smaller than that in [Fe(Htrz)$_2$trz]BF$_4$, for which the size would be about 13.5 nm, considering the HS residual fraction of 5% found by Mössbauer spectroscopy.[33] Also, it has to be compared to the 11 Fe model used in the LAXS study of Verelst et al.,[21] which reproduced very well the experimental data of [Fe(Htrz)$_2$trz]BF$_4$. Therefore, the minimum chain length for the occurrence of rather steep transitions (ΔT_{80} between 5 and 15 K) and small hysteresis, which is a general feature of this family of compound, is below 4 nm. More peculiar behavior, such as that in [Fe(Htrz)$_2$trz]BF$_4$, arises from the addition of strong H-bonding and/or interchain interaction to this "chain" cooperativity.[21]

(37) McGarvey, J. J. TMR-TOSS Meeting 2001, Bordeaux, France, 2001.

(38) Sinditskii, V. P.; Sokol, V. I.; Fogel'zang, A. E.; Dutov, M. D.; Serushkin, V. V.; Porai-Koshits, M. A.; Svtelov, B. S. *Russ. J. Inorg. Chem.* **1987**, *32*, 1149.

(39) Vos, G.; de Graaff, R. A. G.; Haasnoot, J. G.; van der Kraan, A. M.; de Vaal, P.; Reedijk, J. *Inorg. Chem.* **1984**, *23*, 2905−2910.

(40) Kolnaar, J. J. A.; van Dijk, G.; Kooijman, H.; Spek, A. L.; Ksenofontov, V. G.; Gütlich, P.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1997**, *36*, 2433.

(41) Garcia, Y.; Guionneau, P.; Bravic, G.; Chasseau, D.; Howard, J. A. K.; Kahn, O.; Ksenofontov, V.; Reiman, S.; Gütlich, P. *Eur. J. Inorg. Chem.* **2000**, 1531.

The fact that powder X-ray patterns do not compare with the simulated patterns of [Cu(hyetrz)$_3$](ClO$_4$)$_2$·3H$_2$O or with the ones of [Fe(Htrz)$_2$(trz)]BF$_4$ does not rule out a similar structure. These two compounds are original in their strong H-bonding network, which organizes the chains. Moreover, these two compounds have a strict linearity within the chains. Only a small-angle zigzag would change the space group. Indeed, a LAXS study[21] showed that a rhombic distortion of the iron core, which is often observed in iron(II) HS, was likely to yield the disappearance of the strict linear character of the chains, as well as its periodicity. Recent additional EXAFS data indicate, however, that this distortion may simply be a thermal oscillation around the linear state.[42] The calorimetric variations also deserve some discussion, related to the actual cooperativeness of the spin transition in this type of compound. It is generally observed that cooperative spin-transition compounds have high enthalpy and entropy variations; for example, in [Fe(Htrz)$_2$trz]BF$_4$, $\Delta H \sim 27$ kJ mol^{-1},[33] or in [Fe(btr)$_2$(NCS)$_2$]·H$_2$O, $\Delta H \sim 10$ kJ mol^{-1}.[43] The sharp change in spin state of the whole sample is related to a strong modification of the lattice, once some iron-(II) ions change their spin. The better this modification is propagated, the more cooperative the transition is, which is reflected in the importance of elastic terms when modeling the spin-transition behavior.[44] The triple triazole bridge of these polymeric species produces an excellent pathway for such propagation along the chains, yielding the high enthalpy and entropy excesses observed in **1**, which confirm the cooperative character of the spin transition in the polymeric materials of this study. The higher values obtained in the polymeric [Fe-(Htrz)$_2$trz]BF$_4$ probably originate in the presence of a charged bridge in this peculiar compound. An additional explanation for the much higher entropy of the HT phase may arise from the linearity of these materials. Whatever the two reasons advanced above for the disappearance of the 7 Å peak in the HS state in EXAFS, characteristic of three aligned Fe ions, the number of degrees of liberty in the high-temperature state would be higher, which contributes to a higher entropy. Another indication of the strong cooperativeness within these chains is the difficulty to observe the LIESST[45] effect. Only two reports of excitation were published so far, both with high powers and yielding only a partial excitation.[46,47]

Influences of Water. Three of the four compounds of this study change their behavior when losing some or all of the water they contain. The nitrate **4** intrinsically has the same behavior as that of previously reported materials in which loss of water induces a first L → H spin change, with then stable transitions at lower temperatures, without reabsorption of water in normal conditions. When the difference of temperature between the first change to HS and the stable transitions is large enough, as in [Fe(hyetrz)$_3$](3-nitrophenylsulfonate)$_2$·3H$_2$O but unfortunately not in **4**, this can be used as a one-shot application to detect the crossing of a limited temperature. Compound **4** is, nevertheless, original in the fact that all reported similar behaviors were in compounds with phenyl- or naphthylsulfonate anions. Compound **3** does present this property of large difference in temperatures, but it reabsorbs water within minutes in air at RT. The synergy of dehydration–rehydration processes with the corresponding spin states in **3** allows the temporal indication that the temperature has reached an upper limit, here of about 325 K, and so in a reusable fashion. Moreover, because only partial dehydration is necessary to change the LS → HS transition, the loss of water probably dictates the first LS → HS transition. On the other hand, the triflate **1** has an interesting spin transition just above the freezing temperature of water but loses these properties as soon as it becomes partially dehydrated. Its possible application as a detector of the crossing of the 0 °C barrier is ruled out by this loss of water occurring at too low a temperature, although it seems stable in a sealed cell as evidenced by the DSC measurements. It, nevertheless, shows a behavior not reported before. The occurrence of gradual transitions in such polymeric compounds is due to the short size of chains,[17,47] whereas complete and cooperative transitions are related with rather large chains. Compound **1** changes irreversibly even when only a partial dehydration takes place. The passage to more gradual transition curves after dehydration was also observed in [Fe(Htrz)$_3$]-(BF$_4$)$_2$·H$_2$O,[33] but then the temperatures did not change. Because it is not likely that such polymeric chains may break at temperatures of 340 K, it is probable that **1** has only rather short chains, bound to each other by water, yielding cooperative-like behavior. As soon as some water is lost, this behavior would disappear in favor of the gradual transitions of the isolated short chains. This is supported by the fact that, different from compounds **3** and **4**, the original behavior is not observed again after the sample is placed in a water-saturated atmosphere. The argument of short chains strongly bound through a hydrogen-bonding network was indeed already proposed to explain the differences between [Fe(hyetrz)$_3$](3-nitrophenylsulfonate)$_2$·3H$_2$O and its dehydrated form.[29]

One first has to discriminate the two kinds of water molecules that these types of compounds can contain: (i) lattice water and (ii) coordinated water to the outer iron(II) ions of the polymeric chains. The former is likely to be lost easily, whereas the latter should not be removed below 400 K. Therefore, water loss in compounds **1**, **3**, and **4** has to be related to the former kind because it occurs in the 310−400 K range and so do previous reports of water loss in such polymeric compounds.[26−29] Moreover, it has to be emphasized that the end groups can also be monocoordinated triazoles. Studies on mononuclear Fe(II) spin-transition compounds have already revealed that the LS state may be stabilized by interactions with lattice water molecules.[11,48,49] When some lattice water molecules are lost

(42) Moscovici, J. TMR-TOSS Meeting 2001, Bordeaux, France, 2001.

(43) Martin, J.-P.; Zarembowitch, J.; Dworkin, A.; Haasnoot, J. G.; Codjovi, E. *Inorg. Chem.* **1994**, *33*, 2617.

(44) Spiering, H.; Willenbacher, N. *J. Phys. B* **1989**, *1*, 10089−10105.

(45) Decurtins, S.; Gütlich, P.; Köhler, C. P.; Spiering, H.; Hauser, A. *Chem. Phys. Lett.* **1984**, *105*, 1.

(46) Erenburg, S. B.; Bausk, N. V.; Lavrenova, L. G.; Mazalov, L. N. *J. Synch. Rad.* **1999**, *3*, 576.

(47) Garcia, Y. TMR-TOSS Meeting 2001, Bordeaux, France, 2001.

(48) Sugiyarto, K. H.; Craig, D. C.; Rae, A. D.; Goodwin, H. A. *Aust. J. Chem.* **1994**, *47*, 869.

upon heating, the stabilization of the LS state may already diminish. This is why even a partial loss of water, as observed in the present series, may change the transition properties. This was also observed in naphthylsulfonate compounds.[28] The direct relationship between the stabilization of the LS state and the amount of lattice water is also at the origin of the dependence of the first L → H spin change temperature on the kinetics of warming.

In a more general manner, it is not uncommon that solvent molecules are incorporated in coordination compounds, and their influence on the spin crossover behavior of mononuclear species has already attracted much attention.[11,48,50] Very often water is hydrogen bonded to the ligand through a $N-H\cdots OH_2$ interaction or through the interaction with a nitrogen atom of an imine group, $=N\cdots HOH$. In the first case, an increase of the electron density on the nitrogen atom results and, therefore, the metal−ligand interaction is strengthened, with the LS state being favored. The contrary occurs in the latter case. The paramount role of such hydrogen bonds on the supramolecular interactions of a molecular spin crossover material was recently also evidenced, without any solvent molecules, but between two groups of a polynucleating Schiff base.[51] In compounds **1**−**4**, the ligand fatrz does not possess such a free imine group nor a secondary amine; only the amide N−H is likely to form hydrogen bonds. When the amide vibrations in IR of the free ligand and the polymeric compounds are compared, a difference appears between the tetrafluroborate **2** and the three other polymers. In **2** the N−H stretch remains at the same energy and the C=O stretch lowers in energy. On the other hand, in the three other polymers, the two amide stretchings increase in energy, about 20 cm^{-1} for the C=O vibration and about 70 cm^{-1} for the N−H vibration. The latter changes indicate that a hydrogen bonding of the amide group is unlikely in **1**, **3,** and **4**, whereas the lowering in energy of the C=O stretch of the amide group in **2** may indicate the formation of a hydrogen bond through $C=O\cdots HOH$ interaction. This would explain why **2** does not lose water up to 380 K, whereas the other three compounds do. It has to be pointed out, however, that some tosylate compounds of 4-alkyl-substituted 1,2,4-triazole[26] do have striking similarities with the behavior of tosylate compounds of 4-amino-1,2,4-triazole.[27] Therefore, hydrogen bonding of the type discussed above may not be necessary.

Water may play another role than just forming hydrogen bonds. For example, the prototype compound [Fe(Htrz)$_2$trz]BF$_4$ does not have water but has to be synthesized in water to obtain the correct properties. Two explanations were proposed:[33] (i) a very small amount of water is indeed tightly bound to the chains and plays a crucial role in the spin-transition behavior or (ii) the presence of water during the synthesis triggers the crystallinity and/or the crystal structure. The present study reinforces this latter hypothesis because the spin-transition properties were found to be different if the synthesis was done in a solvent other than water, although hydrates of the iron salts were used. This was indeed already mentioned in a study of compounds with long alkyl tails on the triazole molecules.[52] In addition, when such polymeric compounds are synthesized with other solvent molecules and then put in the presence of water, an immediate replacement is observed.[29]

Conclusion

Spin-transition polymeric compounds have already been suggested for possible applications, especially considering the synergy between the loss of noncoordinated water molecules and their L → H spin change. The present family of compounds illustrates the richness of properties of the Fe(II)/4-R-1,2,4-triazole spin-transition polymers. Compounds such as [Fe(fatrz)$_3$](tosylate)$_2$·3H$_2$O (**3**) can be used as a temperature threshold optical indicator. The tuning of the first L → H spin change temperature that occurs when some water is lost can give access to a wide range of temperatures. If, as in compound **3**, the rehydration process is spontaneous, this indicator is reusable, whereas if, as in [Fe(hyetrz)$_3$]-(3-nitrophenylsulfonate)$_2$·3H$_2$O[29] or here in compound **4**, the dehydrated material is stable, it is only a single-shot indicator. The compound [Fe(fatrz)$_3$](triflate)$_2$·3H$_2$O (**1**) can also be used as an optical temperature sensor for the freezing temperature of water, with this application arising from the temperature of its intrinsic spin transition rather than from dehydration−rehydration processes. The tight relation between this class of compounds and coordinated and noncoordinated water molecules has to be emphasized. Whether it is during the synthesis, by increasing cooperativity through hydrogen bonds, or in the synergy of water loss and spin transition, water plays a dominant role in the physical properties and the chemical structure of this whole class of materials.

(49) Buchen, T.; Gütlich, P.; Sugiyarto, K. H.; Goodwin, H. A. *Chem. Eur. J.* **1996**, *2*, 1134.
(50) Gütlich, P.; Köppen, H.; Steinhaüser, H. G. *Chem. Phys. Lett.* **1980**, *74*, 475.
(51) Salmon, L.; Donnadieu, B.; Bousseksou, A.; Tuchagues, J.-P. *C. R. Acad. Sci. Paris II, Sér. C* **1999**, *2*, 305

(52) Armand, F.; Badoux, C.; Bonville, P.; Ruaudel Teixier, A.; Kahn, O. *Langmuir* **1995**, *11*, 3467.