Non-classical Fe^{II} spin-crossover behaviour in polymeric iron(II) compounds of formula $[Fe(NH_2trz)_3]X_2 \cdot xH_2O$ (NH_2trz = 4-amino-1,2,4-triazole; X = derivatives of naphthalene sulfonate)

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A new series of iron(II) spin-crossover materials of formula $[Fe(NH_2trz)_3]X_2 \cdot xH_2O$ [X = 1-naphthalene sulfonate (1ns), 2-naphthalene sulfonate (2ns), 4-hydroxy-1-naphthalene sulfonate (4OH-1ns), 4-amino-1-naphthalene sulfonate ($4NH_2$-1ns) and 6-hydroxy-2-naphthalene sulfonate (6OH-2ns)] are reported. The structure of these compounds consists of linear chains in which the Fe(II) ions are linked by triple N^1,N^2-1,2,4-triazole bridges. All compounds show non-classical spin-crossover behaviour. Optical and magnetic measurements recorded upon heating show an abrupt low-spin to high-spin transition accompanied by a pronounced thermochromic effect occuring between 330 and 340 K depending on the anion. Thermogravimetric analyses show that the transition is induced by the removal of the two lattice water molecules, which initially stabilized the low-spin state. The dynamical character of this transition has been monitored by extended ^{57}Fe Mössbauer spectroscopic studies on $[Fe(NH_2trz)_3](2ns)_2 \cdot xH_2O$. Upon cooling, the dehydrated modifications show classical spin-crossover behaviour with hysteresis at much lower temperatures, ranging from 229 to 297 K depending on the anion. $[Fe(NH_2trz)_3](2ns)_2$ represents one of the first iron(II) spin-crossover materials showing a spin transition in the close vicinity of room temperature (290 K) accompanied by hysteresis (14 K).

Nowadays there is an increasing interest in new bistable iron(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.[1–10] Recently, the use of such materials as molecular-based memory devices and displays has been investigated.[8,11,12] The requirements for this type of application can be formulated as follows: the compound must exhibit abrupt transitions with large hysteresis (*ca.* 50 K), the middle of which should preferably be situated close to room temperature. To allow the material to act as a display, the spin transition should be accompanied by a change in color (thermochromism). Finally, the compound should be stable under normal operating conditions. [2,7,9,11,13,14] A promising class of materials meeting these criteria are the linear chain iron(II) compounds of general formula $[Fe(NH_2trz)_3]X_2 \cdot xH_2O$ (NH_2trz = 4-amino-1,2,4-triazole; X = NO_3^-,[9,15–17] ClO_4^-,[18] BF_4^-,[11,18] I^-,[19] Br^-,[11,18] $CH_3SO_3^-$,[20] tosylate[21]). Although no X-ray crystallographic data are available on these iron(II) compounds, it is obvious that their structure must be comparable to that of $[Cu(NH_2trz)_3](ClO_4)_2 \cdot 0.5H_2O$.[22] The EXAFS study on the related 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) confirms that a similar structure can indeed be obtained with Fe^{II}.[23] Very recently, a detailed EXAFS study finally allowed the acquisition of direct information on the effect of Fe^{II} spin transition on the spatial and electronic structure of $[Fe(NH_2trz)_3]X_2$ (X = NO_3^-, BF_4^-, Br^-, ClO_4^-) and the magnetically diluted phases $[Fe_xZn_{1-x}(NH_2trz)_3](NO_3)_2$.[24–26] In these compounds the Fe^{II} ions are linked by triple N^1,N^2-1,2,4-triazole bridges. This direct linkage of the iron(II) centers results in a large cooperativity of the spin-crossover behaviour, and therefore considerable hysteresis has been found in these materials.[7,9] Variation of the non-coordinated anion in $[Fe(NH_2trz)_3]X_2 \cdot xH_2O$ leads to compounds with significantly different spin-crossover characteristics. The temperature of the transition to the high-spin state increases when the radius of the anion diminishes upon changing in the following order: ClO_4^-, I^-, Br^-, BF_4^-, NO_3^-.[25,27] EXAFS studies on the low-spin forms have shown that the Fe—N bond distances tend to decrease with the above-mentioned order of substitution of the anions.[25,26] Furthermore, ^{57}Fe Mössbauer spectroscopy studies[27] and analyses of the X-ray fluorescence spectra[24] confirm that this decrease in interatomic distances correlates with the covalence of the Fe—N bond in the same series of anions. Therefore, Lavrenova and coworkers concluded that this increase in transition temperatures appears to be associated with the increasing anion–cation interactions, and the thereby arising increasing 'electrostatic pressure' which causes a subsequent increasing compression of the FeN_6 octahedron.[25] Moreover, it appears that a rather low transition temperature (T_c, where 50% high-spin Fe^{II} and 50% low-spin Fe^{II} are present) is accompanied by a rather small hysteresis loop, whereas an increase in T_c leads to an increase in hysteresis width.[28]

Within this family of 4-amino-1,2,4-triazole compounds the derivative containing tosylate[21] shows a rather peculiar Fe^{II} spin-crossover behaviour involving a large apparent hysteresis of about 80 K, which could be ascribed to the synergy between the Fe^{II} spin-crossover behaviour and a dehydration process. In fact, this type of synergy appears to be a general feature particular to Fe^{II} linear chain compounds containing this type of planar aromatic anions. Recently, we have observed the same phenomenon in $[Fe(hyetrz)_3]X_2 \cdot 3H_2O$ (hyetrz = 4-(2′-hydroxyethyl)-1,2,4-triazole; X = 3-nitrophenylsulfonate), which gave rise to an unprecedented apparent hysteresis width of 270 K.[29] The structure of the copper(II) analogue $[Cu(hyetrz)_3](ClO_4)_2 \cdot 3H_2O$ has been elucidated and indeed consists of linear chains in which the Cu^{II} ions are linked by triple N^1,N^2-1,2,4-triazole bridges.[30] It is worth noting that the large thermal hysteresis (60 K) of the mononuclear compound $[Fe\{HB(pz)_3\}]_2$ [$HB(pz)_3$ = tris(1-pyrazolyl)borate][31] is not due to the mechanism mentioned above. In fact, the transition from low-spin to high-spin Fe^{II} occurring at about 400 K is associated with a crystallographic phase transition, whereby the initially well formed crystals shatter into extremely small fragments.[31]

To study the role of planar aromatic anions in further detail in the 4-amino-1,2,4-triazole systems we have selected the sulfonate derivatives of naphthalene. This choice allows a systematic variation of the anion. The sulfonate group can be in two different positions, and other substituents capable of forming hydrogen bonds (such as the hydroxy and the amino group) may be attached to the naphthalene ring system. Here we report on the spin-crossover behaviour of the $[Fe(NH_2trz)_3]X_2 \cdot xH_2O$ derivatives containing the monovalent anions 1-naphthalene sulfonate (abbreviated as 1ns), 2-naphthalene sulfonate (2ns), 4-hydroxy-1-naphthalene sulfonate (4OH-1ns), 4-amino-1-naphthalene sulfonate ($4NH_2$–1ns) and 6-hydroxy-2-naphthalene sulfonate (6OH-2ns) (see Fig. 1).

Experimental

Materials

Commercially available solvents were used without further purification. $FeCl_2 \cdot 4H_2O$, 4-amino-1,2,4-triazole and the sodium salts of 1-naphthalene sulfonic acid and 6-hydroxy-2-naphthalene sulfonic acid were purchased from Aldrich. The sodium salts of 2-naphthalene sulfonic acid, 4-hydroxy-1-naphthalene sulfonic acid and 4-amino-1-naphthalene sulfonic acid were purchased from Acros. The iron(II) salts of the various naphthalene sulfonates were prepared by mixing aqueous solutions of iron(II) chloride and the corresponding naphthalene sulfonate sodium salt.

Measurements

Elemental analyses were performed by the Service Central d'Analyse (CNRS) in Vernaison, France. ^{57}Fe Mössbauer measurements were performed using a constant acceleration Halder-type spectrometer with a room temperature ^{57}Co source (Rh matrix) in a transmission geometry. All isomer shifts reported in this work refer to natural iron at room temperature. The spectra were fitted to the sum of Lorentzians by a least-squares refinement. Thermogravimetric measurements were carried out with a Setaram apparatus in the temperature range 300–400 K under ambient atmosphere. Magnetic susceptibilities were measured in the temperature range 77–400 K with a fully automatized Manics DSM-8 susceptometer equipped with an Oxford instruments DN170 continuous-flow cryostat and a Bruker BE15f electromagnet operating at *ca.* 0.8 Tesla. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants. Optical measurements have been carried out using the device described previously.[7,21]

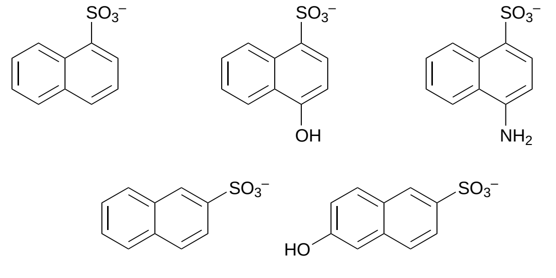

Fig. 1 Structures of 1-naphthalene sulfonate (1ns), 4-hydroxy-1-naphthalene sulfonate (4OH-1ns), 4-amino-1-naphthalene sulfonate ($4NH_2$-1ns), 2-naphthalene sulfonate (2ns), and 6-hydroxy-2-naphthalene sulfonate (6OH-2ns)

Synthesis of $[Fe(NH_2trz)_3]X_2 \cdot 2H_2O$ (X = 1ns, 2ns, 4OH-1ns, $4NH_2$-1ns and 6OH-2ns)

A methanolic solution (40 ml) containing 2 mmol (1.2 g) of $[Fe(H_2O)_6](2ns)_2$ and a small amount of ascorbic acid was added under stirring to a methanolic solution (15 ml) containing 6 mmol (0.5 g) of 4-amino-1,2,4-triazole. Instantaneously, a white precipitate formed, which was filtered and dried in air. During the drying the compound turned pink. Yield: 1.04 g (69%). Elemental analyses. Calc. for $C_{26}H_{30}S_2O_8FeN_{12}$ $\{[Fe(NH_2trz)_3](2ns)_2 \cdot 2H_2O\}$: C, 41.17; H, 3.99; N, 22.16; S, 8.45; Fe, 7.36. Found: C, 39.61; H, 3.88; N, 22.77; S, 8.19; Fe, 7.20%.

The compounds containing other naphthalene sulfonate anions have been prepared analogously. The elemental analyses of these compounds suggest the same composition as for the 2ns derivative. However, in all cases the C and N analyses indicate a small deficit of ligand. This feature has been generally observed for this type of polynuclear iron(II) compounds and may be attributed to the presence of a mixture of linear triply N^1,N^2-1,2,4-triazole bridged compounds differing in chain length.[10] The terminal Fe^{II} ions of such a chain are supposed to have one or more water ligands; consequently, these ions remain in the high-spin state over the whole temperature range. Furthermore, it may not be excluded that the polymeric nature of these compounds gives rise to particular difficulties in the determination of the elemental analyses.

Results and Discussion

The compounds $[Fe(NH_2trz)_3]X_2 \cdot xH_2O$ (X = 1ns, 2ns, 4OH-1ns, $4NH_2$-1ns, 6OH-2ns) appear as purple–pink powders. This pink color is due to the $^1A_{1g} \rightarrow {}^1T_{1g}$ d–d transition of low-spin Fe^{II} occurring at 520 nm. The color of the compounds changes to white upon heating to *ca.* 340 K. This white color is due to the fact that the spin-allowed d–d transition of lowest energy of the compound in high-spin state, $^5T_{2g} \rightarrow {}^5E_g$, occurs at the limit of the visible and IR regions.

Optical measurements

Since these compounds are highly thermochromic, the Fe^{II} spin transition has been studied optically using a home-made device.[7,21] This technique provides an accurate determination of the transition temperatures, however it does not give any information on the percentage of Fe^{II} ions involved in the spin transition. Since the possible use of these materials in molecular electronics requires stability of the physical behaviour of the compounds (*i.e.* retaining of the hysteresis loop) the spin-crossover behaviour has been investigated during at least three thermal cycles. In all cases the temperature has firstly been raised to 400 K followed by additional cooling and heating experiments. The results of these optical measurements are shown in Table 1.

All compounds virtually show the same physical properties. It is worth noting that the spin-crossover behaviour shows a paramount analogy with that of the tosylate derivative.[21] For

Table 1 Results of the optical measurements for $[Fe(NH_2trz)_3]X_2 \cdot xH_2O^a$

	first cycle		second cycle		third cycle	
X	$T_c\uparrow$	$T_c\downarrow$	$T_c\uparrow$	$T_c\downarrow$	$T_c\uparrow$	$T_c\downarrow$
1ns	330	229	235	229	235	229
4OH-1ns	332	230	240	230	240	230
$4NH_2$-1ns	340	225	235	225	235	225
2ns	340	283	297	283	297	283
6OH-2ns	334	260	270	265	270	265

$^a T_c$/K has been taken at the half intensity height.

instance, $[Fe(NH_2trz)_3](1ns)_2 \cdot xH_2O$ (see Fig. 2) shows upon heating a very abrupt low-spin→high-spin transition occurring at 330 K. Decreasing the temperature reveals a very smooth high-spin→low-spin transition with $T_c\downarrow = 229$ K. A second heating of the sample shows a rather smooth low-spin→high-spin transition at $T_c\uparrow = 235$ K. Subsequent heating and cooling cycles indicate that this small hysteresis ($T_c\uparrow = 235$ K, $T_c\downarrow = 229$ K) is retained. Compounds containing the related anions 2ns, 4OH-1ns, $4NH_2$-1ns and 6OH-2ns show a similar behaviour, differing only in the position of the transition temperatures.

Among these compounds the 2ns derivative shows very interesting characteristics of the stable spin-crossover behaviour occurring in the second and further heating and cooling experiments (see Fig. 3). A first heating (1 K min^{-1}) results in an abrupt low-spin→high-spin transition at 340 K. Upon cooling a rather abrupt high-spin→low-spin transition occurs at $T_c\downarrow = 283$ K. Heating the compound once more reveals another abrupt low-spin→high-spin transition, now situated at 297 K. Additional heating and cooling experiments show that this hysteresis of 14 K centered in the close vicinity of room temperature (290 K) remains stable.

The rate of heating has a paramount effect on the spin-crossover behaviour. In fact, when the optical measurements for the 2ns derivative are carried out at a heating rate of 0.1 K min^{-1}, the low-spin to high-spin transition proceeds in an abrupt fashion at 330 K. The increasing of the heating rate above 1 K min^{-1} does not affect the spin-crossover characteristics with respect to the measurements carried out at 1 K min^{-1}: in all cases, the transition takes place abruptly at 340 K. In addition, optical measurements of $[Fe(NH_2trz)_3](2ns)_2 \cdot xH_2O$ have also been carried out by keeping the sample at a fixed temperature lower than 340 K. In a typical experiment the temperature was fixed at 326 K. Interestingly, under these conditions we observed that the compound gradually transforms to its high-spin state. Apparently, even at temperatures lower than 340 K, the temperature at which the low-spin to high-spin transition is found in the heating mode while heating at 1 K min^{-1}, the compound is capable of exhibiting spin-crossover behaviour. This feature may be explained by the mechanism associated with this spin transition in the first heating mode, which will be analyzed in detail in the discussion.

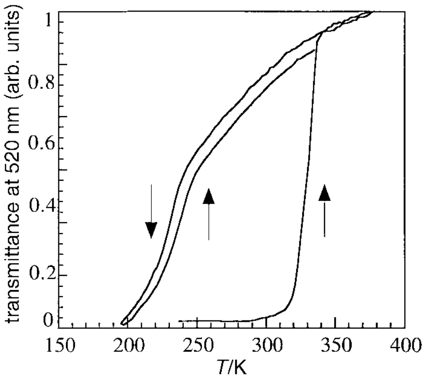

Fig. 2 Optical measurement (intensity *vs.* temperature; recorded at 1 K min^{-1}) for $[Fe(NH_2trz)_3](1ns)_2 \cdot xH_2O$

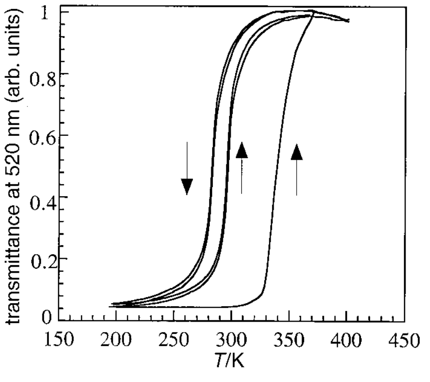

Fig. 3 Optical measurement (intensity *vs.* temperature; recorded at 1 K min^{-1}) for $[Fe(NH_2trz)_3](2ns)_2 \cdot xH_2O$

Thermogravimetry

Thermogravimetric analysis (see Fig. 4) carried out with the same velocity of heating (1 K min^{-1}) as for the optical measurements has been carried out for the 1ns and 2ns derivatives. These measurements reveal a continuous loss of mass starting at room temperature. This decrease in mass proceeds rapidly in the temperature range 315–350 K, after which it continues in a much smoother fashion. It is important to notice that at the transition temperatures T_c, 330 and 340 K for 1ns and 2ns, respectively, the mass% lost corresponds to the removal of 0.5 and 1.3 molecules of lattice water for 1ns and 2ns, respectively. If we assume that the measuring conditions are really identical in the optical and thermogravimetric measurements, this would imply that the spin transition already starts while there are still water molecules present in the sample and proceeds in a moderately abrupt way until all water molecules have been released. This is in sharp contrast to $[Fe(hyetrz)_3](3\text{-nitrophenylsulfonate})_2 \cdot 3H_2O$,[29] where under identical measuring conditions the spin transition has been found to take place in a very abrupt 'explosive' fashion at the moment all water molecules have been removed from the sample. The measurement cell used in the thermogravimetric analyses is in direct contact with the air. Upon cooling to room temperature an increase in the mass of the 1ns and 2ns samples is observed, which indicates that the compounds are being rehydrated: the 1ns compound then has recovered 1.35 molecules of water per formula unit, while the 2ns derivative has only been rehydrated by 1 molecule of water per Fe^{II} ion. On the contrary, $[Fe(hyetrz)_3](3\text{-nitrophenylsulfonate})_2 \cdot 3H_2O$ has been found not to rehydrate under these experimental conditions.[29]

^{57}Fe Mössbauer spectroscopy

^{57}Fe Mössbauer spectra have been recorded for $[Fe(NH_2trz)_3](2ns)_2 \cdot xH_2O$ in the heating mode in the temperature range 293–400 K. Representative Mössbauer spectra are shown in Fig. 5, whereas detailed values of the Mössbauer parameters resulting from the least-squares fitting procedure are listed in Table 2. The area fractions have been calculated

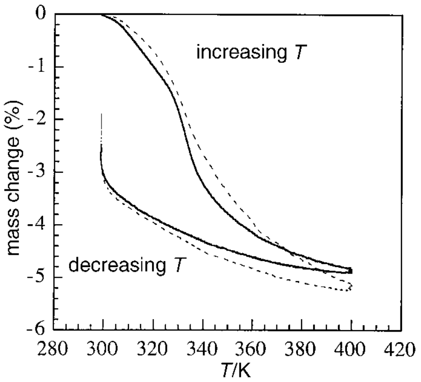

Fig. 4 Thermogravimetric analysis (recorded at 1 K min^{-1}) for $[Fe(NH_2trz)_3](1ns)_2 \cdot xH_2O$ (dotted line) and $[Fe(NH_2trz)_3](2ns)_2 \cdot xH_2O$ (full line)

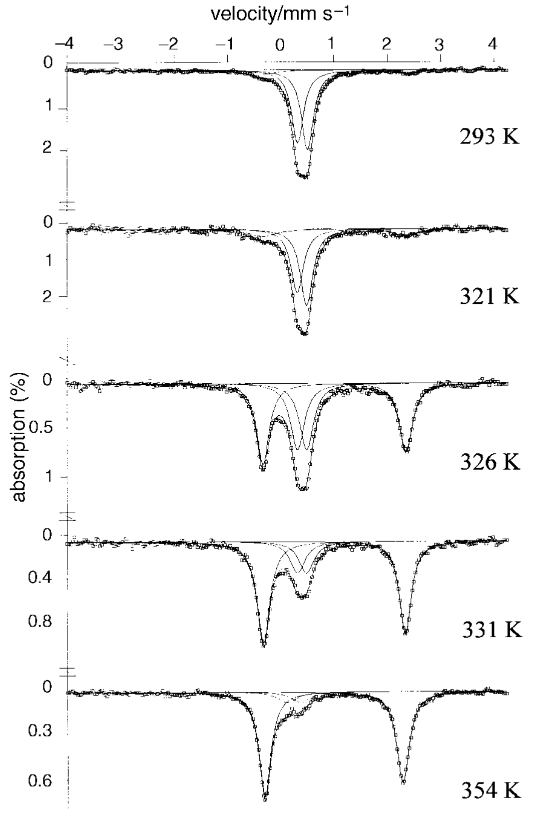

Fig. 5 Selected ^{57}Fe Mössbauer spectra for $[Fe(NH_2trz)_3](2ns)_2 \cdot xH_2O$

assuming identical Lamb–Mössbauer factors for the high-spin and the low-spin state. At 293 K, where according to the optical data the spin transition has not yet started, the spectrum is characterized by a central doublet with a small quadrupole splitting (ΔE_Q) of 0.187(3) mm s^{-1} and an isomer shift (δ) of 0.432(3) mm s^{-1}. The spectral contribution for this doublet is 92%. This doublet may be assigned to Fe^{II} ions in low-spin state. Furthermore, a doublet with a significantly larger quadrupole splitting [2.70(4) mm s^{-1}] and δ of 1.07(4) mm s^{-1} (spectral contribution = 8%) has been observed, which can be attributed to Fe^{II} in high-spin state. At increasing temperatures this Fe^{II} low-spin doublet gradually decreases in intensity, while the doublet with larger quadrupole splitting gains intensity. At 373 K, only 13% of Fe^{II} in low-spin state is present [$\Delta E_Q = 0.341(3)$ mm s^{-1} and $\delta = 0.18(3)$ mm s^{-1}]. The fraction of Fe^{II} in high-spin state is 87% and the doublet is characterized by $\Delta E_Q = 2.532(3)$ mm s^{-1} and $\delta = 0.986(3)$ mm s^{-1}. Similar values for these Mössbauer parameters have also been reported in an extended study on a series of linear iron(II) chain spin-crossover compounds of 4-amino-1,2,4-triazole with the anions NO_3^-, BF_4^-, Br^-, I^- and ClO_4^-.[27] This supports the fact that we are dealing with polynuclear compounds in which the active iron(II) spin-crossover sites are provided by Fe^{II} ions in a six nitrogen environment. The spin transition is neither complete at low temperatures nor at higher temperatures. The percentage of high-spin Fe^{II} detected at lower temperatures may be attributed to 'defects' in the crystal lattice, for instance, caused by terminal Fe^{II} ions having water molecules in the coordination sphere. Indeed, it has already been reported for this type of iron(II) compounds that the residual high-spin Fe^{II} fraction is generally rather high.[10]

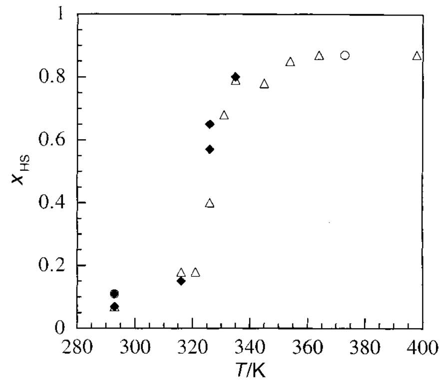

Fig. 6 Temperature dependence of the high-spin area fraction x_{HS} as determined by ^{57}Fe Mössbauer spectroscopy for $[Fe(NH_2trz)_3](2ns)_2 \cdot xH_2O$. Data obtained from the first (○), second (◆) and third (△) heating experiment are included.

Fig. 6 shows the temperature dependence of the relative high-spin area fraction (A_{HS}) as obtained from accumulation of the spectra for about two days. The data obtained from three heating experiments have been included. Interestingly, all measured data fall upon the same curve showing the recovery of the sample after each heating and subsequent cooling. From these data it may be deduced that the transition temperature would be 326 K, a value significantly lower than the 340 K obtained from the optical measurements. On first sight these findings seem to be in contradiction. However, in order to interpret all data recorded during the spin transition it is important to focus on the mechanism of the present Fe^{II} spin crossover. In fact, we are dealing with a non-classical spin-crossover behaviour which is induced by the removal of water molecules (*vide infra*). Clearly, this loss of water molecules is governed by a kinetics that is rather slow at lower temperatures, and increases at higher temperatures. Consequently, the temperature at which the equilibrium value of 50% high-spin and 50% low-spin Fe^{II} is detected significantly depends on the measuring conditions. If the increase of temperature is rather fast, *e.g.* 1 K min^{-1}, in the optical measurements, the transition temperature is found at 340 K. By Mössbauer spectroscopic measurements a time-averaged spectrum is collected over a much longer period of time. This allows the dehydration of

Table 2 Mössbauer parameters (mm s^{-1}) for $[Fe(NH_2trz)_3](2ns)_2 \cdot xH_2O$[a]

T/K	δ(LS)	ΔE_Q(LS)	$\Gamma/2$(LS)	δ(HS)	ΔE_Q(HS)	$\Gamma/2$(HS)	A_{HS}(%)
293	0.432(3)	0.187(3)	0.274(3)	1.07(4)	2.70(4)	0.43(7)	8
316	0.422(4)	0.191(4)	0.261(4)	1.06(3)	2.65(3)	0.39(6)	15
321	0.415(7)	0.178(7)	0.284(7)	1.01(6)	2.67(6)	0.6(1)	18
326	0.413(7)	0.173(7)	0.318(9)	1.017(4)	2.700(4)	0.294(7)	51
331	0.40(1)	0.16(3)	0.34(2)	1.011(3)	2.680(3)	0.284(5)	72
335	0.39(2)	0.12(2)	0.35(3)	1.006(6)	2.664(6)	0.29(1)	80
345	0.26(3)	0.30(3)	0.47(9)	1.002(6)	2.651(6)	0.26(1)	78
354	0.24(4)	0.25(4)	0.44(5)	0.995(2)	2.603(2)	0.278(4)	85
364	0.22(4)	0.30(3)	0.41(8)	0.988(5)	2.561(5)	0.280(9)	87
398	0.18(2)	0.29(2)	0.32(3)	0.971(2)	2.434(2)	0.284(4)	87

[a] = isomer shift, ΔE_Q = quadrupole splitting, $\Gamma/2$ = half-width of the lines, A_{HS} = area fraction of the high-spin doublets.

the sample to occur at a much lower temperature. Therefore, a lower transition temperature of 326 K has been observed. Indeed, these findings are in agreement with the optical measurements performed with a heating rate of 0.1 K min^{-1}, where a transition temperature of 330 K has been found. Furthermore, the optical measurements carried out at a fixed temperature below 340 K (326 K) have shown that the compound is also capable of exhibiting the spin-crossover behaviour at these lower temperatures.

In order to confirm the dynamical character of this non-classical spin transition, additional Mössbauer spectroscopic measurements have been performed. In an experiment, the temperature has been fixed at 326 K and a Mössbauer spectrum has been recorded every 30 minutes. As the measurement proceeds at this fixed temperature, the compound starts to transform to the high-spin state. Probably, the compound slowly starts to loose its lattice water molecules. The Mössbauer data listed in Table 3 show the evolution of the percentage of Fe^{II} in high-spin state as a function of time. The percentages listed correspond to the accumulation of the time-averaged spectra over the total measuring time indicated. After 30 min 40.08% of Fe^{II} in high-spin state is observed. As the time proceeds, the high-spin Fe^{II} fraction gradually increases. Finally, the spectrum recorded after accumulation of the data over 300 min shows 51.00% of high-spin Fe^{II}. Interestingly, the same percentage of high-spin Fe^{II} ions (51%) has been found at 326 K, while accumulating the Mössbauer data for about two days. Apparently, to reach the equilibrium ratio of high-spin and low-spin Fe^{II} under these experimental conditions and at this temperature a measuring time of about 300 min is required, after which this ratio remains stable. These measurements clearly indicate the non-classical character of this spin transition. We may then interpret the identical physical behaviour observed during the three heating experiments (see Fig. 6) by a complete rehydration taking place upon cooling of the sample, which resides in a measurement cell open to the air.

In addition, the significant line broadening of the high-spin absorption observed in the spectrum recorded at 321 K [$\Gamma/2 = 0.6(1)$ mm s^{-1}] may also be indicative of the presence of high-spin Fe^{II} ions in different FeN_6 environments.

For a series of related iron(II) compounds exhibiting classical spin transitions Varnek and Lavrenova have observed a decrease in the isomer shift value for the low-spin state (determined either at 78 K or at 295 K) as a function of increasing transition temperatures.[27] This linear correlation showed a much steeper dependence at 78 than at 295 K. These authors have concluded that this corresponds to a higher degree of covalency of the Fe—N bonds as the transition temperature increases. The δ value at 293 K of 0.432(3) mm s^{-1} for the present compound is somewhat higher than the values for the series of compounds reported by the Russian group, which range from 0.427 to 0.416 mm s^{-1}. This would imply that a transition temperature lower than room temperature would be expected for the present compound. However, it might not be correct to directly compare these δ values, since the variation observed in these values is extremely small and may fall within the uncertainty range. Furthermore, it is certainly not clear whether the present compound would obey this relation, since its non-classical spin-crossover mechanism involving the release of lattice water molecules certainly differs from those of the compounds investigated by the Russian group.

Magnetic measurements

Variable-temperature magnetic susceptibility measurements have been carried out in order to obtain additional informations on the completeness of the non-classical spin transition of $[Fe(NH_2trz)_3](2ns)_2 \cdot xH_2O$. At 307 K the χT value [χ being the magnetic susceptibility per iron(II) ion and T the temperature] is 0.248 cm^3 K mol^{-1}. Upon increasing the temperature, χT attains a value of 3.512 cm^3 K mol^{-1} at 364 K, which roughly corresponds to the value expected for a quintet state.

Concluding remarks

Here we have described a new series of polynuclear iron(II) spin-crossover materials based on the family $[Fe(NH_2trz)_3]X_2 \cdot xH_2O$ (X = 1ns, 2ns, 4OH-1ns, $4NH_2$-1ns and 6OH-2ns). All these compounds which contain derivatives of naphthalene sulfonate as non-coordinating anions show similar characteristics in their spin-crossover behaviour as the previously reported tosylate derivative.[21] In particular, the physical properties of the compounds are determined by the synergy between the Fe^{II} spin-crossover behaviour and a dehydration–rehydration process. For all the compounds, the mechanism describing the physical properties is as follows: at room temperature the thermodynamically stable state for the hydrated compound $[Fe(NH_2trz)_3]$(naphthalene sulfonate derivative)$_2 \cdot xH_2O$ is the low-spin state. Evidently, this low-spin state is stabilized by the hydrated nature of this modification. Indeed, studies on mononuclear iron(II) spin-crossover compounds have already revealed that the low-spin state may be stabilized by interactions with lattice water molecules.[32–35] Upon heating, the compound starts to lose its lattice water molecules, and consequently the stabilization of the low-spin state ceases. For the present series of naphthalene sulfonate compounds, it appears that the destabilization of the low-spin state already occurs while the compounds are not yet completely dehydrated. At first sight this may seem to be in contrast with $[Fe(hyetrz)_3]$(3-nitrophenylsulfonate)$_2 \cdot xH_2O$, where optical and thermogravimetric measurements carried out at an identical heating rate (1 K min^{-1}) have shown that no lattice water molecules are present in the sample as the low-spin to high-spin transition occurs in an extremely abrupt way at 370 K.[29] However, recently, new experiments on $[Fe(hyetrz)_3]$(3-nitrophenylsulfonate)$_2 \cdot xH_2O$ have been carried out: the optical data recorded while fixing the temperature at a value below 370 K show that also at these lower

Table 3 Evolution of the Mössbauer parameters (mm s^{-1}) as a function of time at 326 K for $[Fe(NH_2trz)_3](2ns)_2 \cdot xH_2O^a$

t/min	δ(LS)	ΔE_Q(LS)	$\Gamma/2$(LS)	δ(HS)	ΔE_Q(HS)	$\Gamma/2$(HS)	A_{HS}(%)
30	0.41(3)	0.14(3)	0.28(3)	0.99(3)	2.71(3)	0.26(4)	40.08
60	0.41(1)	0.16(1)	0.28(2)	1.01(2)	2.69(2)	0.26(3)	40.20
90	0.41(1)	0.16(1)	0.31(2)	1.01(1)	2.69(1)	0.28(2)	41.82
120	0.41(1)	0.17(1)	0.28(1)	1.01(1)	2.03(1)	0.27(2)	43.39
150	0.41(1)	0.19(1)	0.28(1)	1.01(1)	2.70(1)	0.28(2)	43.62
180	0.41(1)	0.19(1)	0.28(1)	1.01(1)	2.71(1)	0.27(1)	44.45
210	0.412(9)	0.193(9)	0.29(1)	1.014(9)	2.711(9)	0.29(1)	46.65
240	0.414(9)	0.188(9)	0.29(1)	1.015(9)	2.708(9)	0.30(1)	47.81
270	0.41(1)	0.18(1)	0.29(1)	1.01(1)	2.701(1)	0.30(1)	48.51
300	0.413(7)	0.173(7)	0.318(9)	1.017(4)	2.700(4)	0.294(7)	51.00

[a] δ = Isomer shift, ΔE_Q = quadrupole splitting, $\Gamma/2$ = half-width of the lines, A_{HS} = area fraction of the high-spin doublets.

temperatures the material slowly transforms to the high-spin state.[36] Therefore, also in that case the spin transition is associated with the loss of lattice water molecules. There are indications that $[Fe(NH_2trz)_3](tosylate)_2 \cdot xH_2O$ has similar characteristics for the low-spin to high-spin transition taking place at 361 K. [21] For the series of compounds with derivatives of naphthalene sulfonate as anion, the transition temperatures as determined by optical measurements using a velocity of 1 K min^{-1} are in the range 330–340 K. Obviously, these lower transition temperatures reflect the easier destabilization of the low-spin state in compounds containing naphthalene sulfonates as compared to phenyl sulfonates.

From the proposed mechanism it follows that this spin-crossover behaviour should be entirely governed by the removal of lattice water molecules. Indeed, various experiments have shown that the observed transition temperatures depend very much on the measurement conditions, in particular the heating rate.

For all hydrated naphthalene sulfonate compounds, the transition temperatures for this first low-spin to high-spin transition all occur in a very narrow temperature range. This indicates that the destabilization of the low-spin state or alternatively, the removal of the lattice water molecules occurs in a similar way. This is also supported by the results of the thermogravimetric studies showing very similar dehydration characteristics for the 1ns and 2ns derivatives (see Fig. 4). Therefore, it may be supposed that the anions of the naphthalene sulfonate type also have similar capabilities for hydrogen bonding with the lattice water molecules. On the other hand, compounds containing derivatives of phenyl sulfonate generally show higher transition temperatures.[21,29] Clearly, in these latter compounds the loss of water molecules is more difficult, which may result from a different way of incorporation of the anions in the crystal lattice allowing stronger hydrogen-bonding interactions with the lattice water molecules.

Furthermore, in view of the striking similarities (identical transition temperature for the first low-spin to high-spin transition) between the spin-crossover behaviour of tosylate compounds containing the 4-amino-1,2,4-triazole[21] and 4-alkyl-substituted 1,2,4-triazoles,[37] it may be excluded that hydrogen bonding interactions involving the 4-amino substituent and the lattice water molecules are the determining factor in maintaining these lattice water molecules.

This leads us to the idea that the lattice water molecules in such compounds are bound in a very loose fashion, which might be comparable to the way water molecules are incorporated in zeolites. Indeed, a zeolite is an aluminosilicate with a structure enclosing cavities occupied by large ions and water molecules, both having considerable freedom of movement which permits ion exchange and reversible dehydration. For $[Fe(NH_2trz)_3](aryl\ sulfonate)_2 \cdot xH_2O$ one can propose that the shape and size of the different aryl sulfonates induce the pore size of the polymeric compounds which, in turn, lead to a considerable variation in the rate of water uptake or release. It may be proposed that the stabilization of the low-spin state of Fe^{II} by lattice water molecules results from a cooperative solvation, where hydrogen bonding of these water molecules to the sulfonate group increases the nucleophilicity of the water oxygen atom, and hence its interaction with Fe^{II} maintained in its low-spin state.

Interestingly, the thermogravimetric studies also show that the compounds are easily being rehydrated. Therefore, the spin transition from high-spin to low-spin may also be induced by rehydration. This feature has been tested by several experimental techniques. For the 2ns derivative, the results of the optical, magnetic susceptibility, and ^{57}Fe Mössbauer spectroscopic measurements recorded on a fresh sample have been found to be exactly identical to those obtained on an already measured (*i.e.* dehydrated) sample left in contact with the air for a few minutes. Evidently, ambient vapour pressure is sufficient to completely rehydrate the dehydrated sample back to its initial state. This process of spin crossover induced by dehydration (low-spin to high-spin) and reversible by hydration (high-spin to low-spin) is entirely reproducible. In fact this process may be regarded as a self-assisted process related to the solvate-induced change of spin state, which has already been reported for $[Fe(hyetrz)_3](3\text{-nitrophenylsulfonate})_2 \cdot 3H_2O$.[29]

The dehydrated modifications show spin-crossover behaviour at lower temperatures. The genuine spin transition with stable hysteresis is centered at temperatures ranging from 229 to 297 K for the various compounds. The differences observed in transition temperatures within the series may be due to slight structural variations induced by the anions.

For $[Fe(NH_2trz)_3](2ns)_2$ a stable hysteresis of 14 K centered around 290 K, *i.e.* in close vicinity to room temperature, has been found. Up to now, such features have been observed for a few compounds with 4-amino-1,2,4-triazole. For $[Fe(NH_2trz)_3](CH_3SO_3)_2 \cdot H_2O$, Bronisz *et al.* reported a hysteresis of 26 K centered around 282 K.[20] Surprisingly, these authors also reported that the dehydrated form of this compound shows spin-crossover behaviour with a small hysteresis (4–8 K) centered around *ca.* 296 K.[20] Furthermore, $[Fe(NH_2trz)_3](tosylate)_2$ has been reported to have a hysteresis of 17 K around 290 K.[21] Moreover, the mixed-ligand material $[Fe(Htrz)_{3-3x}(NH_2trz)_{3x}](ClO_4)_2 \cdot xH_2O$ has been reported to exhibit hysteresis of 17 K centered around 304 K. [14] Therefore, $[Fe(NH_2trz)_3](2ns)_2$ represents one of the very few iron(II) spin-crossover materials showing a spin transition and an associated thermochromic effect in close vicinity of room temperature with hysteresis.

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