

Cooperative Spin-Crossover Behaviour in Polymeric 1D Fe^{II} Coordination Compounds: [{Fe(tba)₃}X₂] $\cdot$ *n*H₂O

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A new family of 1D cooperative spin-crossover polymers with general formula [{Fe(tba)₃}X₂] $\cdot$ *n*H₂O [tba = *N*-(4*H*-1,2,4-triazol-4-yl)benzamide; X = CF₃SO₃[−], *n* = 2 (**1**), *n* = 0 (**4**); BF₄[−], *n* = 3 (**2**), *n* = 0 (**5**); 4-CH₃C₆H₄SO₃[−], *n* = 3 (**3**), *n* = 0 (**6**)] has been synthesised and characterised using a series of spectroscopic methods, X-ray powder diffraction, magnetic susceptibility measurements and differential scanning calorimetry. The copper analogue of **1**, [{Cu(tba)₃}(CF₃SO₃)₂] $\cdot$ 3H₂O (**7**), has also been synthesised and its crystal structure solved at 293 K. Compound **7** crystallises in the *P*1 space group. The bidentate *N*-(4*H*-1,2,4-triazol-4-yl)benzamide ligand bridges the copper ions through the 1,2-nitrogen positions leading to a one-dimensional infinite polymer. The EXAFS data collected at 80 K for **1** agree perfectly with a linear chain structure, as observed for **7**, with [Fe(tba)₃] chromophores linked to each other through the adjacent nitrogen atoms of three *N*-(4*H*-1,2,4-triazole-4-yl)benzamide ligands. IR spectroscopic studies confirm the retention of the C_{2v} symmetry for the triazole rings in **2** and **3**, thereby suggesting a similar chainlike arrangement in these compounds. Compound **1** is

low spin (LS) at room temperature while **2** and **3** are high spin (HS). The latter two complexes undergo cooperative thermal spin transition at *T*_c↓ = 250 and *T*_c↑ = 258 K in **2** and *T*_c↓ = 226 and *T*_c↑ = 238 K in **3**. The spin transition in **2** and **3** is accompanied by a change of colour from white in the HS state to violet in the LS state. The thermodynamic parameters associated with the spin transition estimated from DSC measurements are Δ*H* = 17.8 (**2**) and 14.6 kJ mol^{−1} (**3**), and Δ*S* = 67.2 (**2**) and 63.5 J K^{−1} mol^{−1} (**3**). In contrast, the dehydrated compounds **4**, **5** and **6** show very different spin-transition behaviour. Complex **4** exhibits an abrupt spin transition centred at room temperature and is accompanied by a relatively large hysteresis loop with a width of 25 K (Δ*H* = 19.7 kJ mol^{−1} and Δ*S* = 65.6 J K^{−1} mol^{−1}). Like **2** and **3**, **4** shows a dramatic colour change upon the spin transition. Complex **5** shows a continuous and incomplete spin transition, and **6** is HS over the whole temperature range investigated (10–400 K).

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Introduction

Spin crossover (SCO) has turned out to be a particularly appealing phenomenon as it offers one of the best examples of molecular bistability. This reversible change between low-spin (LS) and high-spin (HS) states driven by variation of temperature and/or pressure or also by light irradiation is

mainly observed in pseudo-octahedral iron(II) coordination complexes. SCO compounds have distinct magnetic and optical properties, dielectric constant, colour and structure in the HS and LS states. These properties may be altered drastically in a narrow temperature range for cooperative transitions.^[1–4] Furthermore, hysteresis accompanies a first-order spin transition (ST) when the structural changes are transmitted cooperatively throughout the whole solid.

SCO materials are potentially useful for rewritable optical, thermal or pressure memories at a nanometric scale due to their switching properties.^[5–7] The necessary conditions that an SCO material must fulfil for the construction of devices for thermal displays or recording data include abruptness of spin transition with hysteresis, room-temperature operation, change of colour and chemical stability. Prototypes of thermal displays based on the 1D SCO polymeric systems [Fe(4-Rtrz)₃](ClO₄)₂, [Fe(4-R¹trz)_{3–3x}(4-R²trz)_{3x}](A)₂ $\cdot$ *n*H₂O and [Fe(4-Rtrz)₃](A^{1–x}A^{2–x})₂ $\cdot$ *n*H₂O (4-Rtrz = 4-substituted-1,2,4-triazole), where *x* ≤ 1 and *n* ≥ 0, have been described.^[6,7] These salts, and their closely related

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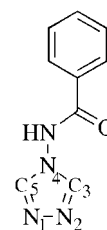
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analogs $[\text{Fe}(\text{Htrz})_3](\text{A})_2$, have been subjected to intense studies because of their interesting properties.^[8] Similarly, 4-substituted triazole ligands like 4-amino-1,2,4-triazole,^[9] 4-(2'-hydroxyethyl)-1,2,4-triazole (hyetrz),^[10] 4-*n*-alkyl-1,2,4-triazoles^[11] and 4-(3'-hydroxypropyl)-1,2,4-triazole (hyptrz)^[12] have also afforded interesting 1D SCO polymers. This family of polymeric compounds has recently been reviewed.^[13] Several of the polymers belonging to this family undergo cooperative SCO at close to room temperature with large hysteresis loops. Furthermore, these materials display dramatic changes in colour from purple to white upon spin transition $\text{LS} \leftrightarrow \text{HS}$, which makes them particularly attractive for memory and sensor devices.^[6,7] Other groups linked to the 4-substituted triazole ligands have yielded 1D SCO polymers exhibiting liquid-crystal properties,^[14] Langmuir–Blodgett films showing spin transition and SCO gels.^[15b,15c] Two more kinds of one-dimensional (1D) Fe^{II} SCO compounds can be distinguished depending on the nature of the N-donating groups involved in the bridges, namely those bearing tetrazole^[13,16,17] or pyridine groups.^[18–21]

In our search for new SCO systems, and in light of the suitability of triazole-based ligands for achieving cooperative spin transitions, we chose the ligand *N*-(4*H*-1,2,4-triazol-4-yl)benzamide (tba). Herein we present the synthesis and physical characterisation by means of magnetic susceptibility measurements, Mössbauer spectroscopy, differential scanning calorimetry, EXAFS and XRD analysis of a new family of 1D spin crossover polymers with general formula $[\{\text{Fe}(\text{tba})_3\}\text{X}_2] \cdot n\text{H}_2\text{O}$ [Scheme 1; $\text{X} = \text{CF}_3\text{SO}_3^-$, $n = 2$ (**1**), $n = 0$ (**4**); BF_4^- , $n = 3$ (**2**), $n = 0$ (**5**); $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$, $n = 3$ (**3**), $n = 0$ (**6**)]. The copper analogue $[\{\text{Cu}(\text{tba})_3\}(\text{CF}_3\text{SO}_3)_2] \cdot 3\text{H}_2\text{O}$ (**7**) has also been synthesised and its crystal structure solved at 293 K.



Scheme 1. Ligand *N*-(4*H*-1,2,4-triazol-4-yl)benzamide (tba).

Results and Discussion

Crystal Structure of $[\{\text{Cu}(\text{tba})_3\}(\text{CF}_3\text{SO}_3)_2] \cdot 3\text{H}_2\text{O}$ (**7**)

As discussed in the Experimental Section, all attempts to obtain single crystals of the $[\{\text{Fe}(\text{tba})_3\}\text{X}_2] \cdot n\text{H}_2\text{O}$ compounds were unsuccessful. However, it proved possible to obtain single crystals of the copper analog $[\{\text{Cu}(\text{tba})_3\}(\text{CF}_3\text{SO}_3)_2] \cdot 3\text{H}_2\text{O}$ (**7**). X-ray diffraction data were collected at 293 K and the structure was solved by direct methods using SHELXS-97^[22] and refined by full-matrix least squares on F^2 using SHELXL-97. Due to the medium quality of the single crystals it was not possible to decrease the *R* factor of the structure below 0.1749. The powder diffraction pattern of **7** was collected at 293 K, where it matches exactly that calculated from the single crystal data (Figure S1, Supporting Information). Compound **7** crystallises in the triclinic space group $P\bar{1}$. The crystallographic data are provided in the Experimental Section and a selection of bond lengths and angles is given in Table 1. Figure 1 displays a fragment of the 1D polymer **7** together with the corresponding atom-numbering scheme. The unit cell contains four crystallographically independent copper ions with an occupancy factor of 0.5 for Cu1 and Cu4, nine tba

Table 1. Selected bond length [Å] and angles [°] for **7** at 293 K.

Cu1–N14	2.011(9)	Cu3–N18	2.016(9)	Cu4–N30	2.008(10)
Cu1–N71	2.151(10)	Cu3–N19	2.029(10)	Cu4–N17	2.036(10)
Cu1–N24	2.242(10)	Cu3–N15	2.043(11)	Cu4–N25	2.035(11)
Cu2–N16	2.044(10)	Cu3–N21	2.080(10)	Cu4–N8	2.053(9)
Cu2–N11	2.159(10)	Cu3–N22	2.329(10)	Cu4–N23	2.329(10)
Cu2–N13	2.259(10)	Cu3–N7	2.365(10)	Cu4–N20	2.351(10)
N14–Cu1–N14 ^[a]	180.0(5)	N18–Cu3–N19	176.7(4)	N30–Cu4–N17	177.7(4)
N14–Cu1–N24	91.0(4)	N18–Cu3–N15	89.1(4)	N30–Cu4–N25	88.9(4)
N14–Cu1–N24 ^[a]	89.0(4)	N19–Cu3–N15	92.3(4)	N17–Cu4–N25	91.4(4)
N24–Cu1–N24 ^[a]	180.0(5)	N18–Cu3–N21	90.5(4)	N30–Cu4–N8	91.3(4)
N14–Cu1–N71	90.0(4)	N19–Cu3–N21	88.0(4)	N17–Cu4–N8	88.4(4)
N71–Cu1–N71 ^[a]	180.0(4)	N15–Cu3–N21	179.6(4)	N25–Cu4–N8	179.5(4)
N71–Cu1–N24	93.5(4)	N18–Cu3–N22	92.1(4)	N30–Cu4–N23	90.7(4)
N71 ^[a] –Cu1–N24	86.5(4)	N19–Cu3–N22	90.8(4)	N17–Cu4–N23	91.6(4)
N16–Cu2–N16 ^[a]	180.0(4)	N15–Cu3–N22	92.8(4)	N25–Cu4–N23	91.9(4)
N16–Cu2–N11	88.3(4)	N21–Cu3–N22	87.0(4)	N8–Cu4–N23	87.7(4)
N16–Cu2–N11 ^[a]	91.7(4)	N18–Cu3–N7	90.2(4)	N30–Cu4–N20	90.1(4)
N11–Cu2–N11 ^[a]	180.0(0)	N19–Cu3–N7	86.9(4)	N17–Cu4–N20	87.6(4)
N16–Cu2–N13	90.4(4)	N15–Cu3–N7	89.3(4)	N25–Cu4–N20	89.1(4)
N16–Cu2–N13 ^[a]	89.6(4)	N21–Cu3–N7	90.9(4)	N8–Cu4–N20	91.3(3)
N11–Cu2–N13	93.1(4)	N22–Cu3–N7	176.9(3)	N23–Cu4–N20	178.7(4)
N11–Cu2–N13 ^[a]	86.9(4)				
N13–Cu2–N13 ^[a]	180.0(0)				

[a] $i = 1 - x, 1 - y, -z$

ligands, six CF₃SO₃[−] anions and nine water molecules. The bidentate *N*-(4*H*-1,2,4-triazol-4-yl)benzamide ligand bridges the copper ions through the 1- and 2-nitrogen atoms to form a one-dimensional infinite polymer. Each Cu^{II} ion is coordinated to six N atoms belonging to six tba ligands with pseudo-octahedral symmetry, as indicated by the bond lengths and angles (Table 1). The axial bond lengths are notably larger than the equatorial ones due to the Jahn–Teller distortion, which are in the range 2.242(10)–2.351(10) Å for the four Cu^{II} ions. The average Cu^{II}–N

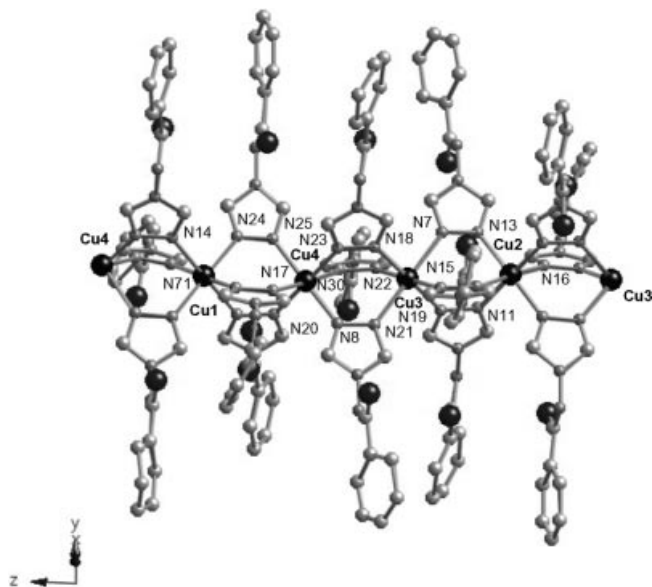


Figure 1. Fragment of the 1D polymer **7** together with the corresponding atom numbering scheme.

bond length is 2.134, 2.154, 2.143 and 2.135 Å for Cu1, Cu2, Cu3 and Cu4, respectively. The Cu–Cu distance through the tba bridge is 3.8915(12) Å. These structural parameters are similar to those observed previously for other Cu^{II}–triazole systems.^[23]

Figure 2 illustrates the crystal packing of **7** in the *xy* plane. The molecular crystal packing of **7** can be described as an infinite hexagonal array of [Cu(tba)₃]²⁺ linear chains along the *z* direction, with water molecules and CF₃SO₃[−] counterions in the vacancies. The distance between the Cu^{II} linear chains is 17.816(2) Å. There are no intermolecular interactions between the chains through the phenyl group of the tba ligands or between the counterions, the water molecules and the tba ligands. The shortest distance between the carbon atoms of two phenyl groups belonging to adjacent chains is 5.219(2) Å. The water molecules are located around the Cu^{II} linear chain at a distance to the Cu^{II} ion between 4.509(2) and 4.951(2) Å.

X-ray Powder Diffraction of Compounds 1–3 and 7

X-ray powder patterns of **1–3** and **7** were recorded at 293 K (Figure 3). Only two compounds have similar profiles, namely compounds **1** and **7**, where small discrepancies between weak peaks can be interpreted as being due to the hydration numbers of both compounds. The profiles of compounds **2** and **3** are not similar and therefore they are not isostructural with **1**. Only two intense peaks located at about the same values (5–6° and 23–24°) were found to be common to all the patterns. This, together with the fact that similar patterns are only found for the triflate complexes of iron(II) and copper(II), shows that, although a chain structure seems to be present in all of these compounds, the dif-

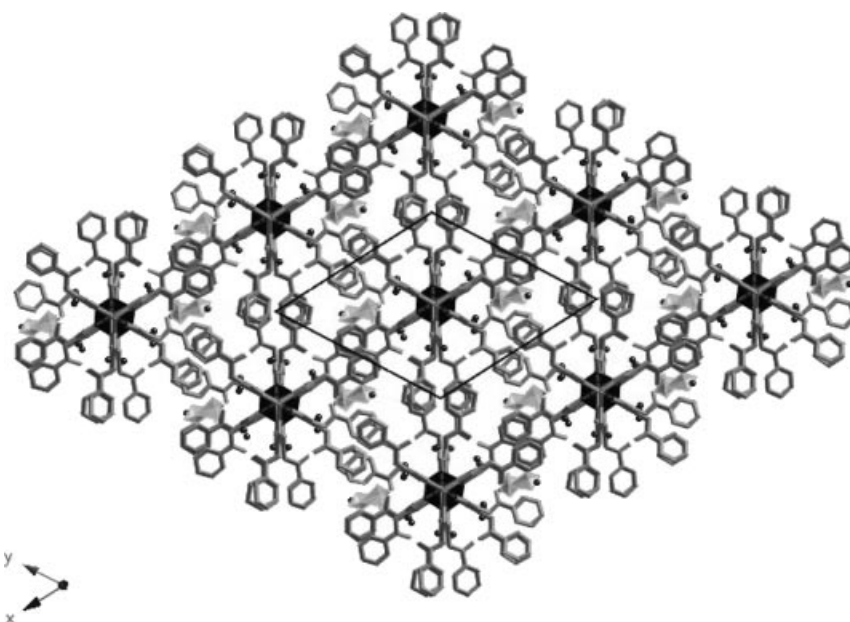


Figure 2. View of the crystal packing of compound **7** in the *xy* plane depicting the packing of the CF₃SO₃[−] anions (light grey polyhedra) and water molecules (black spheres) between the cationic linear chains.

ferent packing and lattice arrangements caused by the different nature of the anions yield completely different crystallographic patterns.^[24]

IR Spectroscopic Studies of 1–3 and 7

Information about the coordination modes of tba in complexes 1–3 and 7 can be derived directly from the room-temperature IR spectra. The intense peaks located at 627, 625, 625 and 628 cm^{-1} for 1–3 and 7, respectively, corre-

spond to torsion vibrations of the triazole rings coordinated in a bridging fashion through N(1) and N(2) (Scheme 1) to neighbouring Fe^{II} or Cu^{II} ions.^[25a] The band at 1207 cm^{-1} assigned to the exocyclic N–N bond stretching in uncoordinated tba ligand should be shifted to higher frequency upon bidentate coordination. Indeed, the value of this band in the linear coordination polymers is typically 15–30 cm^{-1} higher than in the free ligand^[25b] (1228, 1222, 1223 and 1227 cm^{-1} for compounds 1–3 and 7, respectively). These findings confirm the one-dimensional polymeric organisation of 1 and 7 and strongly suggest the same for compounds 2 and 3.

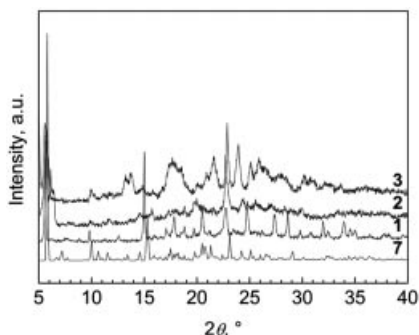


Figure 3. XRD powder diffraction patterns of complexes 1–3 and 7 at 293 K.

EXAFS and XANES Characterisation of Compound 1

The normalised XANES spectrum of 1 recorded at 80 K is typical for an octahedral complex of iron(II) (Figure 4a). It includes absorption in the pre-edge region P assigned to the symmetry-forbidden electronic dipolar $1s \rightarrow 3d$ transition.^[26] The first strong absorption (peak A) is located at 7130 eV and can be attributed to a metal $1s \rightarrow 4p$ dipole-allowed transition.^[26] Further intense shoulders B and M with energies of 7142 and 7154 eV, respectively, are caused by multiple electron-scattering processes.^[27] Finally, absorp-

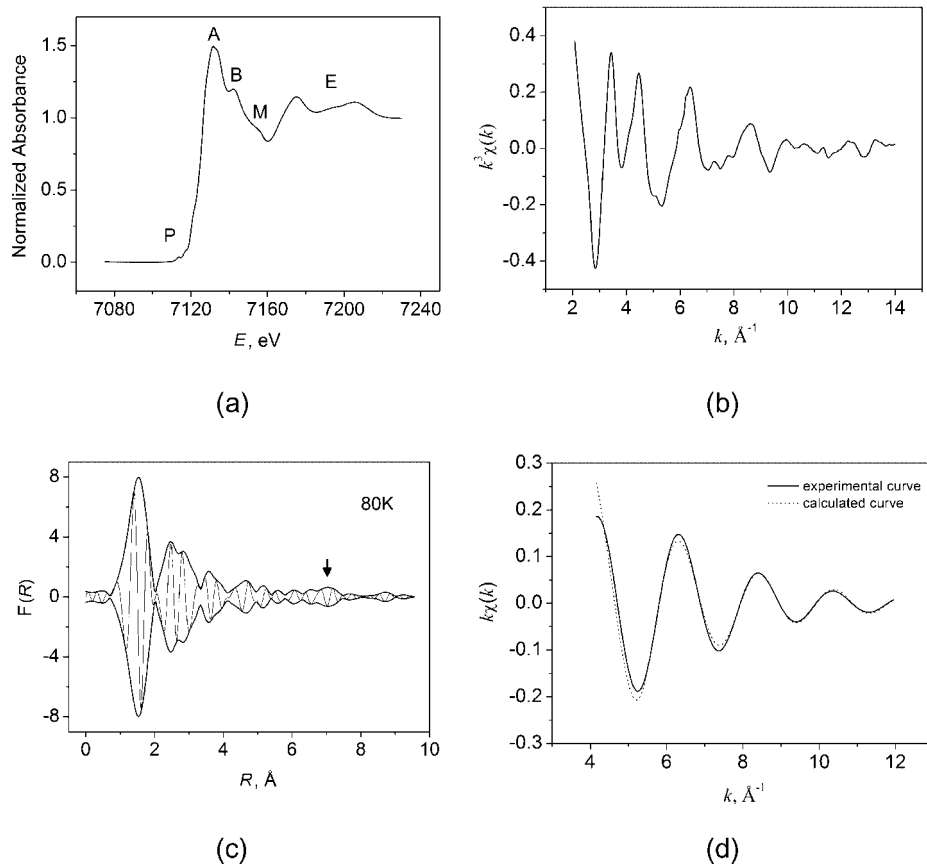
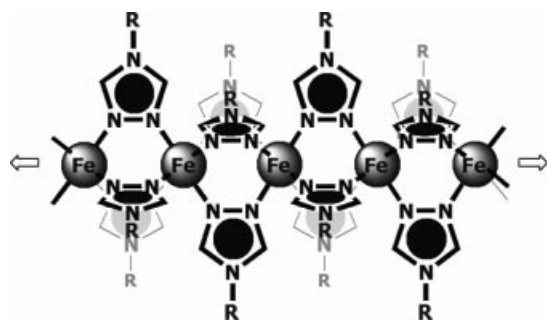


Figure 4. (a) XANES spectrum of complex 1 at 80 K. P: pre-edge; A: top of the edge; B and M: shoulders; E: EXAFS oscillations. (b) $k^3\chi(k)$ spectrum of complex 1. (c) Fourier transforms of the EXAFS spectrum of complex 1 at 80 K including the modulus and imaginary parts. The arrow indicates the peak at about 7 Å that corresponds to the multiple scattering path Fe–Fe–Fe. (d) Comparison of the experimental and calculated $k\chi(k)$ values for the first filtered shell of complex 1 (solid line: experimental; dashed line: fitting curve).

tion E is at the frontier of the XANES and EXAFS regions and, for such molecular systems, is mainly determined by scattering processes inside the first coordination shell. The EXAFS oscillation positioned at relatively high energy (7205 eV) confirms the low-spin character of the iron centre.

The EXAFS spectrum of **1** measured at 80 K is shown in Figure 4b, with its Fourier transform displayed in Figure 4c. The EXAFS signal provides direct information about the radial distribution of the backscattering atoms around the absorbing atom. Similar materials have been investigated by means of EXAFS analysis in previous studies and their linear local structure deduced.^[28–30] The complex shown in Scheme 2 is composed of triazole moieties and iron(II) ions arranged in a one-dimensional fashion, with the N–N groups of the triazoles bridging adjacent metal centres. The spectrum at 80 K consists of five main peaks (Figure 4c). The first intense peak at 1.53 Å can be attributed to the first coordination shell N₆(1) of the iron ion. The peak value is located at a short distance, thus clearly indicating the LS state. Several peaks are distinguishable in the region between 2 and 4 Å. These correspond to several kinds of distances such as Fe–N(2), C(5), Fe–N(3), C(4) (Scheme 1), and Fe with its two nearest Fe neighbours.^[28] According to a previous study,^[29] the peak at about 7.0 Å for the LS triazole-based complexes is ascribed to the Fe–Fe–Fe alignment, the intensity of which is strongly enhanced due to the multiple-scattering focusing effect of the collinearly arranged Fe chains.^[28] The presence of this peak provides confirmation of the polymeric structure of **1**.



Scheme 2. Drawing of the linear chain structure of [Fe(R-trz)₃]²⁺_∞.

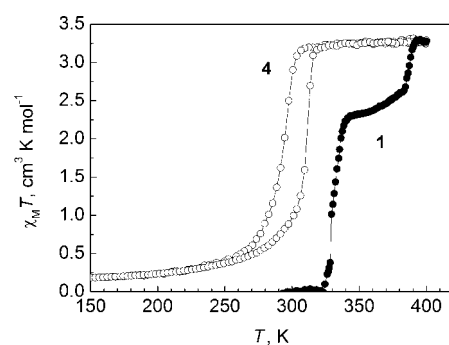
A curve-fitting analysis was performed for the first coordination sphere of iron (Figure 4d). The fitting variables were the Fe–N distance *R*, the edge energy shift ΔE_0 and the Debye–Waller factor σ ; the coordination number *N* was fixed to 6. The obtained values were *R* = 1.96 Å, ΔE_0 = 1.8 eV, σ = 0.068 Å with goodness of fit ρ = 1.2%. The value of the Fe–N contact distance is in good agreement with previously reported data for the same type of compounds.^[28,30]

Magnetic Properties of Compounds 1–6

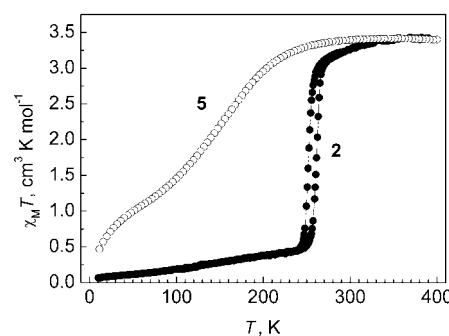
The magnetic data expressed in the form of $\chi_M T$ vs. *T* plots, where χ_M is the molar magnetic susceptibility and *T*

the temperature, are shown in Figure 5 for compounds **1**–**6**. The temperature dependence of the magnetic susceptibility was recorded at a rate of 2 K min^{−1}. Compound **1** is in the LS configuration at 290 K, as shown by the low $\chi_M T$ value. Upon heating, $\chi_M T$ increases abruptly, reaching a value of 3.29 cm³ K mol^{−1} at 400 K. TGA experiments have shown that dehydration takes place in the same temperature region where the change of spin state occurs (Figure S2, Supporting Information). The dehydration and change of spin state take place in two distinct steps. A synergy between dehydration and spin-state change, as observed in this material, has been reported in several other cases.^[1,6,14]

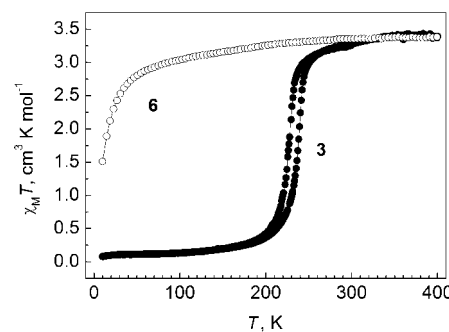
The $\chi_M T$ value for compound **2** at 330 K is 3.41 cm³ K mol^{−1}, which falls into the range of values expected for an Fe^{II} compound in the high-spin configuration. This value decreases abruptly at around 260 K as a conse-



(a)



(b)



(c)

Figure 5. Magnetic properties of compounds **1**–**6** in the form of $\chi_M T$ vs. *T* plots.

quence of a spin transition, reaching a value of $0.43 \text{ cm}^3 \text{ K mol}^{-1}$ at 230 K ($T_c \downarrow = 250 \text{ K}$). The transition is complete at this temperature as the magnetic susceptibility decreases only very gradually down to $0.07 \text{ cm}^3 \text{ K mol}^{-1}$ at 10 K, thus indicating that almost all the Fe^{II} ions are in the LS state. In the warming mode, the measurement reveals a hysteresis width of 8 K ($T_c \uparrow = 258 \text{ K}$).

Like **2**, compound **3** undergoes an abrupt spin transition, although at lower temperatures ($T_c \downarrow = 226$ and $T_c \uparrow = 238 \text{ K}$). The $\chi_M T$ value for **3** at 290 K is $3.30 \text{ cm}^3 \text{ K mol}^{-1}$, which diminishes slightly on lowering the temperature to 250 K ($3.07 \text{ cm}^3 \text{ K mol}^{-1}$). $\chi_M T$ falls to $0.65 \text{ cm}^3 \text{ K mol}^{-1}$ upon further cooling as a consequence of a change of spin state of approximately 90% of the Fe^{II} ions. The $\chi_M T$ value at 145 K is $0.19 \text{ cm}^3 \text{ K mol}^{-1}$, which corresponds to about 95% LS Fe^{II} .

The magnetic properties of the dehydrated complexes **4–6** were also investigated (Figure 5). Dehydration of these complexes is complete at 400 K (Figure S2, Supporting Information). The samples were therefore heated from 300 to 400 K and then kept at this temperature for 15 min in the SQUID magnetometer. Subsequently, the magnetic susceptibility of the dehydrated samples was recorded from 400 K down to 10 K and again up to 400 K. Compound **4** exhibits an abrupt spin transition centred at room temperature. The $\chi_M T$ value at 400 K is $3.28 \text{ cm}^3 \text{ K mol}^{-1}$, which remains practically constant down to the vicinity of $T_c \downarrow$. $\chi_M T$ diminishes suddenly at 300 K, reaching a value of $0.39 \text{ cm}^3 \text{ K mol}^{-1}$ at 250 K and $0.090 \text{ cm}^3 \text{ K mol}^{-1}$ at 10 K. The critical temperatures in the cooling and warming mode ($T_c \downarrow$ and $T_c \uparrow$) are 284 and 309 K, respectively. It is worthwhile mentioning the relatively large hysteresis width of 25 K that accompanies the spin transition in **4**. The reproducibility of the thermal hysteresis loops in **2–4** was confirmed, and they are perfectly reproducible after two or three cooling/warming cycles. Moreover, the spin transition in **2–4** is accompanied by a change of colour from white (HS state) to violet (LS state).

Compound **5** exhibits a very gradual and incomplete spin transition. The $\chi_M T$ value at around 400 K shows that all molecules are in the HS state ($3.41 \text{ cm}^3 \text{ K mol}^{-1}$). This value remains practically constant down to 250 K, where the HS $\rightarrow$ LS transition sets in. A further decrease of the temperature gives rise to a progressive decrease of the magnetic susceptibility due to a spin transition of approximately 50% of the Fe^{II} ions. This spin transition is kinetically blocked below 70 K, and the decrease of $\chi_M T$ below this temperature is due most probably to zero-field splitting (ZFS) of the 50% of Fe^{II} ions that remain in the HS state ($S = 2$). The temperature dependence of the magnetic susceptibility of compound **6** shows a high spin behaviour over the whole temperature range under study (10–400 K). The $\chi_M T$ value at 400 K is $3.38 \text{ cm}^3 \text{ K mol}^{-1}$ and remains constant down to 100 K, where it diminishes most probably due to ZFS.

A weak antiferromagnetic coupling between high-spin iron(II) ions for **5** and **6** cannot be excluded from this explanation. This could, in part, also be responsible for the decrease of the susceptibility on lowering the temperature

since a similar behaviour has been found in the triazole-based copper analogue **7** (Figure S3, Supporting Information) as well as in another copper-based triazole polymer.^[23a]

Mössbauer Spectroscopy of Compounds 1–4

Table 2 collects the Mössbauer parameter values and percentages of populations in the HS and LS states for compounds **1–4** recorded at different temperatures. The Mössbauer spectrum of compound **1** was recorded at 80 K (Figure 6a). This spectrum clearly indicates the presence of only one slightly asymmetrical doublet characterised by an isomer shift and a quadrupole splitting typical of LS iron(II), which matches the data from the magnetic measurements of **1**. The Mössbauer spectrum of **4** recorded at 80 K shows a doublet with parameters typical for HS iron(II) (Table 2), the intensity of which increases dramatically upon heating up to 330 K. The spectrum also reveals the presence of LS Fe^{II} ions, thereby confirming the incomplete character of the spin transition.

Table 2. Mössbauer parameters (IS and ΔE_Q) for **1–4** at different temperatures.

	T [K]	Spin state	IS [mm s ⁻¹]	ΔE_Q [mm s ⁻¹]	A [%]
1	80	d, LS	0.49(0)	0.23(1)	100
2	80	d, LS	0.51(0)	0.27(0)	97
		d, HS	1.22(0)	3.40(0)	3
3	290	d, LS	0.29(0)	0.15(0)	3
		d, HS	1.04(0)	2.80(1)	97
	145	d, LS	0.52(1)	0.28(1)	95
		d, HS	1.15(1)	3.35(0)	5
	290	d, LS	0.40(1)	0.14(0)	8
		d, HS	1.05(0)	2.85(1)	92
4	80	d, LS	0.51(0)	0.25(1)	95
		d, HS	1.17(1)	3.29(0)	5
	330	d, LS	0.32(0)	0.20(0)	14
		d, HS	1.02(0)	2.71(1)	86

The Mössbauer spectra of **2** were recorded above and below T_c (Figure 7a). The spectrum at 290 K shows mainly a doublet characteristic of the HS state of Fe^{II} . The Mössbauer spectrum recorded at 80 K clearly evidences the change of spin state. After cooling, the HS doublet almost disappears and the LS fraction increases significantly. Like the magnetic measurements, the Mössbauer analysis proves that almost 100% of the Fe^{II} ions undergo a spin transition in **2**.

The Mössbauer spectra of **3** were recorded at 290 and 145 K (Figure 7b). Two doublets are observed at 290 K corresponding to the HS and LS states of the Fe^{II} ions. The analysed spectrum at 290 K yields a relative population of 95% HS and 5% LS states. There is a clear inversion of the population distribution at 145 K due to spin transition: practically all the Fe^{II} ions are in the LS state at this temperature (92%). The Mössbauer spectral analyses of **1–4** agree well with the above reported magnetic properties.

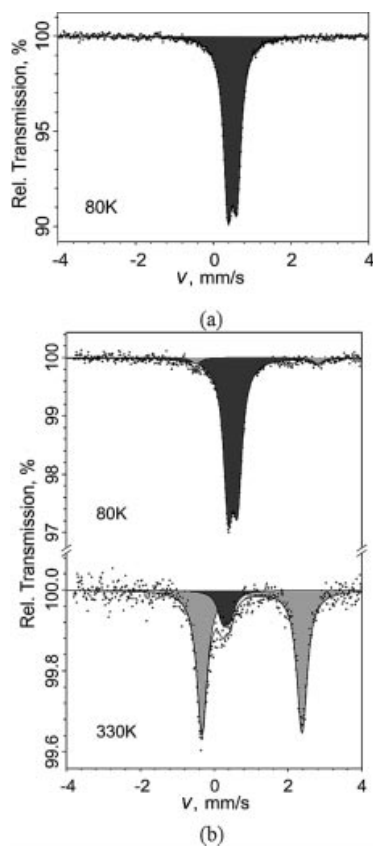


Figure 6. (a) Mössbauer spectrum of **1** at 80 K. (b) Mössbauer spectra of **4** recorded at 80 and 330 K. Dark grey corresponds to the LS doublet; light grey corresponds to the HS doublet.

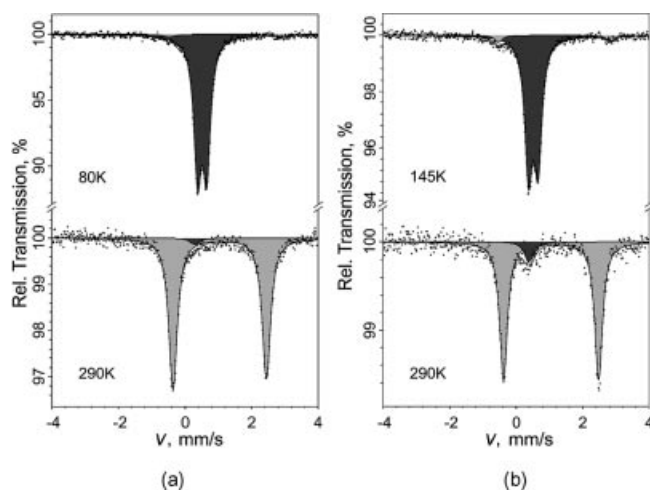


Figure 7. (a) Mössbauer spectra of **2** at 80 and 290 K. (b) Mössbauer spectra of **3** recorded at 145 and 290 K. Dark grey corresponds to the LS doublet; light grey corresponds to the HS doublet.

Differential Scanning Calorimetry of Compounds 2–4

The differential scanning calorimetric measurements were carried out in the 175–400 K temperature range at a rate of 7 K min^{−1}. The temperature dependence of the heat flow in the heating and cooling modes for **2–4** is shown in

Figure 8. The anomalies in the heat flow for compound **2** appear in the cooling mode at $T_c \downarrow = 240$ and $T_c \uparrow = 252$ K in the warming mode, thus indicating the occurrence of a hysteresis with a width of 12 K. These values agree reasonably well with those observed from the $\chi_M T$ vs. T plot. Compounds **3** and **4** exhibit anomalies in the heat flow at $T_c \downarrow = 226$ and $T_c \uparrow = 238$ K and $T_c \downarrow = 290$ and $T_c \uparrow = 310$ K, respectively, which match reasonably well with the reported magnetic data. The small differences in critical temperatures between the DSC and magnetic data are due to the different heating/cooling rates used in the experiments. Table 3 summarises the derived thermodynamic pa-

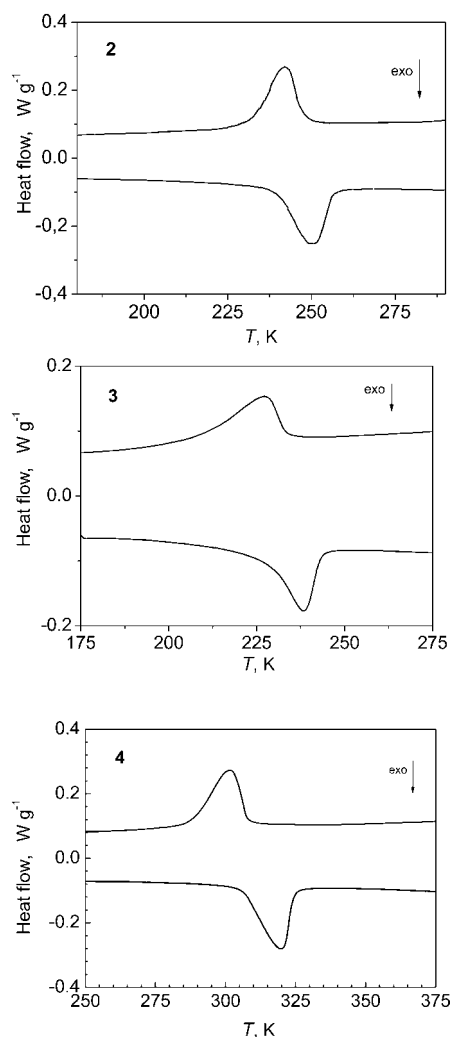


Figure 8. DSC data of complexes **2–4** in the warming and cooling modes recorded at a rate of 7 K min^{−1}.

Table 3. Thermodynamic parameters (ΔH and ΔS) for compounds **2–4**.

	ΔH [kJ mol ^{−1}]	ΔS [J K ^{−1} mol ^{−1}]
2	17.8	67.2
3	14.6	63.5
4	19.7	65.6

rameters ΔH_{SCO} and ΔS_{SCO} for the compounds **2–4**; the values obtained are in the range of values expected for Fe^{II} SCO compounds.^[1,31,32]

Discussion

The linear chain structure of compound **1** has been convincingly derived from EXAFS data, thereby confirming the collinear alignment of the metal ions within the polymeric aggregates formed by alternating triazole bridges. Moreover, the crystal structure of the analog [$\{\text{Cu}(\text{tba})_3\}(\text{CF}_3\text{SO}_3)_2\cdot 3\text{H}_2\text{O}$ (**7**)] confirms the structural features of **1** due to the almost identical powder XRD profiles of these two complexes. The fact that the powder X-ray patterns of **2** and **3** are not similar to those of **1** and **7** does not rule out a similar structure for these complexes as different packing and lattice arrangements would yield different crystallographic patterns even for similar linear chain structures. The final evidence for the similar structural organisation in **1–3** and **7** is provided by IR spectroscopy, namely by the absorption bands assigned to the vibrations of the bridging triazole rings featuring C_{2v} symmetry.

The new family of chainlike 4-substituted-1,2,4-triazole Fe^{II} compounds [$\{\text{Fe}(\text{tba})_3\text{X}_2\}\cdot n\text{H}_2\text{O}$] presents similar SCO characteristics to other complexes reported previously.^[6–13] Three main influences have been reported to play a crucial role in the spin transition and its characteristics in these compounds: (i) the water content in the crystal lattice,^[4,10] (ii) the chemical nature and size of the 4-R substituents^[11] and the counterions,^[12] and (iii) the length of the polymeric chains.^[24a] Stabilisation of the low-spin state by interaction with lattice water molecules has frequently been observed for Fe^{II} SCO compounds, particularly for polymers based on a triazole bridge.^[1,13] This is also the case for compound **1**, which loses its lattice water upon heating and undergoes an abrupt change from the LS to the HS state. When the dehydrated material **4** is cooled, an abrupt HS $\rightarrow$ LS transition occurs at $T_c \downarrow = 284 \text{ K}$ ($T_c \uparrow = 309 \text{ K}$). Subsequent reheating reveals a hysteresis loop of 25 K width centred at room temperature. The length of the chains has been found to be critical for the observation of cooperative and complete spin transition in such triazole polymers.^[6–13] The longer the chains are the lower is the residual HS fraction. The Mössbauer spectrum of compound **4** at 80 K clearly denotes the completeness of the spin transition in this complex, with almost all iron(II) ions in the LS state. For compound **1**, the Mössbauer spectrum recorded at 80 K shows that all iron(II) ions are in the LS state. These facts, together with the observation that all water molecules are removed below 400 K (lattice water), allow us to rule out the possibility of having water coordinated to the outer iron(II) ions of the polymeric chains in **1** and **4**. It is therefore likely that the end groups are monocoordinated tba ligands. Taking into account that the spin-transition properties and thermodynamic parameters of **4** are similar to those observed in $[\text{Fe}(\text{Htrz})\text{trz}](\text{BF}_4)$, one could suggest a similar average chain size for both compounds (around 13 nm).^[24a]

Compounds **2** and **3** undergo abrupt spin transitions at 258 and 238 K, respectively, both with a hysteresis width of about 10 K. A similar cooperative spin transition has also been observed for $[\text{Fe}(\text{fatz})_3](\text{X})_2\cdot n\text{H}_2\text{O}$ ^[24a] and $[\text{Fe}(4\text{-}n\text{-alkyl-trz})_3](\text{X})_2\cdot n\text{H}_2\text{O}$.^[11] The estimated average chain size in these compounds is 7 nm.^[24] Mössbauer spectra recorded for compounds **2** and **3** at liquid-nitrogen temperature indicate that almost all Fe^{II} ions are in the LS state, with a small residual HS fraction. A very different temperature-dependent magnetic behaviour is observed for the corresponding dehydrated compounds **5** and **6**. Thus, complex **5** presents a continuous and incomplete spin transition at $T_{1/2} \approx 100 \text{ K}$, while **6** shows a paramagnetic behaviour over the whole temperature range studied (10–400 K). These results demonstrate that the water contained in the lattices of these compounds plays a dominant role in the SCO behaviour.

Conclusion

The present family of polymeric 4-R-substituted triazole Fe^{II} compounds adds new examples to the richness of spin-transition properties of triazole-based polymers. These materials have been suggested to have possible applications as optical sensors by virtue of their thermochromic properties. Indeed, compound **1** represents a new example of a material with potential applications as a temperature threshold optical indicator. As compound **4** is stable at ambient conditions, however, **1** can only be used as a “single-shot” indicator. On the other hand, compound **4** could be used for thermal displays or recording data as it fulfils the necessary conditions (abruptness, hysteresis, room-temperature operation, change of colour and chemical stability). Compounds **2** and **3** could be useful in another temperature range of operation, namely the freezing-water region.

Experimental Section

Synthesis of Materials: Starting reagents and solvents were obtained commercially from Aldrich and used as received.

Measurements: FTIR spectra (KBr pellets) were recorded with a Bruker Tensor 27 spectrometer in the range of 400–4000 cm^{−1}. Elemental analyses were performed with a Vario EL Mikro Elementaranalysator. NMR spectroscopic measurements were performed with a Bruker DRX 400 spectrometer.

N-(4H-1,2,4-Triazol-4-yl)benzamide (tba): A suspension of 4-amino-4H-1,2,4-triazole (4.2 g, 50 mmol) and benzoyl chloride (7.0 g, 50 mmol) in dry pyridine (100 mL) was refluxed for 24 h. The solvents were then removed in vacuo to provide a cream-coloured solid, which was dissolved in hot water (100 mL) and neutralised with sodium hydrogen carbonate until no further effervescence was observed. The white precipitate obtained on cooling was filtered, washed with water and finally recrystallised from ethanol to give 6.48 g of tba (69%). ¹H NMR (400 MHz, [D₆]DMSO): $\delta = 12.1$ (br. s, 1 H, NH), 8.73 (s, 2 H, CH of trz), 7.89 (dd, $J = 1.36, 7.20 \text{ Hz}$, 2 H, phH), 7.61 (tt, $J = 1.36, 7.20 \text{ Hz}$, 1 H, phH), 7.52 (t, $J = 7.2 \text{ Hz}$, 2 H, phH) ppm. FT-IR (KBr): $\tilde{\nu} = 3113$ [$\nu(\text{CH of trz})$], 2000–1750 [$\nu(\text{Ph})$], 1674 [$\nu(\text{C=O})$] cm^{−1}. C₉H₈N₄O (188.19): calcd.

C 57.44, H 4.28, N 29.77; found C 57.41, H 4.24, N 29.81. EI MS: m/z (%) = 188.2 (2) [M]⁺, 105.0 (100) [M – trzNH]⁺.

Cu(CF₃SO₃)₂·6H₂O: Copper(II) hydroxide, obtained by the methathesis reaction of copper(II) sulfate with sodium hydroxide, was dissolved in a hot aqueous solution of trifluoromethanesulfonic acid. The blue crystals that formed upon cooling were filtered off and air-dried to provide the analytically pure salt in quantitative yield. FT-IR (KBr): $\tilde{\nu}$ = 3473 [br., ν (O–H)], 1255 [s, ν_a (SO₃[–])], 1032 [s, ν (C–F)] cm^{–1}. C₂H₁₂CuF₆O₁₂S₂ (469.76): calcd. C 5.11, H 2.57, S 13.65; found C 5.07, H 2.67, S 13.92.

General Procedure for the Synthesis of the Iron(II) Salts: Iron powder was dissolved in an aqueous solution containing a stoichiometric amount of the corresponding acid by heating. The greenish crystalline precipitate that formed upon cooling was filtered off and air-dried to provide the analytically pure salt in quantitative yield.

[Fe(CF₃SO₃)₂·6H₂O: FT-IR (KBr): $\tilde{\nu}$ = 3473 [br., ν (O–H)], 1188 [ν_a (SO₃[–])], 1035 [s, ν (C–F)] cm^{–1}. C₂H₁₂FeF₆O₁₂S₂ (462.06): calcd. C 5.20, H 2.62, S 13.88; found C 5.25, H 2.60, S 13.89.

[Fe{4-CH₃(C₆H₄)SO₃]₂·6H₂O: FT-IR (KBr): $\tilde{\nu}$ = 3407 [br., ν (O–H)], 1669 (s), 1496 (s), 813 [s, ν (Ph)], 1190 [s, ν_a (SO₃[–])], 3407 [br., ν (O–H)] cm^{–1}. C₁₄H₂₆FeO₁₂S₂ (506.32): calcd. C 33.21, H 5.18, S 12.67; found C 33.24, H 4.93, S 13.05.

General Procedure for the Synthesis of Compounds 1–3 and 7: A methanolic solution of the MA₂ salt (0.53 mmol; M = Cu or Fe; A = 4-CH₃C₆H₄SO₃[–], CF₃SO₃[–], BF₄[–]) was added to a hot methanolic solution of *N*-(4*H*-1,2,4-triazol-4-yl)benzamide (0.3 g, 1.6 mmol). The mixture was refluxed for 5 min, then concentrated by concentrating and cooled to room temperature. The resulting precipitate was filtered off and dried in air. The yields of complexes varied in the range 70–85%.

[{Fe(tba)₃}(CF₃SO₃)₂·2H₂O (1): FT-IR (KBr): $\tilde{\nu}$ = 3483 [br., ν (O–H)], 2000–1750 [ν (Ph)], 1694 [ν (C=O)], 1269 [ν_{as} (SO₃[–])] cm^{–1}. C₂₉H₂₈F₆FeN₁₂O₁₁S₂ (954.57): calcd. C 36.49, H 2.96, N 17.61, S 6.72; found C 36.10, H 2.93, N 17.21, S 6.95.

[{Fe(tba)₃}(BF₄)₂·3H₂O (2): FT-IR (KBr): $\tilde{\nu}$ = 3491 [br., ν (O–H)], 3127 [ν_{as} (C–H)], 2000–1750 [ν (Ph)], 1688 [ν (C=O)], 1093 [ν (B–F)]. C₂₇H₃₀B₂F₈FeN₁₂O₆ (848.06): calcd. C 38.24, H 3.57, N 19.82; found C 38.02, H 3.56, N 19.87.

[{Fe(tba)₃}(4-CH₃C₆H₄SO₃)₂·3H₂O (3): FT-IR (KBr): $\tilde{\nu}$ = 3483 [br., ν (O–H)], 2000–1750 [ν (Ph)], 1694 [ν (C=O)], 1168 [ν_{as} (SO₃[–])] cm^{–1}. C₄₁H₄₄FeN₁₂O₁₂S₂ (1016.84): calcd. C 48.43, H 4.36, N 16.53, S 6.31; found C 47.61, H 4.50, N 16.20, S 6.65.

[Fe(tba)₃](CF₃SO₃)₂ (4), [Fe(tba)₃](BF₄)₂ (5) and [Fe(tba)₃](4-CH₃C₆H₄SO₃)₂ (6): Compounds 4–6 were obtained by heating the hydrated compounds 1–3 in an oven at 400 K for 30 min.

[{Cu(tba)₃}(CF₃SO₃)₂·3H₂O (7): This complex was recrystallised from hot water by slow cooling in a thermostat overnight to provide blue, needle-like crystals. FT-IR (KBr): $\tilde{\nu}$ = 3480 [br., ν (O–H)], 2000–1750 [ν (Ph)], 1697 [ν (C=O)], 1267 [ν_{as} (SO₃[–])] cm^{–1}. C₂₉H₃₂CuF₆N₁₂O₁₃S₂ (998.30): calcd. C 34.89, H 3.23, N 16.84, S 6.42; found C 35.03, H 3.11, N 16.55, S 6.24.

Thermogravimetric Analysis: TGA measurements were performed with a Mettler Toledo TGA/SDTA 851 in tandem with a mass spectrometer in the 300–680 K temperature range under nitrogen with a heating rate of 10 K min^{–1}.

Differential Scanning Calorimetry: DSC measurements were performed with a Mettler model DSC 822e calibrated with metallic indium and zinc. The samples were located in sealed sample pans. DSC profiles were recorded at the rate of 7 K min^{–1} and analysed

with the Netzsch Proteus software (NETZSCH-Geraetebau GMBH; <http://www.e-thermal.com/proteus.htm>).

Magnetic Susceptibility Measurements: The variable-temperature magnetic susceptibility measurements were performed with a Quantum Design MPMS2 SQUID susceptometer equipped with a 5.5 T magnet at 1 T and 1.8–400 K. Experimental data were corrected for diamagnetism using Pascal's constants.^[33]

Mössbauer Spectroscopy: Mössbauer spectra were recorded in transmission geometry with a ⁵⁷Co/Rh source kept at room temperature and a conventional spectrometer operating in the constant-acceleration mode. The samples were sealed in a Plexiglass sample holder and mounted in a nitrogen-bath cryostat. The Recoil 1.03a Mössbauer Analysis Software (Dr. E. Lagarec; <http://www.is-apps.ca/recoil/>) was used to fit the experimental spectra.

X-ray Single-Crystal Crystallographic Study: Diffraction data for complex 7 were collected with a Nonius Kappa-CCD single crystal diffractometer using Mo-*K*_α radiation (λ = 0.71073 Å). A multi-scan absorption correction was found to have no significant effect on the refinement results. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least squares on *F*² using SHELXL-97.^[22] All non-hydrogen atoms were refined anisotropically. Further details can be found in Table 4. CCDC-636097 contains the supplementary crystallographic data for compound 7. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Crystal data for 7 at 293 K.

Empirical formula	C ₂₉ H ₃₀ CuF ₆ N ₁₂ O ₁₂ S ₂
Formula mass	980.31
Space group	<i>P</i> 1
<i>a</i> [Å]	17.8020(3)
<i>b</i> [Å]	17.8160(4)
<i>c</i> [Å]	23.2650(5)
<i>a</i> [°]	89.2120(10)
γ [°]	60.3130(10)
<i>V</i> [Å ³]	6371.8(2)
<i>Z</i>	6
<i>D</i> _{calcd.} [mg cm ^{–3}]	1.533
<i>F</i> (000)	2994
μ (Mo- <i>K</i> _α) [mm ^{–1}]	0.709
Crystal size [mm]	0.02 × 0.02 × 0.05
Temperature [K]	293(2)
Total reflections	16963
Reflections [<i>I</i> > 2σ(<i>I</i>)]	10839
<i>R</i> ₁ ^[a] [<i>I</i> > 2σ(<i>I</i>)]	0.1749
<i>wR</i>	0.4591
<i>S</i>	1.396

[a] $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$; $wR = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (mP)^2 + nP]$ where $P = (F_o^2 + 2F_c^2)/3$, $m = 0.2000$ and $n = 0.0000$.

X-ray Powder Diffraction: X-ray measurements were obtained with a STOE STADI 2 diffractometer equipped with a linear position-sensitive detector (STOE mini PSD). Monochromatic Cu-*K*_α radiation was obtained by using a curved germanium detector (111 plane).

X-ray Absorption Data Recording and Processing: The Fe K-edge XANES (X-ray absorption near-edge structures) and EXAFS (extended X-ray absorption fine structures) data were taken in the conventional transmission mode on beamline A1 at the German Electron Synchrotron (DESY), Hamburg. The spectrum was recorded from 6970 to 7997 eV. The energy scale at the iron K-edge

was calibrated with reference to the strong absorption peak of elemental iron at 7111.2 eV. A water-cooled Si(111) channel-cut crystal was employed as a monochromator. The intensities of the incident and transmitted X-rays were recorded using ionisation chambers. The mass of the sample was calculated to obtain a product $a \times d$ of about 2.5 for energies just above the absorption K-edge of iron (a is the linear absorption coefficient and d is the thickness of the pellet). The calculated amount of sample was ground, then mixed with crystalline cellulose and pressed into a pellet of 13 mm diameter and about 1 mm thickness. The temperature of the experiment was 80 K, which was maintained with a closed-cycle He cryostat. The temperature was measured with an Si diode placed close to the sample. The acquisition time for each data point was 1 s. EXAFS data analysis was performed with the program EXAFS98.^[34] This standard analysis includes linear pre-edge background removal, a smoothing spline atomic absorption energy-dependent procedure, called Lengeler–Eisenberg EXAFS spectrum normalisation, and reduction from the absorption data $\mu(E)$ to the EXAFS spectrum $\chi(k)$ with

$$k = \sqrt{\frac{2m_e}{\hbar^2} (E - E_0)}$$

where E_0 is the energy threshold taken at the absorption maximum (7130 ± 1 eV). The radial distribution function $F(R)$ was calculated by Fourier transformation of $k^3 w(k) \chi(k)$ in the 2–14 Å^{−1} range; $w(k)$ is a Kaiser–Bessel apodisation window with smoothness coefficient $\tau = 3$. After Fourier filtering, the first single-shell Fe–N₆ was fitted in the 4–12 Å^{−1} range to the standard EXAFS formula, without multiple scattering:

$$k_z(k) = -S_0^2 \sum_{i=1,2} \left[\frac{N_i}{R_i^2} (F\pi, k) \right] e^{-2\sigma^2 k^2} e^{\frac{2R_i}{\lambda(k)}} \sin(2kR_i + 2\partial_i(k) + \Psi(k))$$

where S_0^2 is the inelastic reduction factor, N is the number of nitrogen atoms at a distance R from the iron centre, λ is the mean free path of the photoelectron, σ is the Debye–Waller coefficient, characteristic of the width of the Fe–N distance distribution, $\partial_i(k)$ is the central atom phase shift, and $|F\pi(k)|$ and $\psi(k)$ the amplitude and phase of the nitrogen back-scattering factor, respectively. The curve-fitting analysis for the first coordination sphere of the iron atom was performed with the Round Midnight^[35] code after Fourier filtering in the 0.7–2.0 Å range of the EXAFS spectrum with spherical-wave theoretical amplitudes and phase shifts calculated by the McKale^[36] code. Since theoretical phase shifts were used, it was necessary to fit the energy threshold E_0 by adding an extra fitting parameter, ΔE_0 . The goodness of fit was given by:

$$\rho(\%) = \frac{\sum [k\chi_{\text{exp}}(k) - k\chi_{\text{th}}(k)]^2}{\sum [k\chi_{\text{exp}}(k)]^2}$$

Supporting Information (see footnote on the first page of this article): XRD diffraction patterns of **7**, both experimental and calculated from the single crystal data (Figure S1), TGA plots of compounds **1–3** (Figure S2), and magnetic properties of compound **7** in the form of a $\chi_M T$ vs. T plot (Figure S3).

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