PERGAMON

Synthesis, structure and magnetic properties of iron (II), cobalt (II) and nickel (II) complexes of 2,6-bis(pyrazol-3-yl)pyridine and paramagnetic counterions

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Abstract

Iron (II), cobalt (II) and nickel (II) complexes of 2,6-bis(pyrazol-3-yl)pyridine (bpp) with $[Cr(C_2O_4)_3]^{3-}$ have been prepared. They were characterised by single-crystal X-ray diffraction, magnetic susceptibility measurements and thermal gravimetric analyses. All three compounds are isostructural and they are formed by isolated $[M^{II}(bpp)_2]^{2+}$ and $[Cr(C_2O_4)_3]^{3-}$ complexes and free ClO_4^-. As expected, only the salt $[Fe(bpp)_2]_2[Cr(C_2O_4)_3]ClO_4 \cdot 5H_2O$ shows a thermal spin transition with transition temperature ($T_{1/2}$) around 375 K that is correlated to the loss of water molecules.
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1. Introduction

Nowadays, the search for multiproperty molecule-based materials [1] is very important in molecular science, in order to obtain new compounds which show coexistence of interesting properties. Molecule-based layered magnets, such as oxalate networks [2] of the type $[M'^x M^y(C_2O_4)_3]^{x+y-6}$, are used as anionic hosts for inorganic metal cationic complexes which acts as a template from the structural point of view. This type of materials exhibits, in addition to the cooperative magnetism, other interesting properties inferred by the presence of the inserted molecules. In this respect, one of the most interesting properties is bistability, that may be defined as 'a property of a molecular system that allows it to exist in two different electronic states over a certain range of external perturbation' [3]. A typical example of molecular species that exhibit such a molecular bist-

ability are spin crossover compounds. These molecules could be utilised for information processing and information storage. There are a lot of transition metal ($d^n(n = 4-7)$) that show bistability between the high-spin (HS) and low-spin (LS) states. It can be induced by a variation of temperature or of pressure.

At present, one of our aims is to insert a spin crossover complex in these magnetic networks. On the other hand, Decurtins and co-workers [4] in 2000 showed the phenomenon of a thermal spin transition for the $[Co^{II}(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) complex in the three-dimensional oxalate network structure $[Co^{II}(bpy)_3][LiCr(C_2O_4)_3]$, where the host–guest interactions influence the electronic energies of the cationic complex.

We report here the structure and magnetism of some examples of ionic species of the type $[M(bpp)_2]_2$-$[Cr(C_2O_4)_3]ClO_4 \cdot nH_2O$ with M(II) = Fe (**1**), Co (**2**), Ni (**3**). We show also the competition between iron (II), nickel (II) and cobalt (II) by the bpp ligand (bpp = 2,6-bis(pyrazol-3-yl)pyridine) (Fig. 1).

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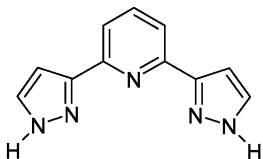*E-mail address:* eugenio.coronado@uv.es (E. Coronado).

Fig. 1. The 2,6-bis(pyrazol-3-yl)pyridine ligand (bpp).

2. Experimental

2.1. Materials

Iron (II)-perchlorate hydrate, cobalt (II)-perchlorate hexahydrate, nickel (II)-perchlorate hexahydrate, silver nitrate, 2,6-diacetylpyridine, dimethylformamide dimethylacetal and hydrazine monohydrate were purchased from Fluka and used as received.

$K_3[Cr(ox)_3]$ (ox = oxalate dianion) was obtained by the method of Bailar and Tones [5]. The silver salt $Ag_3[Cr(ox)_3]$ was precipitated from the potassium salt using an excess of silver nitrate and the product obtained was recrystallised in water.

The 2,6-bis(pyrazol-3-yl)pyridine ligand was synthesised in two steps by the method of Lin and Lang [6].

2.2. Synthesis of [Fe(bpp)₂]₂[Cr(C₂O₄)₃]ClO₄·5H₂O (1)

An ethanolic solution (50%, 30 ml) of $K_3[Cr(C_2O_4)_3]$ (0.071 mmol) was added dropwise to an ethanolic solution (50%, 30 ml) of $Fe(ClO_4)_2\cdot6H_2O$ (0.142 mmol) and bpp (0.284 mmol). Immediately a dark red powder precipitated, that was eliminated by filtration. Evaporation of the mother liquor afforded in a few days red needle-like single-crystals of $[Fe(bpp)_2]_2$-$[Cr(C_2O_4)_3]ClO_4\cdot5H_2O$. IR (cm^{-1}): 478, 619, 921, 1095, 1400, 1615, 1645, 2743, 2918, 3146, 3426. *Elem. Anal.* Found: C, 40.32; H, 3.10; N, 19.15. Calc. for $C_{50}H_{46}ClCrFe_2N_{20}O_{21}$: C, 41.07; H, 3.17; N, 19.15.

2.3. Synthesis of [Co(bpp)₂]₂[Cr(C₂O₄)₃]ClO₄·6H₂O (2)

The procedure mentioned above was adapted by using $Co(ClO_4)_2\cdot6H_2O$ as the divalent metal precursor and $Ag_3[Cr(C_2O_4)_3]$. The compound **2** was obtained by slow evaporation as light green needles. IR (cm^{-1}): 483, 621, 994, 1098, 1399, 1572, 1610, 1652, 2745, 2919, 3144, 3428. *Anal.* Found: C, 41.06; H, 3.25; N, 18.94. Calc. for $C_{50}H_{48}ClCo_2CrN_{20}O_{22}$ $Co_2CrClO_{22}C_{50}N_{20}H_{48}$: C, 40.40; H, 3.25; N, 18.84.

2.4. Synthesis of [Ni(bpp)₂]₂[Cr(C₂O₄)₃]ClO₄·6H₂O (3)

In this case the method was identical to that use for the ferrous compound but using $Ni(ClO_4)_2\cdot6H_2O$ as starting material. Purple needles of **3** were obtained after 1 week. IR (cm^{-1}): 482, 619, 997, 1100, 1399, 1575, 1615, 1654, 2745, 2923, 3143, 3426. *Anal.* Found: C, 40.17; H, 3.25; N, 18.88. Calc. for $C_{50}H_{48}ClCrN_2Ni_{20}O_{22}$: C, 40.18; H, 3.25; N, 18.84.

2.5. Physical techniques

Elemental analysis (C, H, N) were performed on a CE INSTRUMENTS EA 1110 CHNS elemental analyzer The infrared spectra were recorded on a Nicolet 800 FIR spectrophotometer as KBr pellets from 4000 to 400 cm^{-1}.

Magnetic susceptibility measurements of polycrystalline samples were carried out using a magnetometer (Quantum Design MPMS-XL-S) equipped with a SQUID sensor. The d.c. measurements were performed in the temperature range 2–300 K for **2** and **3** and in the range 2–400 K for **1** at a magnetic field of 0.1 T. The field dependence of the magnetisation was performed between 0 and 5 T at 2 K.

Thermogravimetric data of all three compounds were collected on a Mettler Toledo TGA/SDTA/851^e instrument under a dry nitrogen gas atmosphere from ambient temperature up to dehydration. Besides, for **1**, after heating under a dry nitrogen gas atmosphere the dehydration sample was exposed to an air flux allowing the rehydration.

2.6. X-Ray data collection and structure determination

X-ray single-crystal structure has been carried out for needles of all three compounds at room temperature (r.t.). These compounds $[M(bpp)_2]_2[Cr(C_2O_4)_3]ClO_4\cdot$ nH_2O are isoestructural and crystallise in the orthorhombic space group $Pca2_1$. For the compounds **1** and **3** the value of the Flack [7] parameter [0.49(3)] indicated racemic twinning and this was handled via the *TWIN* and *BASF* instructions in SHELXL97 [8]. The relevant single-crystal data and parameters regarding the data collection and structure refinements are given in Table 1. The diffraction data were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation. The structure was solved by direct methods using the SIR 97 program [9] and was refined on F^2 using the SHELXL-97 program. In the structural determination the heavy atoms were found immediately, however the other atoms were located through successive Fourier differences. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were assigned to calculated positions and refined as riding

Table 1
Crystal data and structure refinement data for the compounds $[M(bpp)_2]_2[Cr(C_2O_4)_3]ClO_4 \cdot n\,H_2O$ (M(II) = Fe, Co, Ni)

	$[Fe(bpp)_2]_2[Cr(C_2O_4)_3]ClO_4 \cdot 5H_2O$	$[Co(bpp)_2]_2[Cr(C_2O_4)_3]ClO_4 \cdot 6H_2O$	$[Ni(bpp)_2]_2[Cr(C_2O_4)_3]ClO_4 \cdot 6H_2O$
Empirical formula	$Fe_2CrClO_{21}C_{50}\,N_{20}H_{46}$	$Co_2CrClO_{22}C_{50}\,N_{20}H_{48}$	$Ni_2CrClO_{22}C_{50}\,N_{20}H_{48}$
FW	1462.18	1485.90986	
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$Pca2_1$	$Pca2_1$	$Pca2_1$
Unit cell dimensions			
a (Å)	22.5460(4)	22.6220(4)	22.6300(2)
b (Å)	16.3670(3)	16.5920(3)	16.6020(2)
c (Å)	16.5760(7)	16.7240(7)	16.7600(3)
α (°)	90.000(0)	90.000(0)	90.000(0)
β (°)	90.000(0)	90.000(0)	90.000(0)
γ (°)	90.000(0)	90.000(0)	90.000(0)
$U(Å^3)$	6116.7(3)	6296.79(15)	6277.3(3)
Z	4	4	4
Reflections measured	8739	11 135	20 7961
Independent reflections (R_{int})	8739	11 135	14 442
Observed reflections ($I > 2\sigma(I)$)	6045	8572	9428
R_1(observed)	0.0683	0.0499	0.0459
wR_2(all data)	0.1919	0.1352	0.1310

atoms with a common fixed isotropic thermal parameter. The hydrogen atoms of the water molecules were not calculated.

3. Results and discussion

3.1. Synthesis, characterisation and structure of $[M(bpp)_2]_2[Cr(C_2O_4)_3]ClO_4 \cdot n H_2O$

Combination of ethanolic water solutions containing iron(II) and nickel(II) perchlorates in the presence of bpp and tris(oxalato)chromate(III) results in the formation of needles of $[Ni(bpp)_2]_2[Cr(C_2O_4)_3]ClO_4 \cdot 6H_2O$. Clearly, the stability of the nickel(II) complex is higher, a situation that is rare in polyimine-based metal complexes. Another evidence of the high lability of $[Fe(bpp)_2]^{2+}$ is the partial displacement of bpp when exposing the ferrous complex to a solution containing Co^{2+} cations.

Compounds $[M(bpp)_2]_2[Cr(C_2O_4)_3]ClO_4 \cdot n H_2O$ (M(II) = Fe, Co, Ni) are isostructural and only differ in the number of water molecules of crystallisation. Their crystal structures are composed of isolated $[M^{II}(bpp)_2]^{2+}$ and $[Cr(C_2O_4)_3]^{3-}$ complexes and free ClO_4^- (Fig. 2). In the complex $[M^{II}(bpp)_2]^{2+}$, two tridentate bpp ligands coordinate to the metal center nearly perpendicular to one another in a pseudo C_{2v} symmetry. In the crystal structure the two divalent metal ions are inequivalent. The metal–nitrogen bond distances (d(M–N)) have the following tendency d(Fe–N) < d(Ni–N) < d(Co–N), with values comprised between 1.900(6) and 2.000(8) Å for **1**, 2.004(3) and 2.157(4) Å for **2** and 2.049(4) and 2.174(4) Å for **3**.

As expected, the six Cr–O bond distances are very similar and close to 2 Å in the chromium complex. We can consider these systems as a layered material (Fig. 3) that is made up by alternating layers of cations and anions. The cationic layers contain the $[M(bpp)_2]^{2+}$ complexes. In this layer there are π–π interactions between bpp ligands of neighbouring units. the intermolecular distances between the mean planes of the ligands is 3.4 Å. The anionic layers are segregated in delta (Δ) and lambda (λ) layers due to the chirality of the $[Cr(C_2O_4)_3]^{3-}$ unit. An extensive network of hydrogen bond involving the uncoordinated water molecules, the oxalate oxygens, the perchlorate oxygens and the uncoordinated N–H groups in the bpp ligand is also present.

The thermogravimetric analysis of **1**–**3** under a dry nitrogen gas atmosphere shows a loss of weight that can be attributed to their dehydration (Fig. 4). The weight loss obtained is in agreement with the number of water molecules found by X-ray diffraction for the compounds **1** and **3**. However, the weight loss for the compound **2** is slightly lower than that found by XRD.

The dehydration temperature is 373 K for **1**, 383 K for **2** and 391 K for **3**. These values indicate that the water molecules are uncoordinated.

3.2. Magnetic measurements

The thermal variation of the $\chi_M T$ product in the 2–300 K range (χ_M is the molar magnetic susceptibility, T is the absolute temperature) for **2** and **3** is shown in Figs. 5 and 6, respectively. At r.t., the $\chi_M T$ values (4.72 emu K mol^{-1} for **3** and 7.13 emu K mol^{-1} for **2**) are close to those expected for the sum of uncorrelated spins. For **2**, the $\chi_M T$ product decreases gradually from 200 K, to
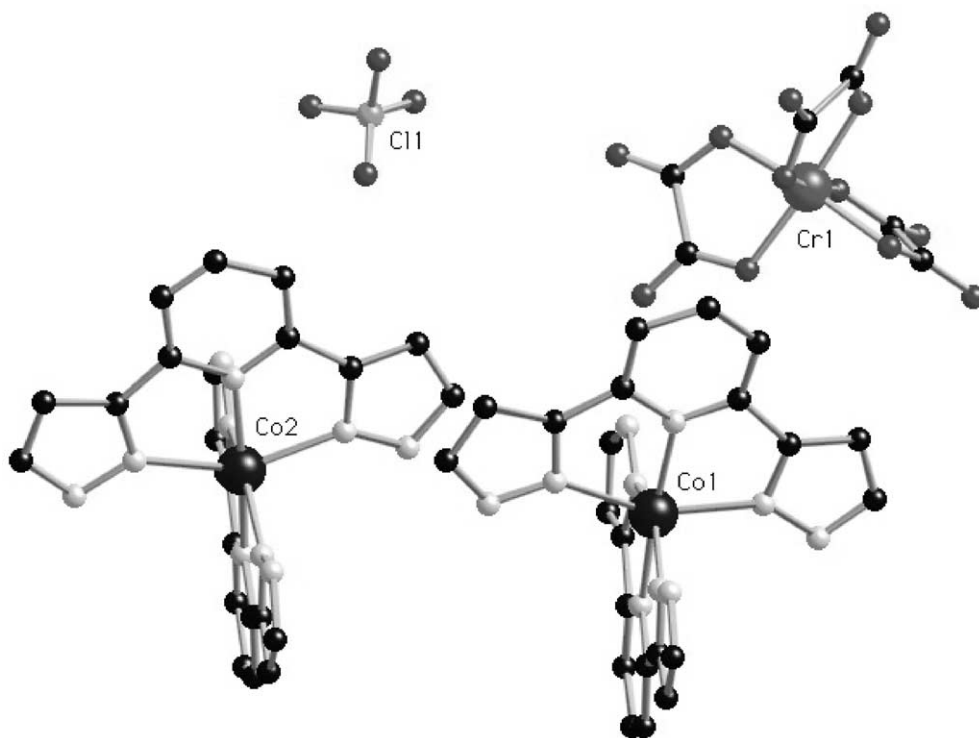
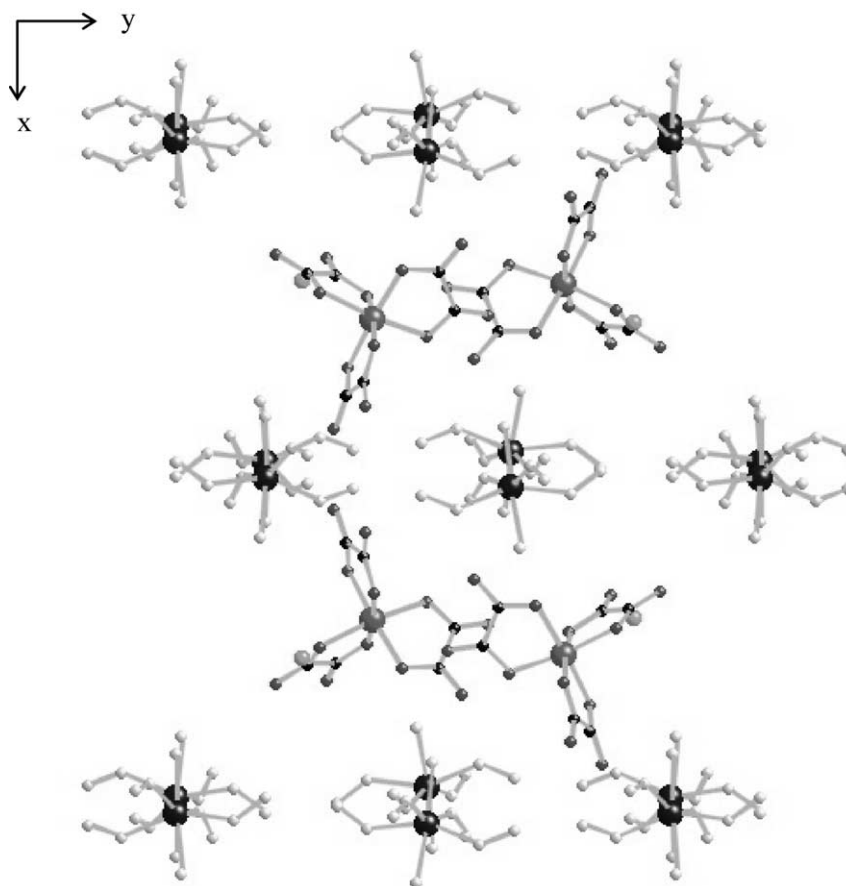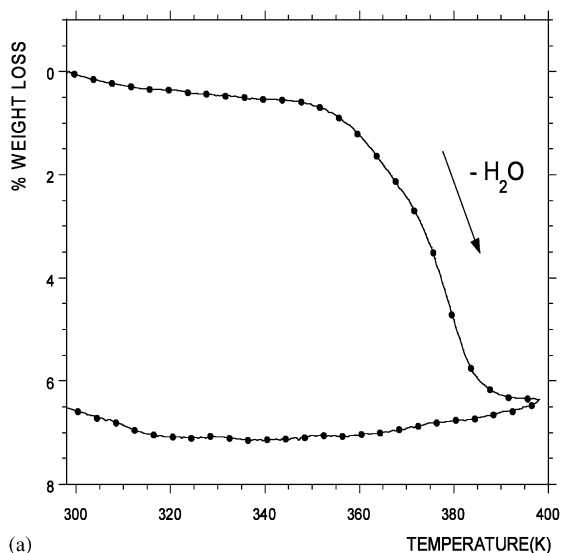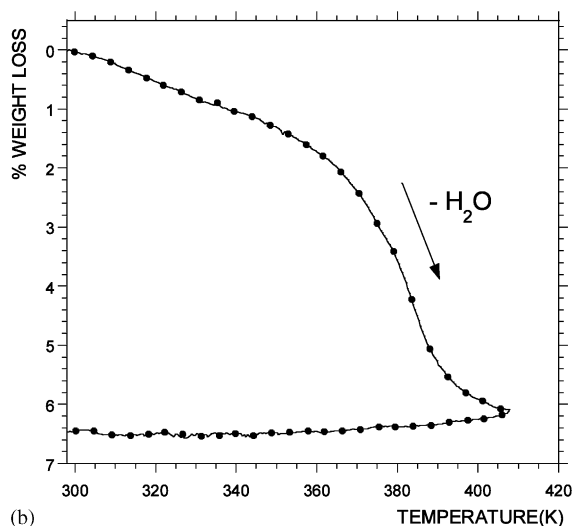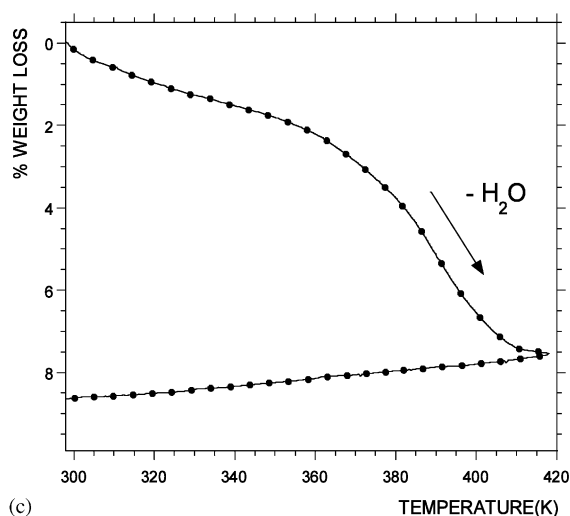Fig. 2. View of the asymmetric unit of the crystal structure of **2**.

Fig. 3. Projection along the *z* axis of the structure of the compound **2** showing the alternating layers of catións and anions. Carbon atoms of bpp have been omitted for the sake of clarity.
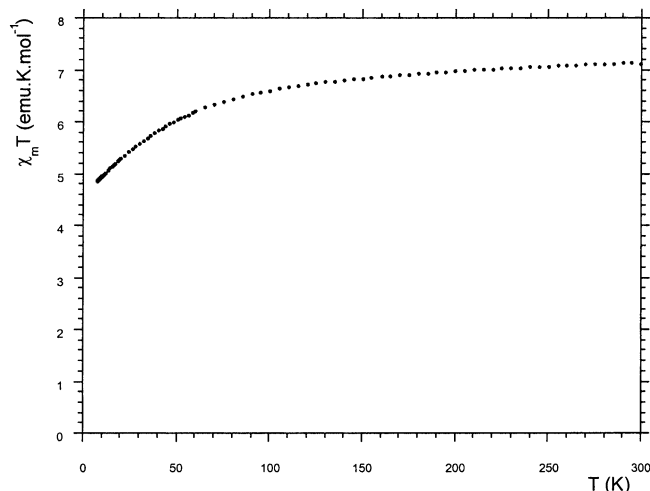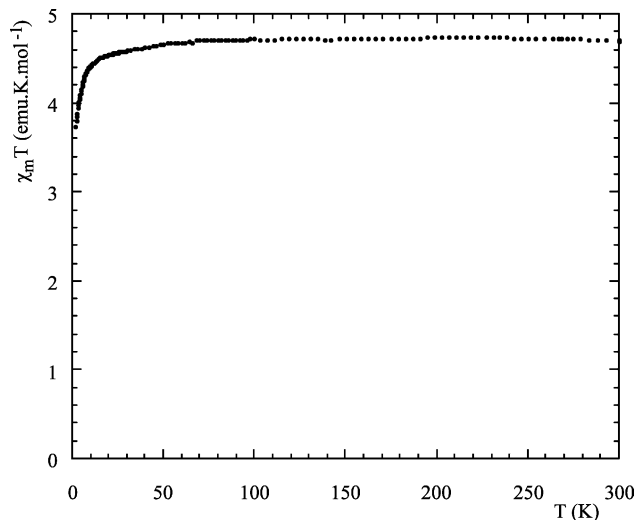
(a)

(b)

(c)

Fig. 4. TGA diagrams of (a) **1**, (b) **2** and (c) **3**.

Fig. 5. $\chi_M T$ versus T for **2**.

Fig. 6. $\chi_M T$ versus T for **3**.

reach 4.8 emu K mol^{-1} at 5 K. This behaviour is due to the spin-orbit coupling of the Co^{2+} cations. On the other hand, the $\chi_M T$ product of **3** remains constant until 68 K. Below this temperature the smooth decrease observed on cooling gets more abrupt. This temperature dependence can be attributed to a zero field-splitting of the Ni^{2+} and Cr^{3+} cations. The magnetic behaviour of **2**–**3** reflects the absence of interactions between spin carriers.

Preliminary magnetic measurements for **1** are shown in Fig. 7. The magnetic susceptibility was measured between 2 and 400 K in the heating and cooling modes. The $\chi_M T$ value for this compound is 3.2 emu K mol^{-1} at 150 K which is higher than the expected contribution of one Cr(III) center. This might be due to the presence of some HS centers. The $\chi_M T$ product remains practically constant on heating up to 300 K, then starts to increase and a thermal spin transition (LS, $^{1}A_{1g} \rightarrow$ HS, $^{5}T_{2g}$) with transition temperature ($T_{1/2}$) around 375 K occurs. The spin transition is directly related to the removal of water molecules since the thermogravimetric analysis reveals a loss of weight around this temperature.
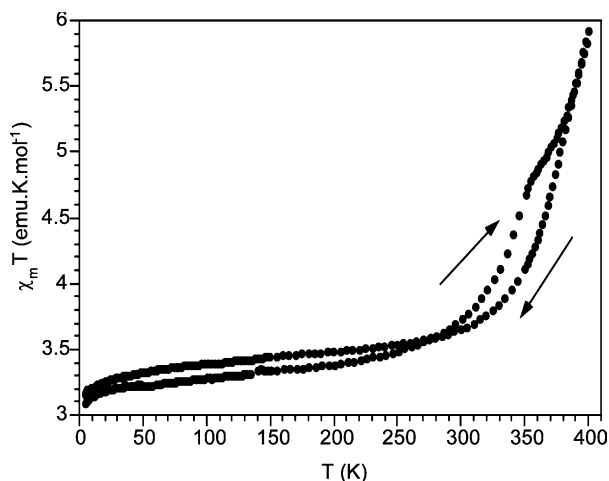
Fig. 7. $\chi_M T$ versus T for **1**. The sample was warmed from 2 to 400 K and then cooled from 400 to 2 K.

The effect of the solvated water is to stabilise the singlet state, similar to that observed in other iron (II) spin crossover complexes with bpp, $Fe(bpp)_2X_2 \cdot nH_2O$ ($X = ClO_4^-$, BF_4^-) [10], where the extent of hydration has a marked influence on the electronic properties.

4. Conclusions

We have shown that the extent of cooperativity of the transition is related to the loss of water molecules in the systems $Fe(bpp)_2X_2 \cdot nH_2O$. Preliminary studies show that the system studied here is able to undergo rehydration, a process that is also associated to a change in the magnetic behaviour. A complete correlation between solvent uptake or removal and the spin transition temperatures is in progress.

5. Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 194933–194935 for compounds **1**, **2** and **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.acuk or www: http://www.ccdc.cam.ac.uk).

References

[1] E. Coronado, J.R. Galán, C.J. Gómez, Mol. Cryst. Liq. Cryst. 334 (1999) 679.
[2] S. Decurtins, H.W. Schmalle, P. Schneuwly, J. Ensling, P. Gütlich, J. Am. Chem. Soc. 116 (1994) 9521.
[3] S. Hayami, Z.-z. Gu, H. Yoshiki, A. Fujishima, O. Sato, J. Am. Chem. Soc. 123 (2001) 11644.
[4] R. Sieber, S. Decurtins, H. Stoeckli, C. Wilson, D. Yufit, J.A.K. Howard, S.C. Capelli, A. Hauser, Chem. Eur. J. 6 (2000) 361.
[5] J.C. Bailar, E.M. Tones, in: H.S. Booth (Ed.), Inorganic Synthesis, vol. 1, Mc Graw-Hill, New York, 1939, p. 35.
[6] Y.-L. Lin, S.A. Lang, Jr., J. Heterocyclic Chem. 14 (1977) 345.
[7] H.D. Flack, Acta Cryst. A 39 (1983) 876.
[8] G.M. Sheldrick, University of Göttingen, Germany, 1997.
[9] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
[10] K.H. Sugiyarto, K. Weitzner, D.C. Craig, H.A. Goodwin, Aust. J. Chem. 50 (1997) 869.