Crystal structure and magnetic properties of a new three-dimensional coordination polymer constructed from (4,4) layers based on dimeric iron(II) subunits

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A new metal-organic polymer [Fe(pydc)(H_2O)] (**1**; H_2pydc = pyridine-2,5-dicarboxylic acid), has been hydrothermally synthesised and characterised by X-ray diffraction, showing that **1** is a three-dimensional framework featuring two-dimensional carboxylate-bridged layers based on canted dimeric iron(II) subunits. Magnetic measurements demonstrate that, although the carboxylate and pyridyl bridges are present in the layer, **1** exhibits only a weak antiferromagnetism.

Introduction

Extended frameworks of coordination polymers based on transition metal ions and multifunctional bridging ligands are currently of great interest[1] because of their intriguing topologies and their potential applications.[2] Multi-carboxylate ligands may exhibit various coordination modes to furnish various structures with higher dimensions.[1,2a–c] We and others have constructed transition metal–organic polymers with new structural features and studied the magnetic properties of these polymers.[3] Pyridine-2,5-dicarboxylic acid (H_2pydc) has unique features besides the respective merits of *m*-pyridinecarboxylate[2b,3b] and *p*-pyridinecarboxylate.[4] Therefore, it is most likely that pydc will form low symmetric structures with metals, such as heterometallic lanthanide–transition metal polymers featuring one-dimensional zigzag chain structures or three-dimensional wavelike structures, showing simple paramagnetism or antiferromagnetic interactions.[5] In this paper, we report the preparation, crystal structure and preliminary magnetic properties of a new three-dimensional polymeric framework compound [Fe(pydc)(H_2O)] (**1**), using iron(II) ions and H_2pydc as the reactants.

Experimental

Materials

All reagents and solvents employed were commercially available and used as received without further purification. The C, H, N microanalyses were carried out with a Perkin–Elmer 240 elemental analyser. The FT-IR spectra were recorded from KBr pellets in the 4000–400 cm^{-1} range on a Nicolet 5DX spectrometer. Magnetic measurements were performed with a Maglab System 2000 magnetometer. Field-cooled magnetisation measurements on **1** were performed with applied fields of 10 KOe between 2 and 300 K, and with applied fields of 200 Oe between 2 and 40 K. The isothermal magnetisation was measured at 1.8 K with applied fields of 0–5 T. The ac magnetisation was measured in an ac field of 5 Oe at 2–10 K. The sample magnetisations were corrected for the intrinsic diamagnetic contributions by using Pascal's constants.

Synthesis

In a typical experiment, H_2pydc (0.167 g, 1 mmol) in an aqueous solution (8 mL) of NaOH (0.040 g, 1 mmol) was mixed with an aqueous solution (2 mL) of $FeSO_4 \cdot 7H_2O$ (0.278 g, 1 mmol). After stirring for 5 min in air, triethylamine (0.07 mL, 0.5 mmol) was added and then the mixture was placed in a 23 mL Teflon-lined autoclave and heated at 140 °C for 120 h. The autoclave was cooled over a period of 12 h at a rate of 5 °C h^{-1}. **1** as reddish-black prismatic crystals was collected by filtration, washed with water, and dried in air. The pure product was obtained by manual separation (*ca.* 35% yield, based on Fe). Anal. (%) calcd for $C_7H_5FeNO_5$ (**1**): C, 35.18; H, 2.11; N, 5.86; found: C, 35.15; H, 2.13; N, 5.84. IR (KBr, cm^{-1}) for **1**: 3351s, 2963m, 1704vs, 1624s, 1607s, 1400m, 1367m, 1234vs, 1170m, 1038w, 880w, 798m.

X-Ray crystallography

Diffraction intensities for complex **1** were collected at 293 K on a Siemens R3m diffractometer using the ω-scan technique. Lorentz polarisation and absorption corrections were applied.[6] The structure was solved with direct methods and refined with full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97 programs, respectively.[7,8] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C–H = 0.96 Å); the aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed and anomalous dispersion corrections were incorporated.[9] Crystal data as well as details of data collection and refinement for the complex are summarised in Table 1. Selected bond distances and angles are listed in the Table 2.†

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† CCDC reference number 217236. See http://www.rsc.org/suppdata/nj/b3/b306872b/ for crystallographic data in .cif or other electronic format.

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Table 1 Crystal and structure refinement data for complex **1**

Empirical formula	$C_7H_5FeNO_5$
Formula weight	238.97
T/K	293(2)
λ/Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	8.791(8)
b/Å	10.577(6)
c/Å	8.663(6)
β/°	95.63(1)
U/Å^3	801.6(10)
Z	4
μ/mm^{-1}	1.874
Reflections collected	1869
Independent reflections	1749
R_{int}	0.0480
$R_1{}^a$ $[I > 2\sigma(I)]$	0.0635
$wR_2{}^a$ $[I > 2\sigma(I)]$	0.1639
$R_1{}^a$ (all data)	0.0944
$wR_2{}^a$ (all data)	0.1839

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Results and discussion

Syntheses and characterisation

The hydrothermal method has been proven to be very effective for the syntheses of zeolites, nano-materials and more recently coordination polymers. It is well-known that small changes in one or more of the hydrothermal parameters, such as temperature, reaction time, pH value and molar ratio of the reactants, may exert a profound influence on the final reaction products. During the past few years, we have explored the synthesis of metal coordination polymers under typical hydrothermal conditions[10] (*i.e.* 120–180 °C and 2–7 days) and found that the syntheses of Fe(II) coordination polymers is more difficult than that of the other spin carrier ions [Cu(II), Co(II), Ni(II)] because the Fe(II) ion has not only an air-sensitive nature but also a hydrolysis-sensitive nature. In this example we found that a pH of 5.5–6.5, together with a moderate reaction temperature and time, is most suitable for the formation of the Fe(II) coordination polymer **1**. We also found that triethylamine is a suitable agent under hydrothermal conditions to keep a relative stable pH value and to serve as a mineraliser.[11]

Crystal structures

X-Ray single-crystal diffraction on **1** reveals the presence of carboxylate-bridged two-dimensional layers extended by pyridyl bridges into a new three-dimensional framework. In the asymmetric unit, there is one iron(II) ion, one pydc and one aqua ligand. The iron(II) ion is located in the centre of a distinctly distorted octahedron formed by one pyridyl nitrogen atom [Fe(1)–N(1) 2.217(5) Å], four oxygen atoms [Fe(1)–O 2.054(5) ~2.206(4) Å] from the carboxylate groups of different pydc ligands and one oxygen atom [Fe(1)–O(1w) 2.149(5) Å] from the terminal aqua ligand (Fig. 1). The two carboxylate groups of pydc in **1** adopt a tetradentate bridging mode to link four iron(II) ions. The dimeric Fe···Fe distance is 4.560(3) Å and the Fe–O–C angles are 145.0(4)° and 149.8(4)°. Each iron(II) ion in the dimeric subunit is linked to two iron(II) ions in two adjacent dimeric subunits by two carboxylate groups in an uncommon skew-skew non-coplanar coordination mode (torsion angles Fe–O–C–O *ca.* 65°),[12] with a Fe···Fe distance of 5.786(3) Å and Fe–O–C angles of 132.9(4)° and 116.8(3)°, being extended into a wrinkly (4,4) net (Fig. 2) with adjacent dimeric subunits canted to each other. The layers are further interconnected (Fe···Fe at 7.118 or 8.791 Å) through the pyridyl rings of pydc, leading to a three-dimensional extended network (Fig. 3) with the terminal aqua ligands pointing into the one-dimensional saddle-like channels (*ca.* 10.6 × 3.5 Å). There are interlayer hydrogen bonds between the aqua ligands and the carboxylate oxygen atoms [O···O 3.053(1) Å]. It is worthy of note that no three-dimensional coordination framework structure featuring dimeric iron(II) ions bridged by carboxylate groups in two-dimensional arrays has been documented so far.[13]

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Fe(1)–O(1)	2.193(4)	O(4)#1–Fe(1)–O(1)	86.2(2)
Fe(1)–O(1W)	2.149(5)	O(3)#2–Fe(1)–O(1)	163.5(2)
Fe(1)–O(2)#3	2.206(4)	O(1W)–Fe(1)–O(1)	94.8(2)
Fe(1)–N(1)	2.217(5)	O(4)#1–Fe(1)–O(2)#3	97.7(2)
Fe(1)–O(3)#2	2.093(4)	O(3)#2–Fe(1)–O(2)#3	84.9(2)
Fe(1)–O(4)#1	2.054(5)	O(1W)–Fe(1)–O(2)#3	172.2(2)
O(4)#1–Fe(1)–O(3)#2	108.4(2)	O(1)–Fe(1)–O(2)#3	85.4(2)
O(4)#1–Fe(1)–O(1W)	90.1(2)	O(4)#1–Fe(1)–N(1)	161.4(2)
O(1)–Fe(1)–N(1)	75.3(2)	O(3)#2–Fe(1)–N(1)	90.2(2)
O(2)#3–Fe(1)–N(1)	82.0(2)	O(1W)–Fe(1)–N(1)	90.5(2)
O(3)#2–Fe(1)–O(1W)	93.0(2)		

Symmetry transformations used to generate equivalent atoms: #1 $x+1, y, z$; #2 $-x, -y, -z$; #3 $x, -y+1/2, z-1/2$; #4 $x, -y+1/2, z+1/2$; #5 $x-1, y, z$

Magnetic properties

Temperature-dependent magnetic susceptibility measurements for **1** were performed on a polycrystalline sample. The magnetic behaviour of **1** in the form of $\chi_M T$ *vs.* T and χ_M *vs.* T plots in the range of 2–306 K at a 10 kOe applied field is shown in Fig. 4. The $\chi_M T$ value is 2.064 cm^3 K mol^{-1} per Fe(II) at 298 K, corresponding to a moment of 4.063 μ_B per Fe(II) ion, which is smaller than that expected for an uncoupled Fe(II) ion ($g = 2.0$, 3.0 cm^3 K mol^{-1}). As expected, this is moderately smaller than the spin-only value of a high-spin Fe(II) ion (4.90 μ_B). When T decreases further to 40 K, the $\chi_M T$ value of **1** remains essentially constant at 2.0 cm^3 K mol^{-1}. Below 40 K the $\chi_M T$ value decreases and reaches 0.926 cm^3 K mol^{-1} at 2 K. The presence of a weak antiferromagnetic interaction and spin-orbit coupling in the high-spin Fe(II) ion are responsible for the reduction of $\chi_M T$ upon further cooling to 2 K.[14] The magnetic behaviour of **1** in the form of $\chi_M T$ *vs.* T and χ_M *vs.* T plots in the range of 2–40 K at a 200 Oe applied field is shown in the inset of Fig. 4. The χ_M value is 0.0605 cm^3 K mol^{-1} per Fe(II) at 40 K and reaches 0.533 cm^3 K mol^{-1} at 2 K. Upon going from 40 K to 2 K, the value of $\chi_M T$ decreases from 2.40 to 1.027 cm^3 K mol^{-1}, suggesting that there is a weak antiferromagnetic interaction among the iron(II) ions through the pydc ligands.[14] No other type of ordering was

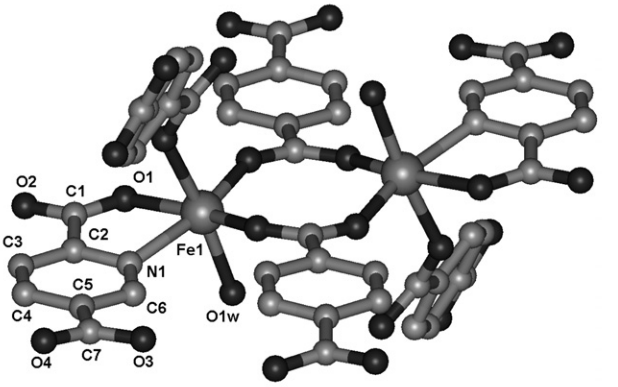

Fig. 1 The Fe(II) coordination environment in the dimeric subunit in **1**. Hydrogen atoms have been omitted for clarity.

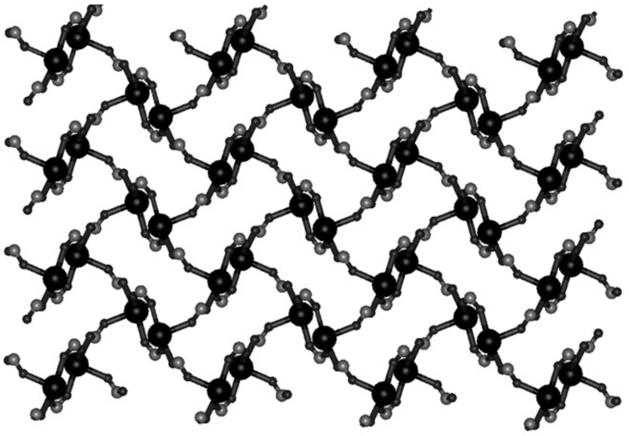

Fig. 2 The (4,4) net constructed by the metal ions and carboxylate groups in **1**. The aqua ligands and pyridyl rings are omitted for clarity.

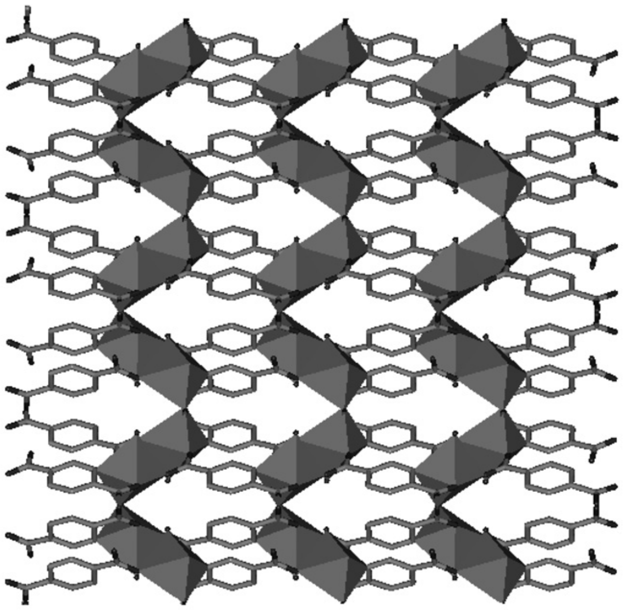

Fig. 3 The three-dimensional framework of **1**.

found based on low field dc and ac data. The field dependence of the magnetisation measured at 1.8 K is shown in Fig. 5. The $M/N\mu_B$ value increases rapidly above 100 Oe and then more gradually tends to 1.787 $M/N\mu_B$ per Fe(II) at the highest applied field of 50 kOe, which tends to a saturation value in the higher fields. The weak antiferromagnetic interaction behaviour indicates that the Fe–O–C–O–Fe connectivity is not efficient enough to transfer strong coupling interactions, as shown in other metal complexes.[15]

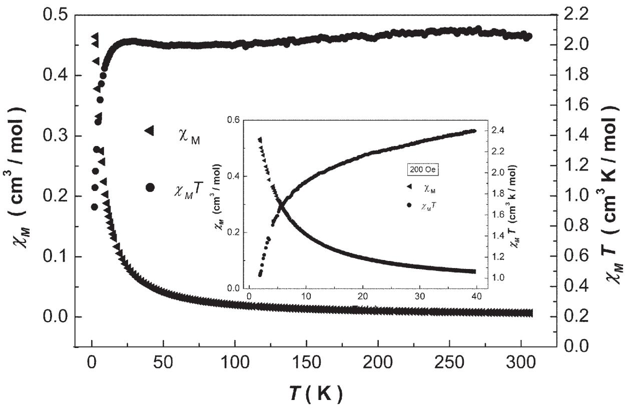

Fig. 4 Temperature dependence of χ_M(◀) and $\chi_M T$(●) values per Fe(II) in **1** at 10 kOe and 200 Oe (inset) applied fields.

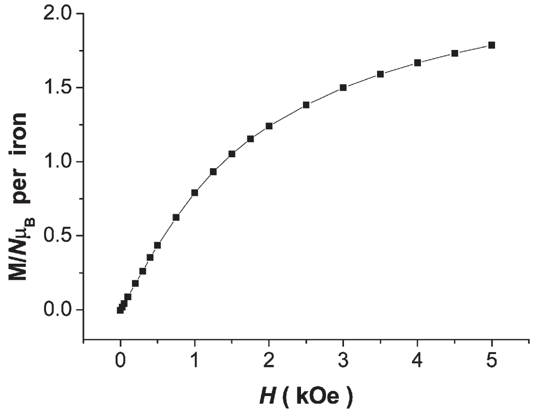

Fig. 5 The field dependence of magnetisation per Fe(II) in **1** at 1.8 K.

In summary, we have demonstrated a new iron(II) three-dimensional coordination polymer produced by a hydrothermal reaction, in which the carboxylate-bridged layers featuring dimeric iron(II) subunits are pillared by the pydc pyridyl bridges. Although the carboxylate and pyridyl bridges are present in the layer, this compound exhibits only a weak antiferromagnetism.

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References

1 D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319.
2 (*a*) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wochter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469; (*b*) W. Lin, O. R. Evans, R.-G. Xiong and Z. Wang, *J. Am. Chem. Soc.*, 1998, **120**, 13 272; (*c*) J. Tao, M.-L. Tong, J.-X. Shi, X.-M. Chen and S.-W. Ng, *Chem. Commun.*, 2000, 2043; (*d*) D. B. Mitzi, S. Wang, C. A. Field, C. A. Chess and A. M. Guloy, *Science*, 1995, **267**, 1473; (*e*) K. Barthelet, J. Marrot, D. Riou and G. Férey, *Angew. Chem., Int. Ed.*, 2002, **41**, 281; (*f*) E.-Q. Gao, S.-Q. Bai, Z.-M. Wang and C.-H. Yan, *J. Am. Chem. Soc.*, 2003, **125**, 4984.
3 (*a*) H.-J. Chen, Z.-W. Mao, S. Gao and X. -M. Chen, *Chem. Commun.*, 2001, 2320; (*b*) H.-Z. Kou, S. Gao, J. Zhang, G.-H. Wen, G. Su, R.-K. Zheng and X.-X. Zhang, *J. Am. Chem. Soc.*, 2001, **123**, 11 809; (*c*) C.-M. Liu, Y.-L. Hou, J. Zhang and S. Gao, *Inorg. Chem.*, 2002, **41**, 140; (*d*) B.-Q. Ma, H.-L. Sun, S. Gao and G. Su, *Chem. Mater.*, 2001, **13**, 1946; (*e*) B.-Q. Ma, D.-S. Zhang, S. Gao, T.-Z. Jin, C.-H. Yan and G.-X. Xu, *Angew. Chem., Int. Ed.*, 2000, **39**, 3644.
4 J.-Y. Lu and A. M. Babb, *Chem. Commun.*, 2002, 1340.
5 (*a*) Y.-C. Liang, R. Cao, W.-P. Su, M.-C. Hong and W.-J. Zhang, *Angew. Chem., Int. Ed.*, 2000, **39**, 3304; (*b*) Y.-C. Liang, M.-C. Hong, W.-P. Su, R. Cao and W.-J. Zhang, *Inorg. Chem.*, 2001, **40**, 4574.
6 C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
7 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.
8 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.
9 T. Cromer, *International Tables for X-ray Crystallography*, Kluwer Academic Publisher, Dordrecht, 1992, vol. C, Tables 4.2.6.8 and 6.1.1.4.

10 (*a*) J. Tao, M.-L. Tong, J.-X. Shi, X.-M. Chen and S. W. Ng, *Chem. Commun.*, 2000, 2043; (*b*) X.-M. Chen and G.-F. Liu, *Chem.-Eur. J.*, 2002, **8**, 4811; (*c*) J. Tao, M.-L. Tong and X.-M. Chen, *J. Chem. Soc., Dalton Trans.*, 2000, 3669; (*d*) J. Tao, Y. Zhang, M.-L. Tong, X.-M. Chen, T. Yuen, C.-L. Lin, X.-Y. Huang and J. Li, *Chem. Commun.*, 2002, 1342; (*e*) M.-L. Tong, L.-J. Li, K. Mochizuki, H.-C. Chang, X.-M. Chen, Y. Li and S. Kitagawa, *Chem. Commun.*, 2003, 428.

11 (*a*) R. M. Barrer, *Hydrothermal Chemistry of Zeolites*, Academic Press, London, 1982; (*b*) S.-H. Feng and R.-R. Xu, *Acc. Chem. Res.*, 2001, **34**, 239.

12 Y.-X. Tong, X.-M. Chen and S.-W. Ng, *Polyhedron*, 1997, **16**, 3363.

13 A. Grirrane, A. Pastor, A. Galindo, A. Ienco, C. Mealli and P. Rosa, *Chem. Commun.*, 2003, 512 and references cited therein.

14 (*a*) R. Boča, *Coord. Chem. Rev.*, 1998, **173**, 167; (*b*) R. L Carlin, *Magnetochemistry*, Springer-Verlag, Berlin, New York, 1986.

15 (*a*) X.-M. Chen, Y.-X. Tong, Z.-T. Xu and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1995, 4001; (*b*) L.-S. Long, X.-M. Chen, M.-L. Tong, Z.-G. Sun, Y.-P. Ren, R.-B. Huang and L.-S. Zheng, *J. Chem. Soc., Dalton Trans.*, 2001, 2888.