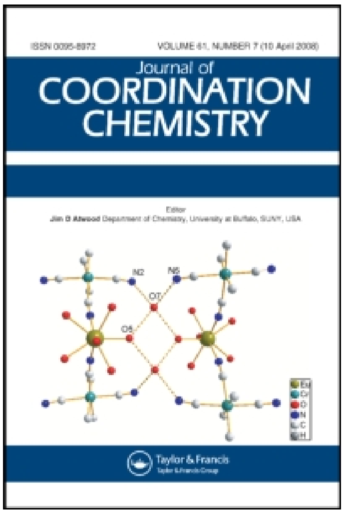

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A three-dimensional supramolecular framework built from two-dimensional wave-shaped layers

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A new metal-organic coordination polymer, $[Fe(4,4'\text{-bpy})(PT)(H_2O)_2]\cdot 2H_2O$ (**1**) (4,4′-bpy = 4,4′-bipyridine, H_2PT = phthalic acid), was prepared by hydrothermal reaction of $FeSO_4\cdot 7H_2O$, 4,4′-bpy and H_2PT at 110°C and characterized by single-crystal X-ray diffraction analysis. The two-dimensional wave-shaped layers are stacked in ABAB sequence, and therefore form a three-dimensional supramolecular architecture. Six-membered rings with the 'chair' conformation, formed *via* hydrogen-bonds, exist between the layers, are symmetrical with respect to the two-fold axes running along *b*.

Keywords: Crystal structure; Supramolecular framework; Mixed ligand; Wave-shaped layer; Hydrothermal synthesis

1. Introduction

The rational design of crystalline solids by self-organization of multiple molecular components is a goal of supramolecular chemistry, owing to their potential application in catalysis, molecular selection, non-linear optics, ion exchange and microelectronics [1–4]. Although some focus aims at the functional aspects, it would be difficult to achieve true advances without understanding the structural aspects of such materials at a molecular or atomic resolution [5–7]. Metal-organic supramolecular networks are constructed from two kinds of weak interaction (H-bond and π–π staking). Hydrogen bonds, O···H, N···H and F···H, are very important in supramolecular chemistry, because they can easily be formed for constructing high-dimensional supramolecular frameworks [8–12]. Multi-carboxylate molecules are not only good hydrogen-bond accepters and hydrogen-bond donors, but also

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coordinate to metal ions, resulting in structures with novel topological features [13]. 4,4′-bipyridine is a linear rigid molecule, easy to construct into a two-dimensional or three-dimensional metal-organic framework in view of the excellent coordination capabilities [14, 15].

To construct a framework with mixed ligands, both must co-coordinate to the metal centers. Because ligands with O-donors or N-donors have different coordinating ability, in the same reaction system there is a competition between them [16, 17]. Our exploratory studies show that hydrothermal environment is very suitable for preparation of novel coordination polymers with mixed ligands [18, 19].

Based on the aforementioned points, the aim of our research is to synthesize a novel high-dimensional metal-organic coordination polymer by means of covalent bonds as well as hydrogen-bonds. In this article, we report a novel three-dimensional supramolecular coordination polymer, $[Fe(4,4'\text{-bpy})(PT)(H_2O)_2] \cdot 2H_2O$ (**1**) based on mixed ligands of phthalic acid and 4,4′-bipyridine under hydrothermal conditions. The three-dimensional framework is built from two-dimensional wave-shaped layers. A six-membered ring, which has the ‘chair’ conformation exists between the layers, connected by H-bonds. In the six-membered ring, two coordinated water molecules, two lattice water molecules and two O atoms from the same carboxylate are centrosymmetric. The rings at both sides of the layers are symmetrical with respect to the two-fold axes running along the *b*-axis.

2. Experimental

2.1. *Materials and methods*

All chemicals purchased were of reagent grade and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The Fe content was determined by a Leaman inductively coupled plasma (ICP) spectrometer. All measurements were performed at room temperature.

2.2. *Preparation of compound*

2.2.1. $[Fe(4,4'\text{-bpy})(PT)(H_2O)_2] \cdot 2H_2O$ (1). A mixture of $FeSO_4 \cdot 7H_2O$ (0.139 g, 0.5 mmol), 4,4′-bpy (0.078 g, 0.5 mmol), H_2PT (0.083 g, 0.5 mmol) and H_2O (10 mL) was stirred for 10 min in air. The mixture was then transferred to a 23 mL Teflon reactor and kept at 110°C for 4 days under autogenous pressure, then cooled to room temperature at a rate of $10^{\circ}C\,h^{-1}$. Yellow crystals of compound **1** were obtained (yield: 61% based on Fe). The element analysis found: C, 48.1%; H, 4.1%; N, 6.1%; Fe, 12.3% (Calcd: C, 48.21%; H, 4.46%; N, 6.25%; Fe, 12.47%).

2.3. *X-ray crystallography*

A yellow single crystal with dimensions $0.323 \times 0.224 \times 0.253\,mm^3$ was glued on a glass fiber. Data were collected on a Rigaku R-axis RAPID IP diffractometer at 293 K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and IP technique in the range $3.20^{\circ} < \theta < 27.49^{\circ}$. An empirical absorption correction was applied. The structure was solved by the direct method and refined by full-matrix least-squares on F^2 using the SHELXTL 97 crystallographic

Table 1. Crystal data and structure refinements for compound **1**.

Empirical formula	$C_{18}H_{20}FeN_2O_8$
Formula weight	448.21
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2/n$
a (Å)	7.6500(15)
b (Å)	11.390(2)
c (Å)	10.790(2)
Volume (Å^3)	939.1(3)
Z	2
P_{calcd} (mg m^{-3})	1.585
Absorption coefficient (mm^{-1})	0.854
F(000)	464
Crystal size (mm)	0.38 × 0.35 × 0.31
θ range (°)	3.20–27.49
Limiting indices	$-9 \leq h \leq 9$, $-14 \leq k \leq 14$, $-13 \leq l \leq 14$
Reflections collected	8402
Independent reflections	2088
Max. and min. transmission	0.7778 and 0.7374
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2088/4/147
Goodness-of-fit on F^2	1.041
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0324$, $wR_2 = 0.0741$
R indices (all data)	$R_1 = 0.0408$, $wR_2 = 0.0793$
Largest diff. peak and hole (e Å^{-3})	0.352 and −0.272

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **1**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Fe(1)	7500	7195(1)	75007500	22(1)
O(1)	5333(2)	7077(1)	8706(1)	33(1)
O(2)	2582(2)	6578(1)	9001(1)	45(1)
N(1)	7500	5279(2)	7500	28(1)
N(2)	7500	−902(2)	7500	25(1)
C(1)	8984(3)	4670(2)	7715(2)	33(1)
C(2)	9041(3)	3467(2)	7745(2)	33(1)
C(3)	7500	2837(2)	7500	27(1)
C(4)	7500	1548(2)	7500	26(1)
C(5)	8199(3)	914(2)	8505(2)	30(1)
C(6)	8157(3)	−289(2)	8471(2)	30(1)
C(7)	3712(2)	7256(2)	8612(1)	25(1)
C(8)	3078(2)	8384(1)	8015(1)	22(1)
C(9)	3612(3)	9445(2)	8536(2)	33(1)
C(10)	3045(3)	10,492(2)	8029(2)	43(1)
OW1	5820(2)	7170(1)	5843(1)	30(1)
OW2	7844(2)	5866(2)	4366(1)	48(1)

software package [20, 21]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps. Further details of the X-ray structural analysis are given in table 1. Atomic positional parameters and isotropic temperature factors are given in table 2. Selected bond lengths

Table 3. Bond lengths [Å] and bond angles [°] for complex **1**.

Fe(1)–OW1	2.1525(14)
Fe(1)–O(1)	2.1588(14)
Fe(1)–N(1)	2.182(2)
OW1–Fe(1)–O(1)	93.12(5)
OW1–Fe(1)–N(1)	89.23(4)
O(1)–Fe(1)–N(1)	86.45(4)
C(7)–O(1)–Fe(1)	136.39(11)
Fe(1)–OW1–HW1A	119.8(16)
Fe(1)–OW1–HW1B	109.9(17)
C(1)–N(1)–Fe(1)	121.16(11)

and angles are listed in table 3. Crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters are available in supplementary crystallographic data.

3. Results and discussion

3.1. *The crystal structure of compound 1*

The single-crystal structural analysis shows that the structure of **1** is a novel three-dimensional supramolecular framework, in which the asymmetric unit contains one iron atom, one 4,4′-bpy ligand, one PT ligand, two coordinated water molecules and two lattice water molecules (figure 1). The iron(II) atom is coordinated by two oxygen atoms (Fe(1)–O(1) and Fe(1)–O(1A) = 2.1588(14) Å) from carboxylate groups of two PT ligands, two nitrogen atoms (Fe(1)–N(1) = 2.182(2) Å, Fe(1)–N(2) = 2.168(2) Å) from two 4,4′-bpy ligands and two coordinated water molecules (Fe(1)–OW(1) and Fe(1)–OW(1A) = 2.1525(14) Å), to complete an octahedral coordination environment. The octahedral geometry is only slightly distorted.

The valence sum calculations [22] give the value of 1.887 for Fe atom, suggesting that Fe center is in the +2 oxidation state. OW(1) has bond valence sum of 0.323, showing it is a coordinated water molecule. The results of bond valence sum calculations are consistent with the charge balance considerations.

The assembly of **1** occurs through two steps: the first is the construction of the two-dimensional layers and the second is the formation of the three-dimensional framework by hydrogen-bonding interaction. The iron atoms are connected together *via* oxygen atoms (O1) of the carbonyl groups from PT ligands to form one-dimensional chains. The two carbonyl groups of PT adopt the same coordination mode, namely one O atom of the carbonyl group coordinated to iron and the other O atoms uncoordinated. The PT molecules and the iron atoms are arranged as a wave-shaped chain due to the coordinated PT ligands. Then the chains are connected together by the linear ligand, 4,4′-bpy, to form a two-dimensional layer. The 2D layer exhibits a wave-shape in an ABAB sequence (figure 2). Lattice water molecules are located between the layers and form multipoint hydrogen-bonds with the nearest carboxyl oxygen atoms (O1 and O2) and coordinated water molecules; representative hydrogen-bonds are OW(2)–HW(2A) $\cdots$ O(1), OW(2)–HW(2B) $\cdots$ O(2)

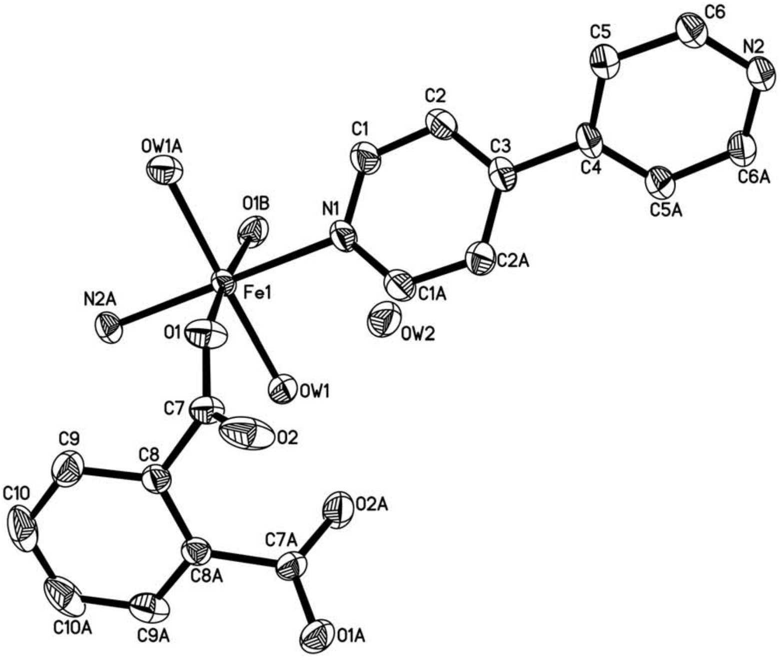
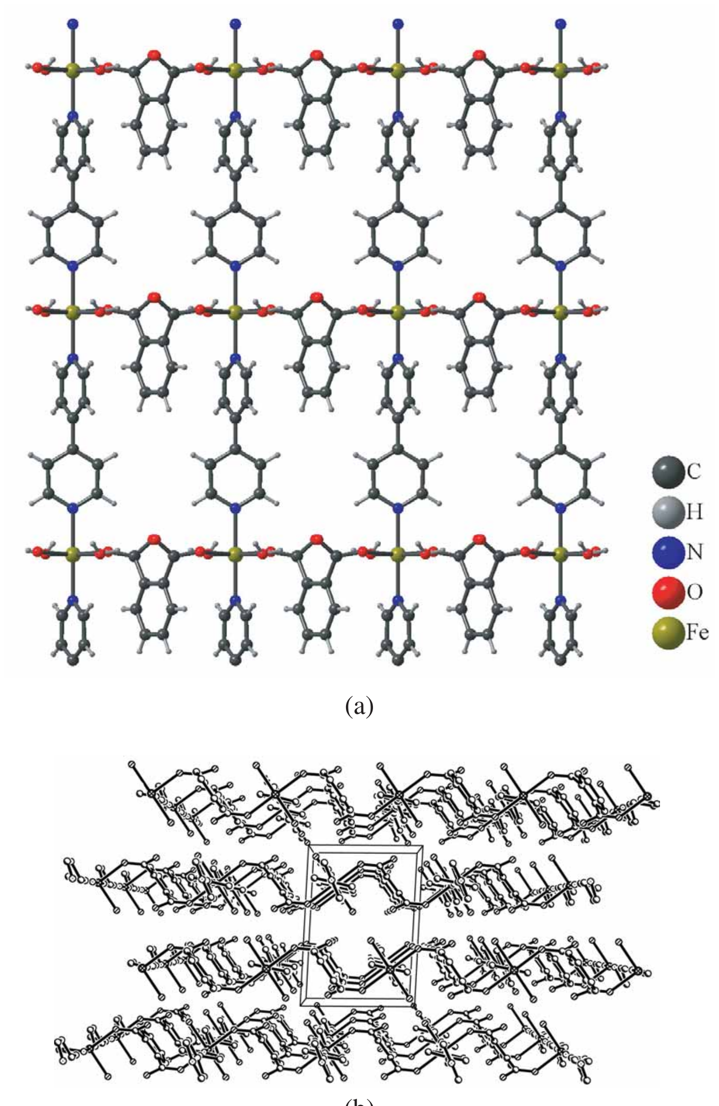


Figure 1. The coordination environment of iron in **1**.

and OW(1)–HW(1B)···OW(2), whose lengths are 2.812, 2.817 and 2.715 Å, respectively. Through these hydrogen-bonds existing between the layers, a three-dimensional supramolecular framework is formed. Besides the aforementioned hydrogen-bonds, coordinated waters also form multipoint hydrogen-bonds with the nearest O atoms (O2) with a representative hydrogen-bond are OW(1)–HW(1A)···O(2), whose length is 2.701 Å. Interestingly, a six-membered ring, consisting of two O atoms of the carbonyl group, two lattice water molecules and two coordinated water molecules, is observed between adjacent wave-shaped layers, formed *via* the hydrogen-bonds OW(1)–HW(1B)···OW(2), OW(2)–HW(2B)···O(2) and OW(1)–HW(1A)···O(2). The six molecules and atoms are centro-symmetric, and the ring has the 'chair' conformation. The rings are symmetrical with respect to the two-fold axis running along the *b*-axis (figure 3).

3.2. *Magnetic properties of compound 1*

The thermal variations of $\chi_m T$, and χ of **1** are displayed in figure 4. The $\chi_m T$, continuously decreased as the temperature is lowered from 300.0 to 2.0 K, indicating the presence of antiferromagnetic interactions. At 300 K, the $\chi_m T$ value is ca 3.23 emu K mol^{-1}, slightly higher than the value (3.00 emu K mol^{-1}) of $S = 2$ spins of Fe^{2+}. The magnetic susceptibility is characteristic of an overall antiferromagnetic interaction. It is too difficult to fit the experimental magnetic data of this complex system using a suitable theoretical model, and further studies on magnetic properties of similar systems are ongoing in our lab.



(a)

(b)

Figure 2. (a) View of the wave-shaped layer of compound **1**. (b) Side view of the layers, showing a beautiful wave shape.

4. Conclusions

In this article, a novel three-dimensional supramolecular framework with wave-shaped layers, formed by covalent bonds and hydrogen-bonding interactions, has been synthesized and structurally characterized. The successful synthesis of compound **1** not only shows that the efficiency of hydrothermal reactions in preparing novel metal-organic framework with different ligands but also proves that the H-bonding interaction contributes to the formation of higher-dimensional frameworks.

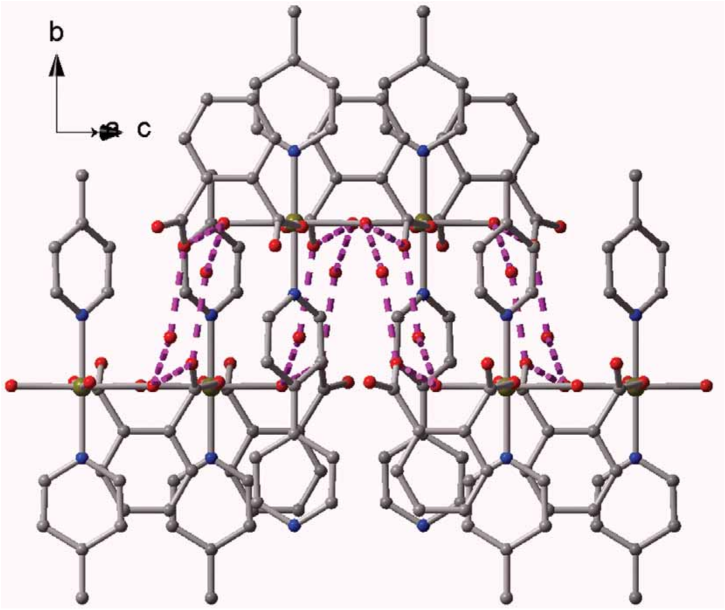


Figure 3. H-bonds in the six-membered rings with 'chair' conformation, and the rings are symmetrical with respect to the two-fold axis running along *b*-axis.

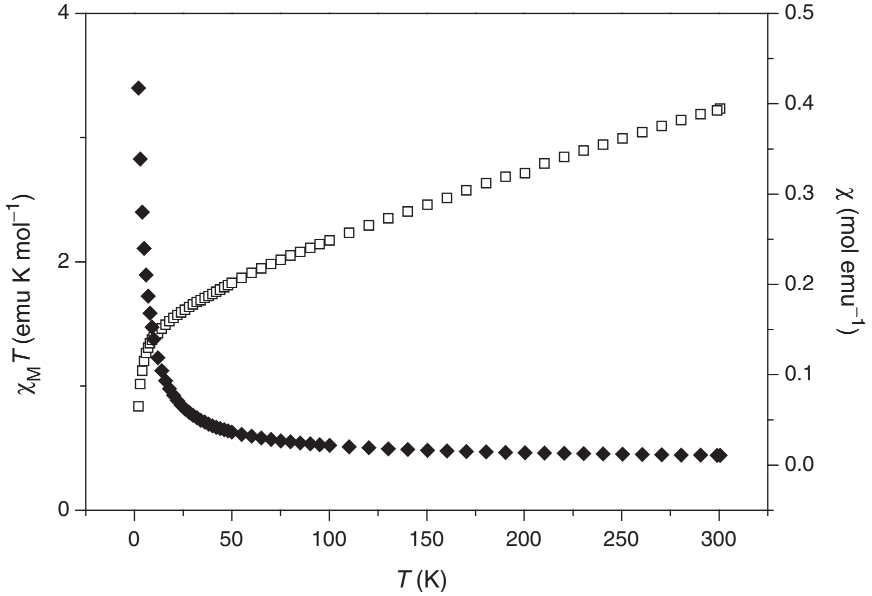


Figure 4. The temperature dependence of magnetic susceptibility χ_M (diamond) and the product $\chi_M T$ (square) for compound **1**.

The rational combination of the two aspects will enrich the chemistry of metal-based coordination polymers.

Supplementary material

H contains hydrogen coordinates and isotropic displacement parameters, and anisotropic displacement parameters for **1**.

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References

[1] O.M. Yaghi, H. Li, C. David, D. Richardson, T.L. Groy. *Acc. Chem. Res.*, **474**, 31 (1998).
[2] P.J. Hagrman, D. Hagrman, J. Zubieta. *Angew. Chem. Int. Ed.*, **38**, 2638 (1999).
[3] S.R. Batten, R. Roboson. *Angew. Chem. Int. Ed.*, **37**, 1461 (1998).
[4] S. Noro, S. Kitagawa, M. Kondo, K. Seki. *Angew. Chem. Int. Ed.*, **39**, 2082 (2000).
[5] O.R. Evans, W. Lin. *Acc. Chem. Res.*, **35**, 511 (2002).
[6] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi. J. Kim. *Nature*, **423**, 705 (2003).
[7] S.L. James. *Chem. Soc. Rev.*, **32**, 276 (2003).
[8] U. Kortz, S.S. Hamzeh, N.A. Nasser. *Chem. Eur. J.*, **9**, 2945 (2003).
[9] S.R. Batten, B.F. Hoskins, R. Robson. *New, J. Chem.*, **22**, 173 (1998).
[10] H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi. *Nature*, **402**, 276 (1999).
[11] X.M. Zhang, M.L. Tong, M.L. Gong, X.M. Chen. *Eur. J. Inorg. Chem.*, 138 (2003).
[12] X.M. Chen, G.F. Liu. *Chem. Eur. J.*, **8**, 4811 (2002).
[13] D.M. Shin, I.S. Lee, Y.K. Chung, M.S. Lah. *Inorg. Chem.*, **42**, 5459 (2003).
[14] C.H. Huang, L.H. Huang, K.H. Lii. *Inorg. Chem.*, **40**, 2625 (2001).
[15] L. Zheng, X. Fang, K.H. Lii, H.H. Song, X.Q. Xin, H.K. Fun, K.Chinnakali, I.A. Razak. *J. Chem. Soc., Dalton Trans.*, **14**, 2311 (1999).
[16] P.J. Hagrman, D. Hagrman, J. Zubieta. *Angew. Chem. Int. Ed.*, **38**, 2638 (1999).
[17] D. Hagrman, K.R. Hammond, R. Haushalter, J. Zubieta. *Chem. Mater.*, **10**, 2091 (1998).
[18] Y.G. Li, N. Hao, E.B. Wang, Y. Lu, C.W. Hu, L. Xu. *Eur. J. Inorg. Chem.*, 2567 (2003).
[19] Y.G. Li, N. Hao, E.B. Wang, Z.H. Kang, C.W. Hu. *Inorg. Chem.*, **42**, 3119 (2003).
[20] G.M. Sheldrick. *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany (1997).
[21] G.M. Sheldrick. *Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany (1997).
[22] I.D. Brown, D. Altermatt. *Acta Crystallogr. Sect. B*, **41**, 244 (1985).