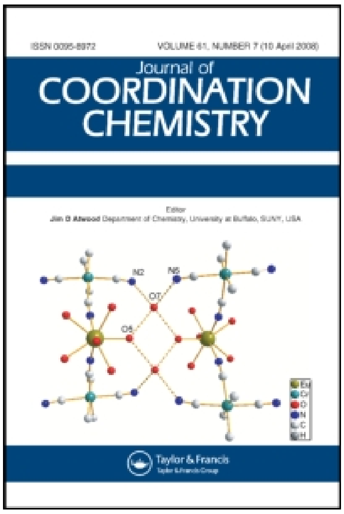

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Syntheses and crystal structures of two Zn(II) complexes, [Zn(Fura)$_2$(2,2'-bipy)(H$_2$O)] and [Zn(μ-dnbc)$_2$] (Fura=Furoic acid, 2,2'-bpy=2,2'-bipyridine, dnba=3,5-dinitrobenzoic acid)

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Syntheses and crystal structures of two Zn(II) complexes, $[Zn(Fura)_2(2,2'\text{-bipy})(H_2O)]$ and $[Zn(\mu\text{-dnbc})_2]$ (Fura = Furoic acid, 2,2′-bpy = 2,2′-bipyridine, dnba = 3,5-dinitrobenzoic acid)

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Two Zn(II) complexes, $[Zn(Fura)_2(2,2'\text{-bpy})(H_2O)]$ (**1**) and $[Zn(\mu\text{-dnbc})_2]$ (**2**), have been synthesized and characterized by X-ray diffraction and IR spectra. **1** is a quaternary Zn(II) complex with ZnN_2O_3 configuration distorted square pyramid geometry; **2** is a Zn(II) coordination polymer with 1D double-helical chains bridged by 3,5-dinitrobenzoic acid.

Keywords: Zn(II) complex; Furoic acid; Coordination polymer; 3,5-dinitrobenzoic acid

1. Introduction

Design and synthesis of metal-organic coordination polymers are of great interest due to their applications in sorption and separation, non-linear optical materials, electrical conductivity and catalysis [1–4]. The fascinating properties have prompted studies of the architectures of metal–organic coordination polymers [1]. In many cases, metal–organic frameworks with micropores or channels could be constructed from transition or rare earth metals with carboxylate or polypyridine linkages [5–8]. Coordination polymers or clusters constructed from carboxylate linkages have proven to be sufficiently strong to stabilize networks against collapse because carboxylate can coordinate to metal ions as terminal, chelate, bridging, or chelate-bridging ligands [9–11] and also have a role in charge compensation. Metal coordination with polypyridine linkages, although widely employed, generally have not stabilized open frameworks against channel collapse; furthermore, a drawback of polypyridine-only frameworks is that ions required for charge compensation may block channels [9]. Hupp *et al*. reasoned that both problems might be overcome by combining polypyridine coordination with carboxylate coordination in mixed-ligand framework compounds, which could also facilitate the incorporation of functionality [9]. In order to construct

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coordination polymers with new metal–organic frameworks and probe the effect of electron-attracting substituents on aromatic ring of aromatic carboxylic acids we now report the syntheses, crystal structures and some properties of [Zn(Fura)$_2$(2,2′-bipy)(H$_2$O)] (**1**) and [Zn(μ-dnbc)$_2$] (**2**) prepared from zinc oxalate reaction with 2,2′-bipyridine and furoic acid, 2,2′-bipyridine and 3,5-dinitrobenzoic acid, respectively.

2. Experimental

2.1. *Materials and physical measurements*

We prepared zinc oxalate. Other reagents and solvents for syntheses of the complexes are analytically pure, purchased from the Chemical Reagent Company and used without further purification.

IR spectra were recorded on a Nicolte IR-470 Spectrophometer as KBr pellets in the range 4000–400 cm^{-1}. Thermal analysis was measured on NETZSCH TG209 instrument. The single crystal structure was measured on a Rigaku-Raxis-IV X-ray Diffractometer.

2.2. *Synthesis of [Zn(Fura)$_2$(2,2′-bipy)(H$_2$O)] (1)*

A solution of 2,2′-bipyridine 0.0625 g (0.4 mmol) dissolved in 10 mL methanol was added to a suspension solution of zinc oxalate 0.0613 g (0.4 mmol) and 20 mL water in a 100 mL triangular bottle with stirring for 20 min. A methanol solution (20 mL) containing furoic acid 0.09 g (0.8 mmol) neutralized to pH = 7 with 0.5 mol L^{-1} NaOH was added dropwise to the above-mentioned solution with stirring. The reaction mixture was heated and refluxed at 60°C for 3 h, cooled to room temperature and filtered. The filtrate was allowed to evaporate at ambient temperature. Colourless block crystals of **1** were obtained after one month with the yields of 0.089 g (48.13%). IR (KBr, cm^{-1}) : υ(O–H) 3420 w, υ(C–H) 3122 m, υ_{as}(COO$^-$) 1597 s, υ_s(COO$^-$) 1363 s, υ(C=C) 1580 vs, υ(C=N) 1566 vs, υ(C–O) 1009 m.

2.3. *Synthesis of [Zn(μ-dnba)$_2$] (2)*

Except for replacing furoic acid by 3,5-dinitrobenzoic acid, the synthesis of complex **2** is similar to the procedure for 1. The colourless column crystals of **2** were obtained after two months with yields of 0.167 g (42.8%). IR (KBr, cm^{-1}) : υ(C–H) 3101 m, υ_{as}(COO$^-$) 1629 s, υ_s(COO$^-$) 1472 vs, υ(C=C) 1609 vs, υ_{as}(NO$_2$) 1415 vs, υ_s(NO$_2$) 1344 vs.

2.4. *X-ray crystallography*

Intensity data of complex **1** (0.20 × 0.18 × 0.17 mm^3) and **2** (0.20 × 0.18 × 0.18 mm^3) were measured with a Rigaku-Raxis-IV X-ray Diffractometer using monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at 291 K. Reflections (5696) were measured over the ranges $0 \leq h \leq 8$, $-20 \leq k \leq 20$, $-19 \leq l \leq 19$ yielding 3224 unique reflections for **1**. Reflections (4297) were measured over the ranges $-11 \leq h \leq 13$, $-13 \leq k \leq 0$, $-13 \leq l \leq 13$ and yielding 1550 unique reflections for **2**. The raw data were corrected with direct methods and the structure was solved using the SHELX-97 program. Non-hydrogen atoms were located by direct phase determination and subjected to anisotropic refinement. The full matrix least-squares calculations on F^2 were applied to the final refinement. The refinement converged at $R_1 = 0.0347$ and $wR_2 = 0.0826$ values for reflections with $I > 2\sigma(I)$ for **1**, and $R_1 = 0.0272$ and $wR_2 = 0.0646$ values for reflections with $I > 2\sigma(I)$ for **2**. Details of the crystal structural determinations are summarized in tables 1 and 2 of this article. Full atomic data are available as a file in CIF format.

3. Results and discussion

3.1. *Synthesis and discussion*

Oxalate forms stable complexes with alkaline earth metals, transition metals and rare earth metals, but many of these complexes are insoluble. We attempted to synthesize new complexes with new configuration and specific properties not only containing oxalate but other interesting ligands. Our results suggests that aromatic carboxylate with electron-attracting substituents possess strong coordination. Coordination was enhanced due to the electron-attracting substituent reducing electric charges repelling the oxygen atoms of carboxylate,

3.2. *Description of the crystal structure of complex 1*

The crystal cell parameters and selected bond distances and angles relevant to the Zn(II) coordination sphere and the hydrogen bond distances and angles of the complex **1** are

Table 1. Crystallographic data and structural refinement for complexes **1** and **2**.

	1	**2**
Empirical formula	$C_{20}H_{16}N_2O_7Zn$	$C_{14}H_6N_4O_{12}Zn$
Formula weight	461.72	487.60
Crystal system	Monoclinic	Hexagal
Space group	$P2(1)/c$	$P3(1)2(1)2$
a (Å)	6.8707(14)	11.1241(16)
b (Å)	17.129(3)	11.1241(16)
c (Å)	16.429(3)	11.620(2)
α (°)	90	90
β (°)	95.99(3)	90
γ (°)	90	120
V (Å^3)	1923.0(7)	1245.3(4)
D_c (Mg m^{-3})	1.595	1.951
Z	4	3
μ (mm^{-1})	1.32	1.564
Reflections collected/unique	5696/3224	4297/1550
Data/restraints/parameters	3224/0/280	1550/0/142
R_1	0.0347	0.0272
wR_2	0.0826	0.0646
Goodness-of-fit on F^2	1.100	1.052
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ (e Å^{-3})	0.396 and −0.457	0.231 and −0.357

Table 2. Selected bond distances (Å) and angles (°) for complexes **1** and **2**.

1		**2**	
Zn(1)–O(6)	2.028(2)	Zn(1)–O(1)	1.935(2)
Zn(1)–O(3)	2.0514(19)	Zn(1)–O(1)#1	1.935(2)
Zn(1)–N(1)	2.109(2)	Zn(1)–O(2)#2	1.9608(19)
Zn(1)–N(2)	2.176(2)	Zn(1)–O(2)#3	1.9608(19)
Zn(1)–O(7)	2.030(2)	O(2)–Zn(1)#4	1.9608(19)
O(3)–C(5)	1.272(3)	O(1)–C(7)	1.261(3)
O(2)–C(5)	1.249(3)	O(2)–C(7)	1.260(3)
O(6)–C(10)	1.269(3)		
O(5)–C(10)	1.254(3)		
O(6)–Zn(1)–O(3)	93.28(8)	O(1)–Zn(1)–O(1)#1	121.66(15)
O(3)–Zn(1)–N(1)	93.57(8)	O(1)–Zn(1)–O(2)#2	101.67(9)
N(1)–Zn(1)–N(2)	76.28(8)	O(1)#1–Zn(1)–O(2)#2	111.07(9)
O(7)–Zn(1)–O(3)	93.07(10)	O(1)–Zn(1)–O(2)#3	111.07(9)
O(6)–Zn(1)–O(7)	101.94(10)	O(1)#1–Zn(1)–O(2)#3	101.67(9)
O(7)–Zn(1)–N(1)	104.97(10)	O(2)#2–Zn(1)–O(2)#3	109.63(13)
O(7)–Zn(1)–N(2)	102.16(10)	O(1)–C(7)–O(2)	125.8(2)
C(5)–O(3)–Zn(1)	124.07(18)	O(3)–N(1)–O(4)	124.3(3)
C(10)–O(6)–Zn(1)	109.54(16)	C(7)–O(1)–Zn(1)	128.15(18)
O(2)–C(5)–O(3)	126.4(3)	C(7)–O(2)–Zn(1)#4	141.06(18)
O(5)–C(10)–O(6)	124.1(2)		

Symmetry transformations used to generate equivalent atoms for the complex **2**, **1**: y, x, $-z$, #2: $-y+2$, $x-y+1$, $z-1/3$, #3: $x-y+1$, $-y+2$, $-z+1/3$, #4: $-x+y+1$, $-x+2$, $z+1/3$.

Table 3. Hydrogen-bonds for *P*21*c* (Å and °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(7)–H(7F)···O(5)#1	0.83(5)	1.89(5)	2.714(3)	173(5)
O(7)–H(7E)···O(2)	0.78(4)	1.93(4)	2.675(4)	160(4)

Symmetry transformations used to generate equivalent atoms, #1: $x-1$, y, z.

given in tables 1–3, respectively. Figures 1 and 2 show the ORTEP drawing and 1D network formed by hydrogen bonding and π–π stacking interaction for **1**, respectively. The crystal cell of **1** consists of one 2,2′-bpy, two furoate and one water with a Zn(II) centre with ZnN_2O_3 distorted square pyramid geometry. Two nitrogen atoms of 2,2′-bpy and two oxygen atoms from two furoates are located in the square pyramid bottom; oxygen of coordinated water lies at the top of the pyramid. Zn(1)–N(1) and Zn(1)–N(2) are longer than those in the literature [12], Zn(1)–O(6), Zn(1)–O(3) and Zn(1)–O(7) are shorter than literature values [12].

There are three kinds of hydrogen bond in the structure of **1**. One is an intramolecular hydrogen bond [O(7)–H(7E)···O(2) = 2.675(4) Å] formed from one hydrogen of the coordinated water with an uncoordinated oxygen of one furoate of the same crystal cell. Another is an intermolecular hydrogen bond [O(7)–H(7F)···O(5)#1 = 2.714(3) Å] formed from the other hydrogen with an uncoordinated oxygen of one an furoate of adjacent crystal cell, by which the structural units were linked into a 1D chain along the *a* axis; additionally, a strong π–π stacking interaction existed between pyridine rings of neighbouring chains with centroid

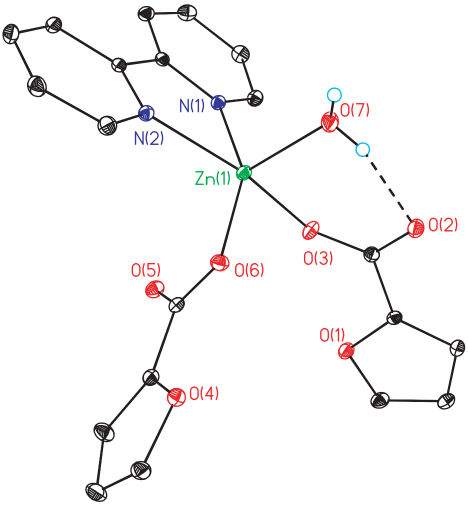

Figure 1. The ORTEP drawing of complex **1**.

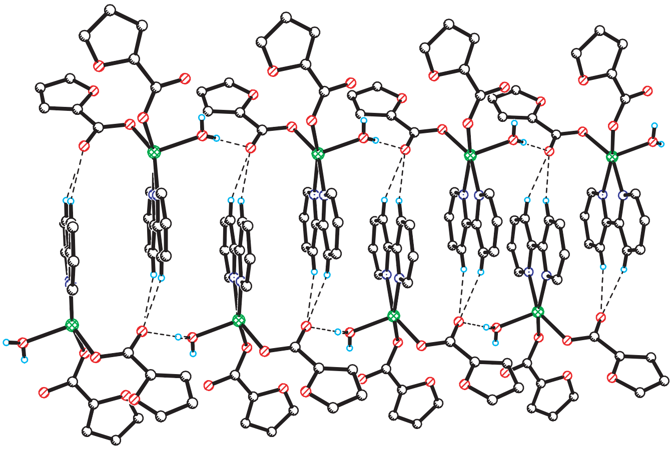

Figure 2. A view of the structure with hydrogen bonding and π–π stacking interaction for **1**.

to centroid distance 3.4185 Å and dihedral angle 0°. Due to the intermolecular hydrogen bonding and π–π stacking interactions, a double-chain structure was formed (as shown in figure 2). Additionally, there is a weak intermolecular hydrogen bond [C(14c)–H, 14c] $\cdots$ O(5b) = 3.355 Å, C(17c)–H(17c) $\cdots$ O(5b) = 3.472 Å] formed from 3,3′- dihydrogen atoms of 2,2′-bpy with an uncoordinated oxygen of one furoate of an adjacent chain, stabilizing the double-chain structure. There is also an intermolecular hydrogen bond [C(6a)–H(6a) $\cdots$ O(1c) = 3.196 Å] formed from hydrogen of furan with an oxygen of the adjacent furan ring, together with the π–π stacking interaction between furan rings of neighbouring chains with centroid to centroid distance 3.584 Å and dihedral angle 0°, resulting in the chain linking into a 3D structure (as shown in figure 3).

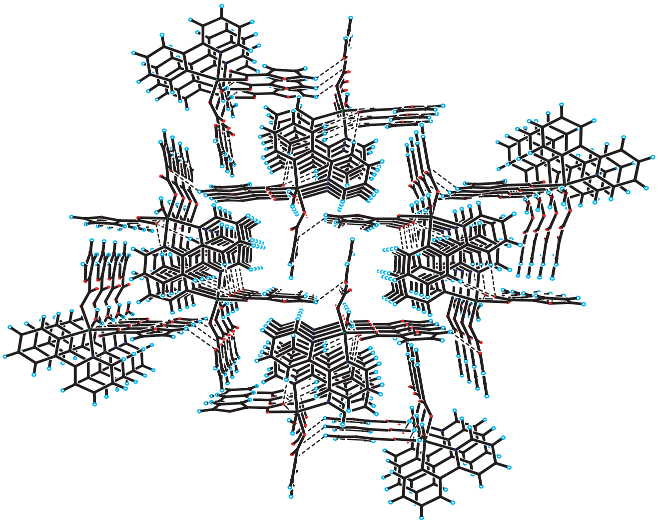

Figure 3. A view of the packing diagram of complex **1**.

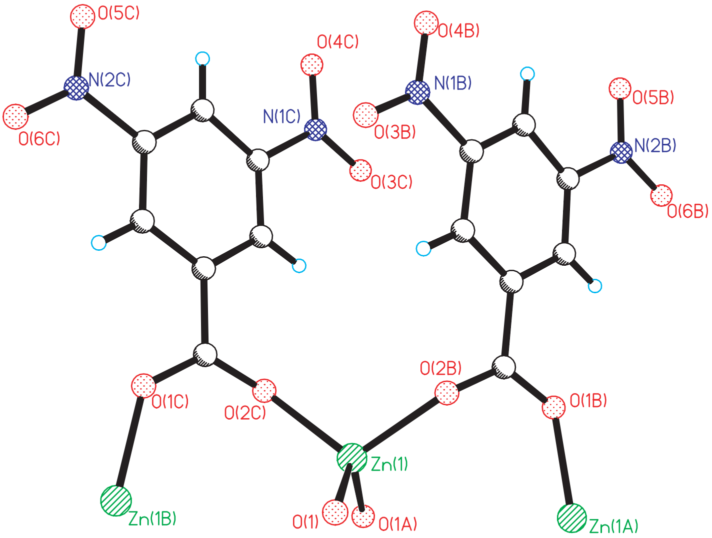

Figure 4. The ORTEP drawing of complex **2**.

3.3. *Description of the crystal structure of complex 2*

The crystal cell parameters and selected bond distances and angles relevant to the Zn(II) coordination of **2** are given in tables 1 and 2, respectively. The crystal cell consists of two dnba and one Zn(II) centre with ZnO_4 in a distorted tetrahedron (figure 4). Four oxygen atoms from four dnba form the top of the tetrahedron, two oxygen atoms of carboxylate of each dnba bridge adjacent two Zn(II); Zn–O distances are 1.935(2)–1.9608(19) Å; the range is shorter than literature values [13]. Bond angles of **2** are different from the literature value (109.5°) [14], indicating a distorted tetrahedron.

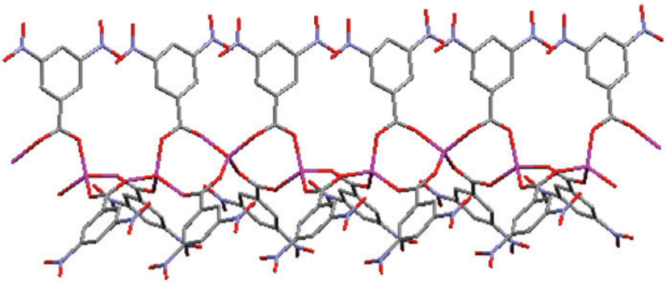

Figure 5. A view of the structure with double-helical chains of **2**.

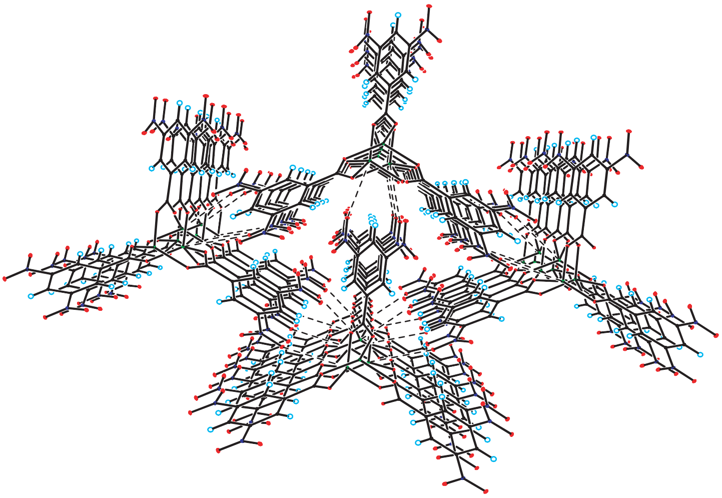

Figure 6. A view of the packing diagram of complex **2**.

Due to bridging dnba, Zn(II) arranges alternately in three directions of the C_3 axis and the crystal structural units are expanded into 1D chain twisted double-helical chains along the *c* axis (as shown in figure 5). Interestingly, one oxygen atom of each nitro-group of each dnba in 1D double-helical chain with Zn(II) of adjacent chain have secondary bonding, by which the 1D chains are expanded into the three-dimensional crystal structure (as shown in figure 6).

3.4. *IR spectra*

In the IR spectrum of complex **1**, υ(O–H) of coordinated water appeared at 3420 cm^{-1}, $\upsilon_{as}(COO^-)$ and $\upsilon_s(COO^-)$ of fura were observed at 1597 and 1363 cm^{-1}, respectively, the characterization absorption bands of 2,2′-bpy were displayed at 3122 and 1566 cm^{-1} respectively. $\Delta_{\upsilon_{as}(coo^-)-\upsilon_s(coo^-)}$ is larger than 200 cm^{-1}, suggesting unidentate carboxylate [15, 16]. For **2** $\upsilon_{as}(COO^-)$ and $\upsilon_s(COO^-)$ of dnba appeared at 1629 and 1472 cm^{-1} respectively, the characterization absorption bands of NO_3^- were observed at 1415 and 1344 cm^{-1} respectively. $\Delta_{\upsilon_{as}(coo^-)-\upsilon_s(coo^-)}$ is 157 cm^{-1}, indicating that dnba

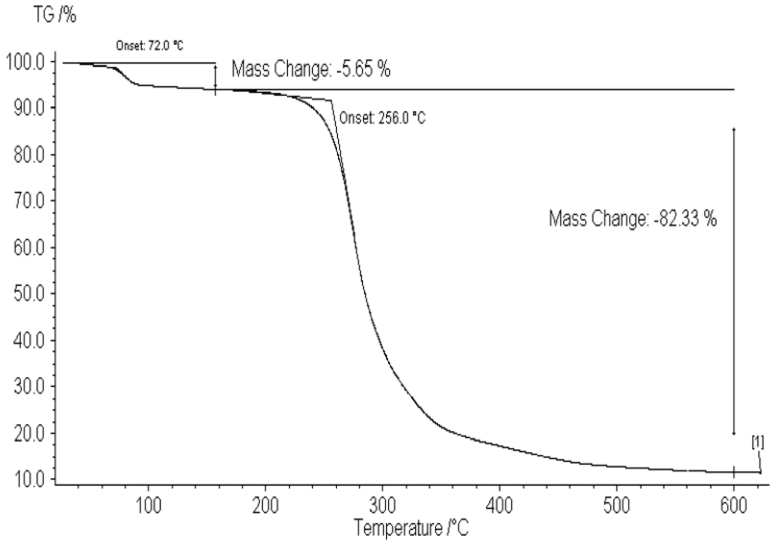

Figure 7. TG graph of **1**.

is bridging bidentate [17]. The results of IR spetral analyses are consistent with those of X-ray diffraction analysis.

3.5. *Thermal analysis*

Thermal decomposition of **1** in nitrogen was carried out at the heating rate of 10°min^{-1}. The TG curve (figure 7) shows decomposition at 72°C, to 256°C with mass loss of 5.65%, corresponding to losing one water (3.9%). The remains continuously decomposed, to 580°C with total mass loss of 82.33%, from fura and 2,2′-bpy separating from the parent complex (Calcd 82.30%). The total mass loss of 87.98% is quite close to the theoretical mass loss (86.2%) calculated by taking zinc as the final product.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 280096 for the complex **1**, 290244 for the complex **2**. Copies of these informations may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk or at http://www.ccdc.cam.ac.uk).

References

[1] D. Sun, R. Cao, W. Bi, J. Weng, M. Hong, Y. Liang. *Inorg. Chim. Acta*, **357**, 991 (2004).
[2] (a) A.J. Cheethan. *Science*, **264**, 794 (1994); (b) R.C. Finn, J. Zubieta. *Inorg. Chem.*, **40**, 2466 (2001).

[3] (a) J.M. Thomas. *Chem. Comm.*, **8**, 675 (2001); (b) S.L. Suib. *Chem. Rev.*, **93**, 803 (1993).

[4] G.K.H. Shimizu, GD. Enright, C.I. Ratcliffe, K.F. Preston, J.L. Reid, J.A. Ripmeester. *Chem. Comm.*, **16**, 1485 (1999).

[5] H. Mao, C. Zhang, G. Li, H. Zhang, H. Hou, L. Li, Q. Wu, Y. Zhu, E. Wang. *Dalton Trans.*, **22**, 3918 (2004).

[6] H.-L. Liu, H.-Y. Mao, H.-Y. Zhang, C. Xu, Q.-A. Wu, G. Li, Y. Zhu, H.-W. Hou. *Polyhedron*, **23**, 943 (2004).

[7] H.-Y. Mao, X.-Q. Shen, G. Li, H.-Y. Zhang, C. Xu, H.-L. Liu, E.-B. Wang, Q.-A. Wu, H.-W. Hou, Y. Zhu. *Polyhedron*, **23**, 1961 (2004).

[8] B.-L. Wu, H.-Q. Zhang, H.-Y. Zhang, Q.-A. Wu, H.-W. Hou, Y. Zhu, X.-Y. Wang. *Aust. J. Chem.*, **56**, 335 (2003).

[9] B.-Q. Ma, K.L. Mulfort, J.T. Hupp. *Inorg. Chem.*, **44**, 4912 (2005).

[10] C.N.R. Rao, S. Natarajan, R. Vaidhyanathan. *Angew. Chem. Int. Ed.*, **43**, 1466 (2004).

[11] (a) O.M. Yaghi, M. O'Keeffe, N.W. Ockwing, H.K. Chae, M. Eddaoudi, J. Kim. *Nature*, **423**, 705, (2003); (b) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J.M. Wachter, M. O'Keeffe, O.M. Yaghi. *Science*, **295**, 469, (2002).

[12] W.-G. Li, Z.-W. Wang, Y. Cai, Z.-J. Xu, Y.-Z. Li, H.-G. Zheng. *Chinese J. Inorg. Chem.*, **21**, 1857 (2005).

[13] X.-J. Li, R. Cao, D.-F. Sun, D.-Q. Yuan, W.-H. Bi, X. Li, Y.-Q. Wang. *J. Mol. Struct.*, **694**, 205 (2004).

[14] Beijing Normal University, *Inorganic Chemistry*, p. 318, People's Education Publishing House, Beijing, (1981).

[15] G.B. Deacon, R.J. Phillips. *Coord. Chem. Rev.*, **88**, 227 (1980).

[16] Z.-P. Deng, S. Gao, L.-H. Huo, H. Zharo. *Chinese J. Inorg. Chem.*, **22**, 567 (2006).

[17] Y. Zheng, D.-M. Xu, S.-X. Liu. *Inorg. Chem. Acta*, **294**, 163 (1999).