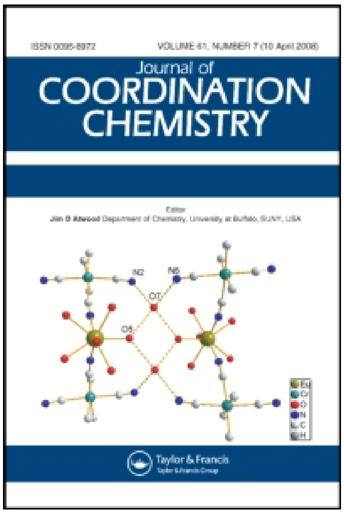

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Three porous coordination polymers of Co^{2+} and dpdo ligands with channels hosting polyanion chains

Meilin Wei[a]; Haiyun Xu[b]; Ruiping Sun[a]
[a] College of Chemistry and Environmental Science, Henan Normal University, Xinxiang, P.R. China [b] Department of Chemistry, Shangqiu Normal University, Shangqiu, P.R. China

To cite this Article Wei, Meilin , Xu, Haiyun and Sun, Ruiping(2009) 'Three porous coordination polymers of Co^{2+} and dpdo ligands with channels hosting polyanion chains', Journal of Coordination Chemistry, 62: 12, 1989 — 2002
To link to this Article: DOI: 10.1080/00958970902744982
URL: http://dx.doi.org/10.1080/00958970902744982

Journal of Coordination Chemistry
Vol. 62, No. 12, 20 June 2009, 1989–2002

Taylor & Francis
Taylor & Francis Group

Three porous coordination polymers of Co^{2+} and dpdo ligands with channels hosting polyanion chains

MEILIN WEI*†, HAIYUN XU‡ and RUIPING SUN†

†College of Chemistry and Environmental Science,
Henan Normal University, Xinxiang, 453007, P.R. China
‡Department of Chemistry, Shangqiu Normal University,
Shangqiu 476000, P.R. China

(*Received 13 August 2008; in final form 2 October 2008*)

Three porous coordination polymers, $\{[Co(dpdo)_4(H_2O)_2][H(H_2O)_6](PMo_{12}O_{40})\}_n$ (**1**), $\{[Co(dpdo)_4(H_2O)_2][H_3O(CH_3OH)_4](PMo_{12}O_{40})\}_n$ (**2**) and $\{[Co(dpdo)_4(H_2O)_2][K(CH_3OH)_4](PMo_{12}O_{40})\}_n$ (**3**) (where dpdo is 4,4′-bipyridine-*N*,*N*′-dioxide), with special channels for the chain-like assembly of polymeric Keggin-type anions have been synthesized through self-assembly of Co^{2+} and dpdo ligands in acetonitrile/water or methanol/water solutions and characterized by single crystal X-ray diffraction. Based on layers constructed by $[Co(dpdo)_4(H_2O)_2]^{2+}$ and different bridging units for charge compensation between layers, the three compounds exhibit similar noninterwoven networks with large channels occupied by the poly-Keggin-anion chains. Thermogravimetric analyses suggest that the three supramolecular networks have different thermal stabilities based on different cationic bridging units.

Keywords: Coordination polymer; Supramolecular structure; Polyoxometalate; 4,4′-Bipyridine-*N*,*N*′-dioxide; Cobalt complex

1. Introduction

Porous metal–ligand coordination polymers are a promising new class of materials that often have crystalline, well-defined cavities (or channels) and can be used for including various guest species [1, 2]. Bearing unique properties and exhibiting diverse compositions, polyoxometalates (POMs) represent an outstanding class of molecular building blocks for construction of such materials [3–12]. Remarkable progress on construction of 3-D porous 4,4′-bipyridine-*N*,*N*′-dioxide (dpdo)-based organic–inorganic hybrid materials with discrete single- or double-Keggin anions as guests has been made [8, 10, 11]. Representative examples include $[Co_4(dpdo)_{12}][H(H_2O)_{27}(CH_3CN)_{12}][PW_{12}O_{40}]_3$ [11a], $\{Gd(dpdo)_4(H_2O)_5(PMo_{12}O_{40})(CH_3CN)\}_n$ [11b], $\{[Ni(dpdo)_2(CH_3CN)(H_2O)_2]_2(SiMo_{12}O_{40})(H_2O)_2\}_n$ [11b], $\{[Tb(dpdo)_4(H_2O)_3]H(SiMo_{12}O_{40})(dpdo)_{0.5}(CH_3CN)_{0.5}(H_2O)_4\}_n$ [11c] and $\{[Tb(dpdo)_4(H_2O)_3](PMo_{12}O_{40})(H_2O)_2CH_3CN\}_n$ [11c]. However, the design and assembly of POM-based open metal–ligand coordination polymers with special channels for assembly of polymeric

---

*Corresponding author. Email: weimeilin@henannu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970902744982

polyanions remain an arduous task for coordination chemists due to the large number of potential coordination sites and the relatively weak coordination ability of POMs. To correlate the influence of polyanions on resultant structures in different organic solvents, herein, Co^{2+} ions, dpdo and Keggin-type $[PMo_{12}O_{40}]^{3-}$ polyanions were chosen to construct open supramolecular networks with special channels for the assembly of polymeric Keggin-type anions in mixtures such as acetonitrile/water or methanol/water. The presence of nanosized, highly charged anions as building blocks prevented lattice interpenetration, resulting in three similar porous networks with large cavities occupied by the polymeric Keggin-type anions.

2. Experimental

2.1. *Materials and measurements*

All organic solvents and materials used for syntheses were of reagent grade and used without purification. α-$H_3PMo_{12}O_{40} \cdot 6H_2O$ was prepared according to a literature method [13] and characterized by an IR spectrum and TG analysis. Elemental analyses were carried out on a Perkin–Elmer 240C analyzer for C, H, and N, as well as on a J-A1100 ICP analyzer for Co, P, Mo, and K. IR spectra were recorded on a VECTOR 22 Bruker spectrophotometer with KBr pellets from 400 to 4000 cm^{-1}. Thermogravimetric analyses were carried out on a Perkin–Elmer thermal analyzer in an atmosphere of N_2 with a heating rate of 10°C min^{-1}.

2.2. *Synthesis of* $\{[Co(dpdo)_4(H_2O)_2][H(H_2O)_6](PMo_{12}O_{40})\}_n$ *(1)*

The formation of heteropolyacid cobalt salt was accomplished by neutralization of the acid. α-$H_3PMo_{12}O_{40} \cdot 6H_2O$ (63 mg, 0.03 mmol) and $CoCl_2 \cdot 6H_2O$ (7.5 mg, 0.03 mmol) was dissolved in water (2 mL) and the solution was heated to 80°C in a water bath. Red crystals formed after cooling the saturated solution and slowly evaporating at room temperature, were characterized by an IR spectrum. A buffer layer of a solution (10 mL) of acetonitrile : water (3 : 2, v/v) was carefully layered over 4 mL of an aqueous solution of dpdo hydrate (33 mg, 0.15 mmol). Then an acetonitrile : water (3 : 1, v/v) solution (4 mL) of the resultant heteropolyacid cobalt salts was carefully layered over the buffer layer. Red crystals appeared after 4–5 weeks and were collected and dried in air after being quickly washed with water. Yield: 82% based on α-$H_3PMo_{12}O_{40} \cdot 6H_2O$. $C_{40}H_{49}N_8O_{56}PCoMo_{12}$ (%): Calcd C 17.29, H 1.78, N 4.03; found C 17.36, H 1.86, N 4.18. IR (KBr): four characteristic vibrations resulting from heteropolyanions with the Keggin structure: ν(Mo=Ot)(960 cm^{-1}), ν(Mo–Ob)(880 cm^{-1}), ν(Mo–Oc) (800 cm^{-1}) and ν(P–Oa)(1060 cm^{-1}); four characteristic vibrations resulting from dpdo molecules: ν(N–O)(1229 cm^{-1}), ν(ring)(1471 cm^{-1}), δ(C–H, in plane)(1182 cm^{-1}) and δ(N–O)(838 cm^{-1}), respectively.

2.3. *Synthesis of* $\{[Co(dpdo)_4(H_2O)_2][H_3O(CH_3OH)_4](PMo_{12}O_{40})\}_n$ *(2)*

Compound **2** was prepared in the same way as for **1**, using methanol instead of acetonitrile. A buffer layer of a solution (10 mL) of methanol : water (1 : 1, v/v) was carefully layered over a 4 mL aqueous solution of dpdo hydrate (33 mg, 0.15 mmol). Then a methanol solution (4 mL) of resultant heteropolyacid cobalt salt was carefully layered over the buffer layer. Orange crystals appeared after 4 weeks and were collected and dried in air after quickly being washed with methanol : water (1 : 1, v/v). Yield: 75% based on α-$H_3PMo_{12}O_{40} \cdot 6H_2O$. Anal. Calcd for $C_{44}H_{55}N_8O_{55}CoMo_{12}P$ (%): C, 18.76; H, 1.97; N, 3.98. Found: C, 18.58; H, 1.81; N, 4.18. IR(KBr): four characteristic asymmetric vibrations resulting from heteropolyanions with the Keggin structure: ν(Mo–Oc)(798 cm^{-1}), ν(Mo–Ob)(882 cm^{-1}), ν(Mo=Ot)(960 cm^{-1}) and ν(P–Oa)(1063 cm^{-1}); four characteristic vibrations resulting from dpdo molecules: ν(N–O)(1228 cm^{-1}), ν(ring)(1472 cm^{-1}), δ(C–H, in plane)(1180 cm^{-1}) and δ(N–O) (838 cm^{-1}), respectively.

2.4. *Synthesis of* $\{[Co(dpdo)_4(H_2O)_2][K(CH_3OH)_4]\ (PMo_{12}O_{40})\}_n$ *(3)*

Compound **3** was prepared in the similar way as for **2**, except adding KCl (3 mg, 0.03 mmol) to the 4 mL aqueous solution of dpdo hydrate. Orange single crystals appeared after 4 weeks and were collected and dried in air after quickly being washed with methanol : water (1 : 1, v/v). Yield: 78% based on α-$H_3PMo_{12}O_{40} \cdot 6H_2O$. Anal. Calcd for $C_{44}H_{52}N_8O_{54}CoMo_{12}PK$ (%): C, 18.63; H, 1.85; N, 3.95; K, 1.38; Co, 2.08; P, 1.09; Mo, 40.58. Found: C, 18.55; H, 1.76; N, 3.83; K, 1.30; Co, 2.01; P, 1.01; Mo, 40.49. IR(KBr): four characteristic vibrations resulting from heteropolyanions with the Keggin structure: ν(Mo–Oc)(794 cm^{-1}), ν(Mo–Ob)(880 cm^{-1}), ν(Mo=Ot)(960 cm^{-1}), ν(P–Oa)(1062 cm^{-1}); four characteristic vibrations resulting from dpdo molecules, ν(N–O)(1233 cm^{-1}), ν(ring)(1472 cm^{-1}), δ(C–H, in plane)(1181 cm^{-1}), and δ(N–O) (838 cm^{-1}).

2.5. *Crystal structure and determination*

Intensity data of **1–3** were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo-Kα radiation $\lambda = 0.71073$ Å using SMART and SAINT programs [14]. The structures were solved by direct methods and refined on F^2 by using full-matrix least-squares methods with SHELXTL version 5.1 [15]. For **1**, all nonhydrogen atoms except solvent water were refined anisotropically. For **2**, all non-hydrogen atoms except one solvent water and methanol were refined anisotropically. For **3**, all nonhydrogen atoms except methanol and potassium were refined anisotropically. Hydrogen atoms of the organic ligands were localized in their calculated positions and refined using a riding model. Hydrogen atoms of coordinated water molecules and methanol molecules were localized by difference Fourier maps and refined by fixing the isotropic temperature factors to 1.2 times that of the mother atoms attached. For **1**, hydrogen atoms of solvent water molecules were not treated. For **2**, hydrogen atoms of the solvent water molecule were localized by difference Fourier maps and refined by fixing the isotropic temperature factors as 1.2 times that of the mother atoms. The crystal parameters, data collection, and refinement results for three compounds are summarized in table 1. Selected bond lengths and angles are listed in tables 2–4, respectively.

Table 1. Crystal data and structure refinements for **1–3**.

	1	**2**	**3**
Formula	$C_{40}H_{45}N_8O_{54}CoMo_{12}P$	$C_{44}H_{55}N_8O_{55}CoMo_{12}P$	$C_{44}H_{52}N_8O_{54}CoKMo_{12}P$
Fw	2779.05	2817.14	2837.22
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cells and dimensions (Å, °)			
a	9.957(2)	9.958(1)	9.953(1)
b	13.746(3)	13.884(1)	13.844(1)
c	14.245(3)	14.212(3)	14.180(1)
α	92.887(3)	89.228(1)	89.584(1)
β	100.395(4)	77.885(1)	77.832(1)
γ	94.472(3)	86.002(1)	85.865(1)
$V(\text{Å}^3)$	1907.7(8)	1916.4(3)	1905.0(2)
Z	1	1	1
$Dc(\mathrm{g\,cm^{-3}})$	2.419	2.441	2.473
$\mu(\mathrm{mm^{-1}})$	2.248	2.239	2.305
$F(000)$	1339	1361	1369
Reflection measured	9570	9758	9639
Reflection unique	5502	5228	5521
R_{int}	0.0810	0.0431	0.0384
Parameters refined	538	554	555
GOF	0.931	1.028	1.079
$R_1/\mathrm{w}R_2$ $[I \geq 2\sigma(I)]$	0.0663/0.1842	0.0406/0.1034	0.0437/0.1179
$\Delta\rho_{\mathrm{fin}}$ (max/min) (e Å^{-3})	1.866/−1.388	0.860/−0.980	2.021/−1.353

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

P(1)–O(1′)	1.475(10)	CO(1)–O(21)	2.078(8)	CO(1)–O(1W)	2.043(8)
P(1)–O(1)	1.495(10)	Co(1)–O(23)	2.104(8)	O(13)–Mo(1)–O(1′)	64.5(3)
P(1)–O(2)	1.539(10)	O(1′)–P(1)–O(1)	113.4(6)	O(7)#1–Mo(1)–O(1′)	89.7(4)
P(1)–O(2′)	1.554(10)	O(1′)#1–P(1)–O(2)	110.2(5)	O(11)–Mo(1)–O(1′)	94.9(4)
Mo(1)–O(18)	1.658(6)	O(1)#1–P(1)–O(2)	109.2(5)	O(16)–Mo(1)–O(1′)	65.6(4)
Mo(1)–O(11)	1.809(7)	O(1′)–P(1)–O(2′)#1	109.6(5)	O(13)#1–Mo(1)–O(1)	90.9(4)
Mo(1)–O(16)	1.825(7)	O(1)–P(1)–O(2′)#1	108.3(6)	O(16)–Mo(1)–O(1)#1	94.3(4)
Mo(1)–O(7)#1	1.970(7)	O(2)–P(1)–O(2′)	106.0(5)	O(7)#1–Mo(1)–O(13)	81.9(3)
Mo(1)–O(13)	2.000(7)	O(11)–Mo(1)–O(7)#1	87.3(3)	O(16)–Mo(1)–O(13)	86.0(3)
Mo(1)–O(1)#1	2.436(10)	O(18)–Mo(1)–O(13)	99.2(4)	O(1W)–Co(1)–O(21)	89.0(3)
Mo(1)–O(1′)	2.471(10)	O(1W)–Co(1)–O(23)	94.6(3)	O(21)–Co(1)–O(23)	90.5(4)

Note: #1: $-x+1$, $-y+2$, $-z$.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

P(1)–O(1′)	1.491(7)	Co(1)–O(21)	2.094(5)	Co(1)–O(1W)	2.047(5)
P(1)–O(1)	1.559(8)	Co(1)–O(23)	2.139(5)	O(3)#1–Mo(1)–O(20)	80.5(2)
P(1)–O(2)	1.466(7)	O(1′)–P(1)–O(1)	108.9(4)	O(16)–Mo(1)–O(1′)	65.7(3)
P(1)–O(2′)	1.566(7)	O(2)#1–P(1)–O(1′)	114.2(4)	O(3)#1–Mo(1)–O(1′)	88.8(2)
Mo(1)–O(18)	1.656(5)	O(2)#1–P(1)–O(1)	110.5(4)	O(20)–Mo(1)–O(1′)	63.9(2)
Mo(1)–O(19)	1.814(5)	O(1′)#1–P(1)–O(2′)	107.8(4)	O(19)–Mo(1)–O(2)	66.1(2)
Mo(1)–O(16)	1.807(5)	O(1)–P(1)–O(2′)	105.6(4)	O(16)–Mo(1)–O(2)	94.1(3)
Mo(1)–O(20)	1.994(5)	O(2)–P(1)–O(2′)	109.4(4)	O(3)#1–Mo(1)–O(2)	64.5(2)
Mo(1)–O(3)#1	1.979(5)	O(19)–Mo(1)–O(3)#1	87.2(2)	O(20)–Mo(1)–O(2)	89.6(3)
Mo(1)–O(2)	2.437(8)	O(16)–Mo(1)–O(20)	85.8(2)	O(1W)–Co(1)–O(21)	90.2(2)
Mo(1)–O(1′)	2.481(8)	O(1W)–Co(1)–O(23)	92.8(2)	O(21)–Co(1)–O(23)	90.3(2)

Note: #1: $-x+1$, $-y+1$, $-z+1$.

Table 4. Selected bond lengths (Å) and angles (°) for **3**.

P(1)–O(1′)	1.472(8)	Co(1)–O(21)	2.091(5)	Co(1)–O(1W)	2.046(5)
P(1)–O(1)	1.557(8)	Co(1)–O(23)	2.131(6)	O(3)#1–Mo(1)–O(20)	80.5(2)
P(1)–O(2)	1.504(7)	O(1′)–P(1)–O(1)	109.3(4)	O(16)–Mo(1)–O(1′)#1	94.4(3)
P(1)–O(2′)	1.564(8)	O(2)#1–P(1)–O(1)	108.7(4)	O(3)#1–Mo(1)–O(1′)	80.2(2)
Mo(1)–O(18)	1.661(4)	O(1′)#1–P(1)–O(2)	113.4(4)	O(18)–Mo(1)–O(3)#1	99.7(3)
Mo(1)–O(19)	1.814(5)	O(1′)#1–P(1)–O(2′)	111.6(4)	O(19)–Mo(1)–O(1′)#1	65.8(3)
Mo(1)–O(16)	1.817(5)	O(1)–P(1)–O(2′)	105.0(4)	O(16)#1–Mo(1)–O(2)	65.6(3)
Mo(1)–O(20)	1.990(5)	O(2)–P(1)–O(2′)	108.4(4)	O(3)#1–Mo(1)–O(2)	64.5(2)
Mo(1)–O(3)#1	1.978(4)	O(19)–Mo(1)–O(3)#1	87.3(2)	O(20)#1–Mo(1)–O(1′)	90.3(3)
Mo(1)–O(2)	2.476(7)	O(16)–Mo(1)–O(20)	86.4(2)	O(1W)–Co(1)–O(21)	90.7(2)
Mo(1)–O(1′)	2.445(7)	O(1W)–Co(1)–O(23)	93.0(2)	O(21)–Co(1)–O(23)	90.5(2)
K(1)–O(25)	2.44(3)	K(1)–O(26)	2.81(2)		

Note: #1: $-x+1$, $-y+1$, $-z+1$.

3. Results and discussion

3.1. *Structure description*

Reaction of cobalt phosphomolybdates and dpdo with a Co : dpdo : $[PMo_{12}O_{40}]^{3-}$ stoichiometry of 1 : 4 : 1 in acetonitrile/water by the layering method gave **1**. Compound **2** was prepared in the same stoichiometry as for **1** using methanol instead of acetonitrile. Reaction of cobalt phosphomolybdates, dpdo and KCl with Co : KCl : dpdo : $[PMo_{12}O_{40}]^{3-}$ in stoichiometries of 1 : 1 : 4 : 1 in methanol/water gave **3**. The results of the single crystal X-ray diffractions suggested that three compounds exhibit similar 3-D noninterwoven networks with large channels occupied by the poly-Keggin-anion chains. These composite compounds have the same layers constructed by the coordinated cation $[Co(dpdo)_4(H_2O)_2]^{2+}$, the same poly-Keggin-anion chain as guests and different bridging units for charge compensation between layers. The bridging units are $[H(H_2O)_6]^+$ (the proton added to balance the charge) cluster for **1**, the $[H_3O(CH_3OH)_4]^+$ (the proton added to balance the charge) cluster for **2**, and $[K(CH_3OH)_4]^+$ cluster for **3**, respectively.

A representative $[Co(dpdo)_4(H_2O)_2]^{2+}$ unit is shown in figure 1. The Co^{2+} is coordinated by six oxygens from two waters [Co–O(water) 2.043(8) Å for **1**, 2.047(5) Å for **2**, and 2.046(5) Å for **3**] and from four independent dpdo ligands [mean Co–O(dpdo) 2.091(8) Å for **1**, 2.117(5) Å for **2**, and 2.111(5) Å for **3**]. The N–O–Co angles range from 122.1(7)° to 124.5(6)° for **1**, from 122.0(5)° to 123.8(4)° for **2**, and from 122.0(5)° to 123.2(4)° for **3**. The dihedral angles between the N(1)-containing pyridine ring and the N(2) ring, as well as between the N(3) ring and the N(4) ring of the dpdo ligands are 35.6° and 7.0° for **1**, 31.6° and 17.8° for **2**, and 31.6° and 17.8° for **3**, respectively. In the three compounds, coordinated cations form the same 2-D layer with metal square grids through hydrogen bonding interactions between the oxygens belonging to the coordinated water molecules and the noncoordinated oxygens of the ligands (figure 2). Each coordinated water is a donor of double hydrogen bonds connecting with two noncoordinated terminal oxygens of dpdo belonging to two adjacent metal centers [O(1W)$\cdots$O(22) ($-x+2$, $-y+2$, $-z+1$) 2.59(2) Å and O(1W)$\cdots$O(24) ($-x+2$, $-y+3$, $-z$) 2.64(2) Å for **1**, O(1W)$\cdots$O(22) ($-x+2$, $-y+2$, $-z+1$) 2.58(2) Å and O(1W)$\cdots$O(24) ($-x+2$, $-y+3$, $-z$) 2.61(2) Å for **2** and O(1W)$\cdots$O(22) ($-x+2$, $-y+2$, $-z+1$) 2.57(2) Å and O(1W)$\cdots$O(24) ($-x+2$, $-y+3$, $-z$) 2.61(2) Å for **3**]. Face-to-face π–π stacking interactions within the bridging

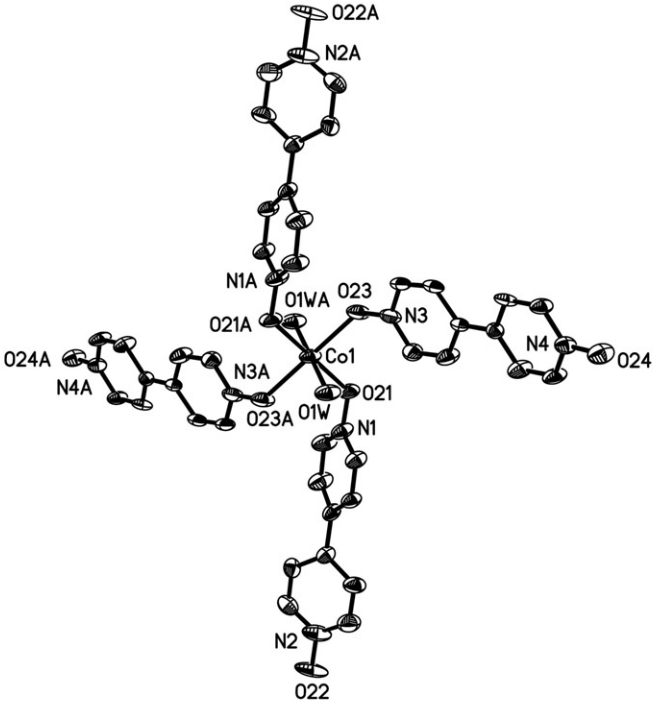

Figure 1. Representative coordinated cation $[Co(dpdo)_4(H_2O)_2]^{2+}$. Hydrogen atoms are omitted for clarity.

dpdo pairs also stabilize the layers. Partially overlapping arrangements between neighboring dpdo ligands are observed in the crystals. As shown in table 5, the centroid distances between the N(3)-ring and the symmetry-related N(4)-ring clearly suggest the existence of aromatic π–π stacking interactions in the frameworks. These stacked aromatic rings divide the frameworks into voids with a single polyanion embedded in each of these voids (figure 3).

Being heavy "building stones" for charge compensation, $[PMo_{12}O_{40}]^{3-}$ anions position at two sides of each layer above and below the voids of the tetragons (figure 4) and connect adjacent layers together through weak hydrogen bonds between coordinated waters O(1W) and terminal oxygens O(18) of polyanions [O(1W)$\cdots$O(18) $(-x+1, -y+2, -z)$ 3.62(2) Å for **1**, O(1W)$\cdots$O(18) $(-x+2, -y+1, -z+1)$ 3.82(2) Å for **2** and O(1W)$\cdots$O(18) $(-x+2, -y+1, -z+1)$ 3.83(2) Å for **3**]. In other words, $[PMo_{12}O_{40}]^{3-}$ anions are pillars in the wave-like channels. In each compound, direct incorporation of the $[PMo_{12}O_{40}]^{3-}$ anions between the 2-D cationic framework embedding within the cavities is formed. For each void, the Co$\cdots$Co separation bridged by dpdo oxygens O(21) and O(22) is 13.8 Å, the one bridged by the dpdo ligand containing oxygens O(23) and O(24) is 14.2 Å, and the upright one between two adjacent layers is 10.0 Å. Thus, each compound forms a supramolecular network with channels of *ca* $10.0 \times 13.8 \times 14.2$ Å based on the Co$\cdots$Co separations, indicating that each pore could only accommodate a single Keggin anion. Co$\cdots$Co separations bridged by dpdo are longer than between two adjacent layers, thus, each cavity is heavily condensed along the *a*-axis. As a result, the Keggin-type $[PMo_{12}O_{40}]^{3-}$ anions are embedded in the voids of the tetragons and

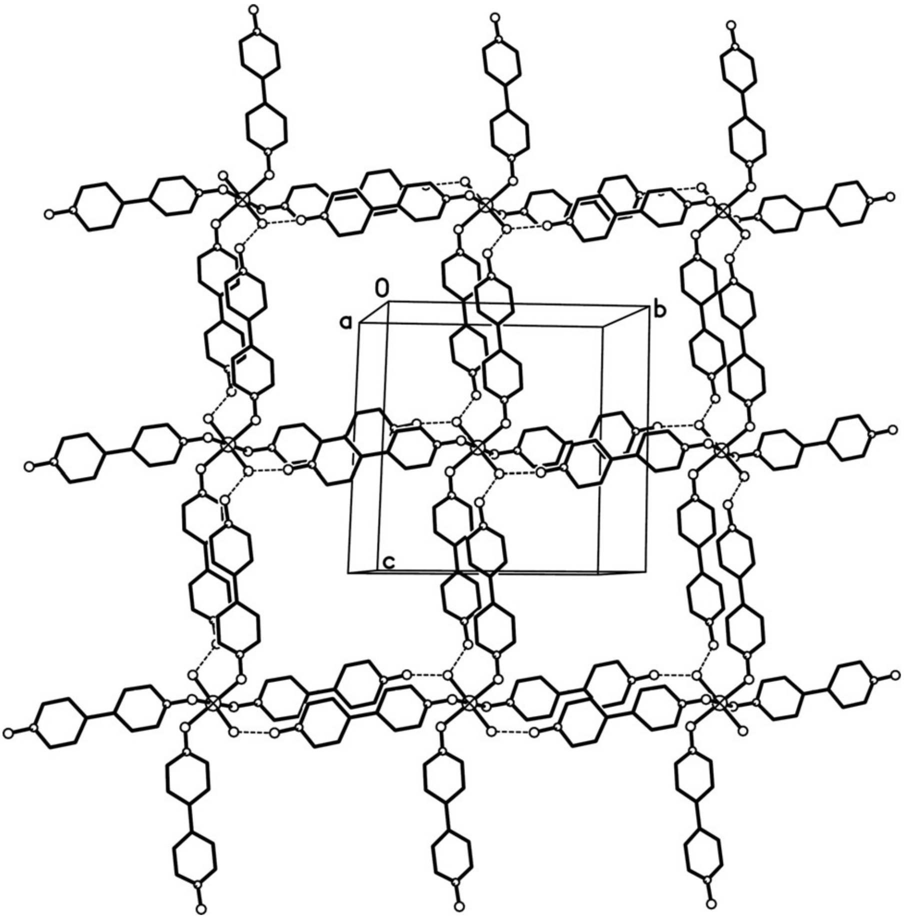

Figure 2. Representative 2-D sheet with square lattices down *a*-axis in the title compounds. Hydrogen atoms are omitted for clarity.

Table 5. π–π Stacking interaction distances (Å) in **1**–**3**.

Cg(I) $\cdots$ Cg(J)	Symmetry code of Cg(J)	Center-to-center distance		
Cg(3) $\cdots$ Cg(4)	$-x+2, -y+3, -z$	4.154(1)	3.987(2)	3.986(3)
Cg(4) $\cdots$ Cg(3)	$-x+2, -y+3, -z$	4.154(1)	3.987(2)	3.986(3)

Notes: Cg(3): N(3) → C(11) → C(12) → C(13) → C(14) → C(15) → ; Cg(4): N(4) → C(16) → C(17) → C(18) → C(19) → C(20) →. (1): compound **1**; (2): compound **2**; (3): compound **3**.

connect to one another leading to a poly-Keggin-anion chain in the channel along the *a*-axis (figure 4). In the polymeric polyanion, there are some short atom $\cdots$ atom separations: O(14) $\cdots$ O(16B) 2.91(2) and O(14) $\cdots$ O(18B) 3.12(2) Å for **1**, O(14) $\cdots$ O(16B) 2.86(2) and O(14) $\cdots$ O(18B) 3.15(2) Å for **2**, and O(14) $\cdots$ O(16B) 2.85(2) and O(14) $\cdots$ O(18B) 3.14(2) Å for **3**.

In all the three compounds, the two adjacent layers are further bridged by different cationic units for charge compensation through hydrogen bonding interactions (table 6).

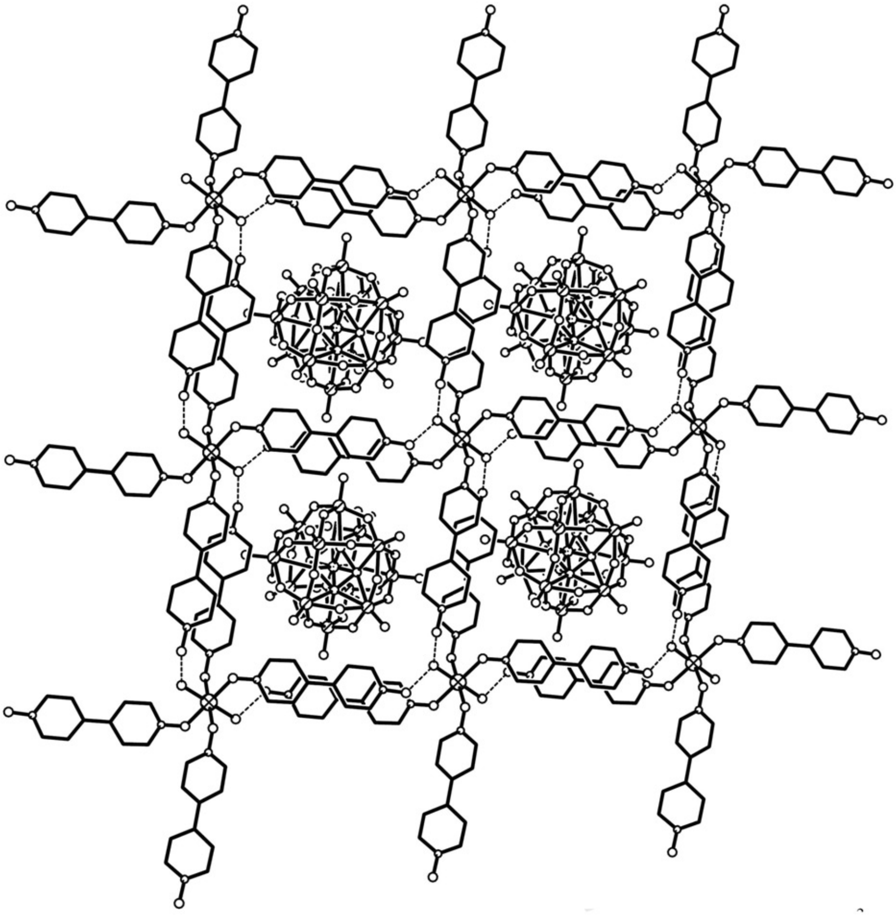

Figure 3. Representative 2-D sheet showing square lattices occupied by $[PMo_{12}O_{40}]^{3-}$ anions. Hydrogen atoms are omitted for clarity.

In **1**, the two adjacent layers are further bridged by $[H(H_2O)_6]^+$ clusters through hydrogen bonding interactions between the oxygens belonging to the solvent water [O(2W)] and the oxygens [O(21) and O(22)] of the ligands, as well as between the oxygens belonging to the solvent water [O(2W)] and the oxygens belonging to the coordinated water [O(2W) $\cdots$ O(1W) 3.00(2) Å], leading to a 3-D cationic framework [figure 5(a)]. The crystal water molecules O(3W) and O(4W) are around the crystal water molecule O(2W) to form a small water cluster $[H(H_2O)_6]^+$ with O(2W) $\cdots$ O(3W) 3.96(2), O(2W) $\cdots$ O(4W) $(-x+3, -y+3, -z+1)$ 3.73(2) Å [figure 5(b)]. In **2**, the two adjacent layers are further bridged by the $[H_3O(CH_3OH)_4]^+$ clusters [figure 6(b)] through hydrogen bonds, leading to a 3-D network [figure 6(a)]. In **3**, the two adjacent layers are further bridged by the $[K(CH_3OH)_4]^+$ clusters [figure 6(c)] through hydrogen bonds, leading to a 3-D network similar to that in **2** [figure 6(a)]. The compounds present three similar metal–ligand networks with large cavities occupied by the polymeric Keggin-type anions (figure 7), constructed by the coordinated cation $[Co(dpdo)_4(H_2O)_2]^{2+}$ and the polyanion $[PMo_{12}O_{40}]^{3-}$, as well as different cationic units for charge compensation. In contrast with the structure of the $[K(CH_3OH)_4]^+$ cluster in **3**, the most possible position

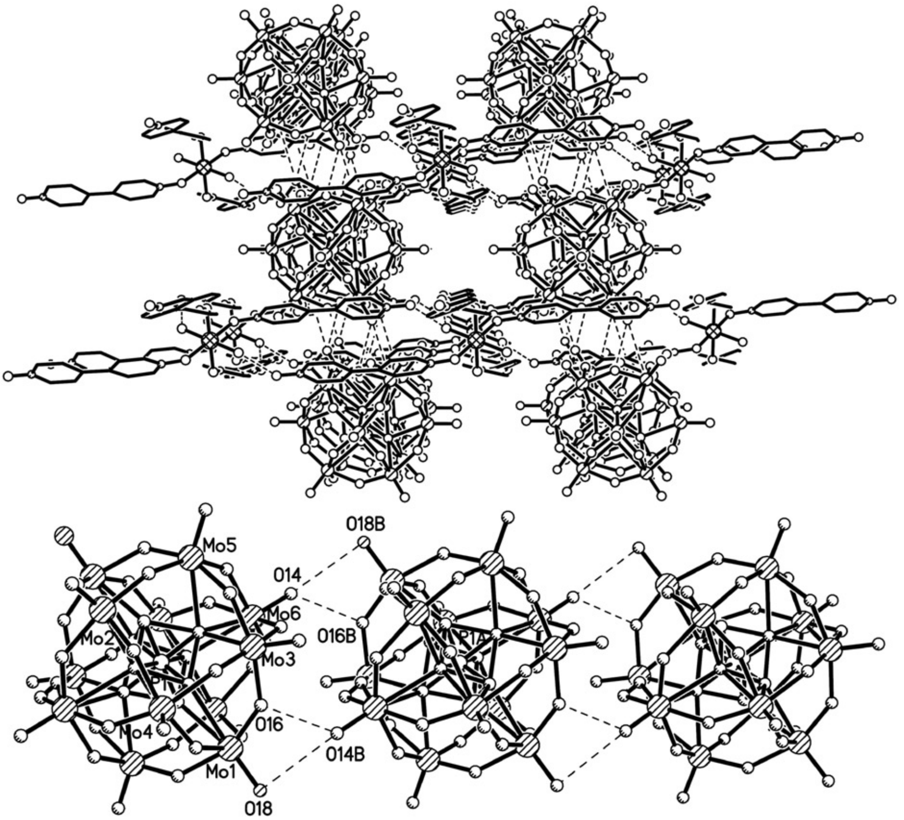

Figure 4. Representative 3-D network showing $[PMo_{12}O_{40}]^{3-}$ anions positioning at the two sides of each layer above and below the voids of the tetragons (top), and view of the poly-anion chain (bottom). Hydrogen atoms are omitted for clarity.

of the excess protons added to balance charge in **1** and **2** are at the O(2W) centers, resulting in the $[H(H_2O)_6]^+$ and $[H_3O(CH_3OH)_4]^+$ clusters. Similar results were obtained in related literature [11, 16, 17]. The positively charged species attract the polyanions together to form a poly-Keggin-anion chain in the channel. The accessible porosity for the guest molecule ($[PMo_{12}O_{40}]^{3-}$ anion) calculated through PLATON [18] is 868 Å^3 mol^{-1} (46%) in **1**, 819.9 Å^3 mol^{-1} (42.8%) in **2**, and 818 Å^3 mol^{-1} (43%) in **3**. The different void volumes and occupancy in three compounds indicated that different cationic units for charge compensation play important roles in controlling pore size of the POM-based coordination polymers.

In **1**, the P–O and Mo–O bond lengths are 1.475(10)–1.554(10) and 1.636(6)–2.507(10) Å, respectively; in **2**, 1.466(7)–1.566(7) and 1.644(4)–2.514(7) Å, respectively; and in **3**, 1.472(8)–1.564(8) and 1.645(5)–16(8) Å, respectively, comparable to those of 1.524(5)–1.535(5) and 1.662(6)–2.446(5) Å, respectively, in $\{Gd(dpdo)_4(H_2O)_5(PMo_{12}O_{40})(CH_3CN)\}_n$ [11b]. In addition, the O–P–O angles are in the range 105–114°. All these results indicate that the $[PMo_{12}O_{40}]^{3-}$ units have a normal Keggin structure in the polymeric-polyanion chains. Compared with 3-D porous dpdo-based organic–inorganic hybrid materials with discrete single- or double-Keggin anions as guests [11], **1–3** give similar metal–ligand networks with large cavities occupied by the

Table 6. Selected hydrogen bond lengths (Å) in **1**–**3**.

1			**2**			**3**		
D···A	d(D···A)	Symmetry	D···A	d(D···A)	Symmetry	D···A	d(D···A)	Symmetry
O(2W)···O(21)	2.72	$(-x+2, -y+3, -z+1)$	O(2W)···O(25)	2.69		O(25)···O(23)	2.92	
O(2W)···O(22)	2.90	$(-x+2, -y+2, -z+1)$	O(2W)···O(26)	2.83	$(-x+1, -y+2, -z+2)$	O(26)···O(22)	2.82	$(-x+3, -y+1, -z+2)$
O(2W)···O(1W)	3.00		O(25)···O(23)	2.94	$(x-1, y, z)$			
O(46)···O(9W)	2.76		O(26)···O(22)	2.87	$(-x+2, -y+1, -z+2)$			

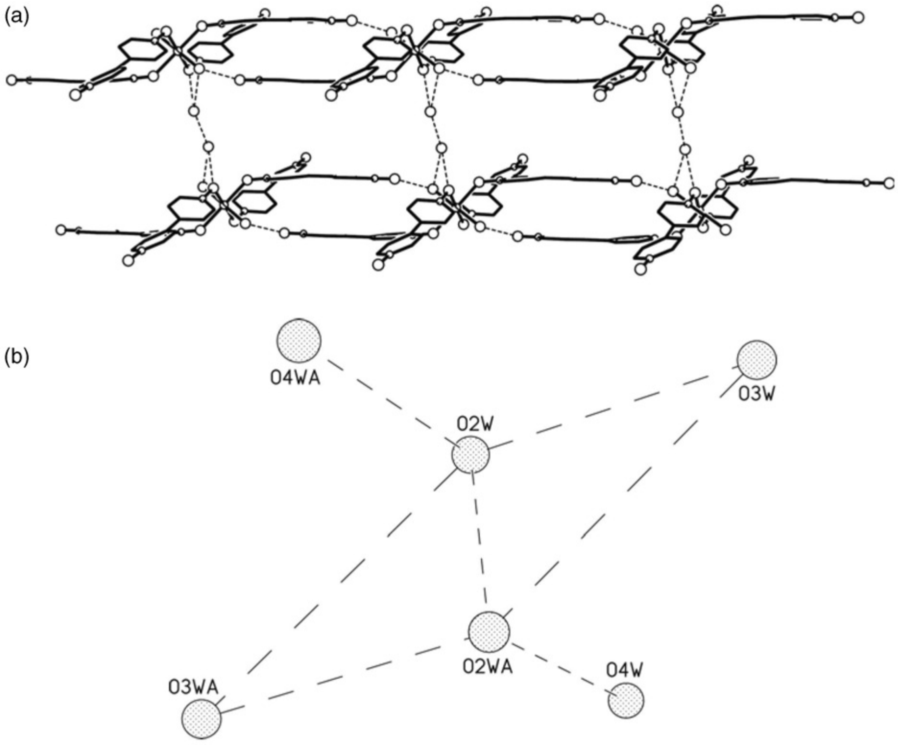

Figure 5. The 3-D cationic network (a) in **1** showing two adjacent layers bridged by $[H(H_2O)_6]^+$, (b) through hydrogen bonding interactions. Hydrogen atoms are omitted for clarity.

polymeric Keggin-type anions, indicating that Co^{2+} ions, dpdo, and Keggin-type $[PMo_{12}O_{40}]^{3-}$ polyanions could construct open supramolecular networks with special channels for the assembly of polymeric Keggin-type anions through carefully adjusting the stoichiometric proportion of the highly charged POMs and the metal-organic units. Methanol is more suitable organic solvent than acetonitrile for forming such open supramolecular networks. As a result, the noncoordinating poly-Keggin-type anions play not only a charge-compensating role, but also dramatically influence the overall solid-state architecture through their templating function; the cationic networks with special channels also influence the polymerization of polyanions through their host functions. Thus, this strategy provides a synthetic approach in understanding the formation of poly-Keggin anions within the resultant structures constructed by transition metal ions and dpdo ligands.

3.2. *Thermogravimetric analyses*

Thermogravimetric analysis of the powder of the crystalline samples is provided in Supplementary material. Compound **1** in an atmosphere of N_2 shows a weight loss of 5.06% in the temperature range 20−200°C, corresponding to four solvent waters and two coordinated waters (Calcd 5.18%). The weight loss in the temperature range 200−600°C corresponds to the loss of dpdo ligands and the disruption of the structural

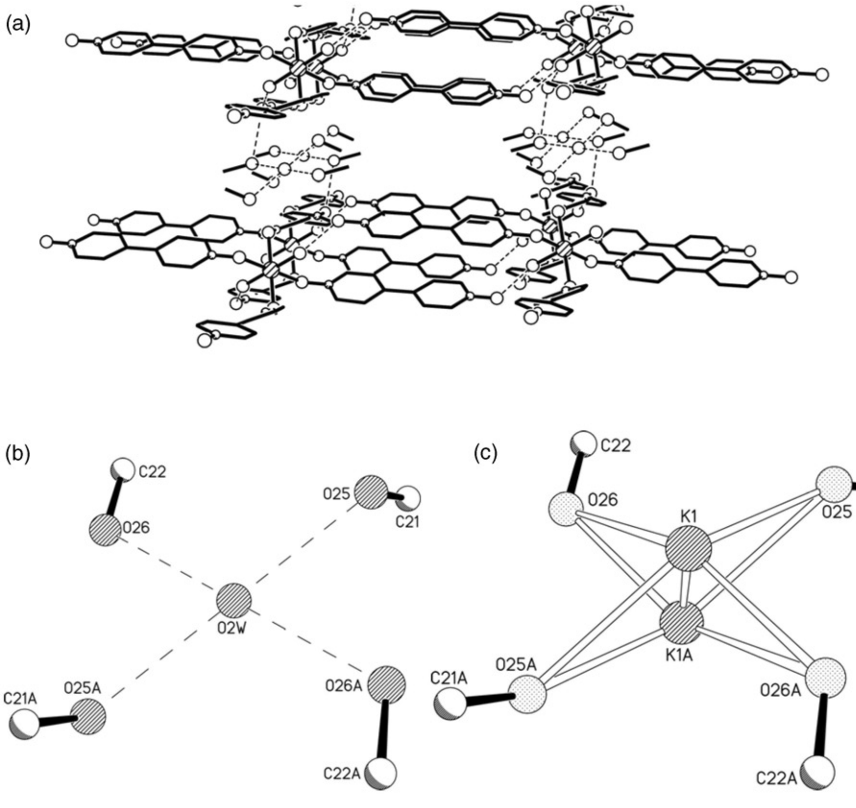

Figure 6. Representative 3-D cationic network (a) in **2** and **3** showing two adjacent layers bridged by the $[(H_3O)(CH_3OH)_4]^+$ (b) or $[K(CH_3OH)_4]^+$ clusters (c) through hydrogen bonding interactions. Hydrogen atoms are omitted for clarity.

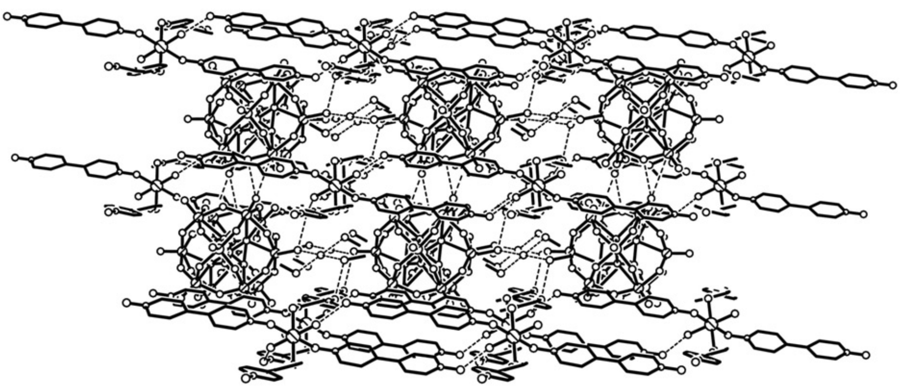

Figure 7. Direct incorporation between the 3-D cationic network and the $[PMo_{12}O_{40}]^{3-}$ anions embedding within the cavities in **2** and **3**.

skeletons of $[PMo_{12}O_{40}]^{3-}$. Compound **2** shows a weight loss of 6.35% in the temperature range 20−255°C, corresponding to four methanols, one solvent water, and two coordinated waters (Calcd 6.46%). A slow weight loss in the temperature range 20−150°C and a rapid weight loss in the temperature range 150−255°C occur. Weight loss from 255°C to 700°C corresponds to the loss of dpdo ligands and disruption of the structural skeleton of $[PMo_{12}O_{40}]^{3-}$. Compound **3** shows weight loss of 5.65% from 20°C to 255°C, corresponding to four solvent methanols and two coordinated waters (Calcd 5.78%), with slow weight loss from 20°C to 200°C and rapid weight loss from 200°C to 255°C. Weight loss from 255°C to 700°C corresponds to loss of dpdo and disruption of structural skeletons of $[PMo_{12}O_{40}]^{3-}$. The thermogravimetric analyses suggest that the supramolecular networks have different thermal stabilities based on different cationic bridging units, with $[H(H_2O)_6]^+$ having weaker stability than $[H_3O(CH_3OH)_4]^+$ and $[K(CH_3OH)_4]^+$ clusters.

4. Conclusions

In summary, we have synthesized three porous metal coordination polymers with similar architectures from dpdo and Co^{2+} ions in methanol/water or acetonitrile/water solutions directed by polyanion chains as templates. These compounds provided examples for understanding the template effect of polyanion chains on the resultant structures in different mixture solvents.

Supplementary material

Crystallographic data for **1**–**3** have been deposited at the Cambridge Crystallographic Data Centre, CCDC-672203 (**1**), CCDC-698122 (**2**), and CCDC-698123 (**3**). The data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk or www: http:ccdc.cam.ac.uk/conts/retrieving.html

Acknowledgments

This work is supported by the Natural Science Foundation of Henan Province (No. 082300420170) and the Start-up Foundation of Henan Normal University (No. 0707).

References

[1] M. Eddaoudi, D.B. Moler, H.L. Li, B.L. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi. *Acc. Chem. Res.*, **34**, 319 (2001).

[2] B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001).

[3] (a) S. Kitagawa, R. Kitaura, S. Noro. *Angew. Chem. Int. Ed.*, **43**, 2334 (2004); (b) J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim. *Nature*, **404**, 982 (2000).

[4] (a) C.D. Wu, A. Hu, L. Zhang, W. Lin. *J. Am. Chem. Soc.*, **127**, 8940 (2005); (b) L. Pan, D.H. Olson, L.R. Ciemnolonski, R. Heddy, J. Li. *Angew. Chem. Int. Ed.*, **45**, 616 (2006).

[5] D. Long, E. Burkholder, L. Cronin. *Chem. Soc. Rev.*, **36**, 105 (2007).

[6] (a) T. Rüther, V.M. Hultgren, B.P. Timko, A.M. Bond, W.R. Jackson, A.G. Wedd. *J. Am. Chem. Soc.*, **125**, 10133 (2003); (b) A. Müller, S.K. Das, S. Talismanov, S. Roy, E. Beckmann, H. Bögge, M. Schmidtmann, A. Merca, A. Berkle, L. Allouche, Y. Zhou, L. Zhang. *Angew. Chem. Int. Ed.*, **42**, 5039 (2003).

[7] (a) S. Uchida, R. Kawamoto, T. Akatsuka, S. Hikichi, N. Mizuno. *Chem. Mater.*, **17**, 1367 (2005); (b) R. Kawamoto, S. Uchida, N. Mizuno. *J. Am. Chem. Soc.*, **127**, 10560 (2005); (c) C. Jiang, A. Lesbani, R. Kawamoto, S. Uchida, N. Mizuno. *J. Am. Chem. Soc.*, **127**, 14240 (2006).

[8] (a) H.-A. An, E.-B. Wang, D.-R. Xiao, Y.-G. Li, Z.-M. Su, L. Xu. *Angew. Chem. Int. Ed.*, **45**, 904 (2006); (b) Y.-G. Li, L.-M. Dai, Y.-H. Wang, X.-L. Wang, E.-B. Wang, Z.-M. Su, L. Xu. *Chem. Commun.*, 2593 (2007); (c) J. Lu, E.-H. Shen, Y.-G. Li, D.-R. Xiao, E.-B. Wang, L. Xu. *Cryst. Growth Des.*, **5**, 65 (2005).

[9] (a) J. Kang, B. Xu, Z. Peng, X. Zhu, Y. Wei, D.R. Powell. *Angew. Chem. Int. Ed.*, **44**, 6902 (2005); (b) J.M. Knaust, C. Inman, S.W. Keller. *Chem. Commun.*, 492 (2004).

[10] (a) Y.-P. Ren, X.-J. Kong, X.-Y. Hu, M. Sun, L.-S. Long, R.-B. Huang, L.-S. Zheng. *Inorg. Chem.*, **45**, 4016 (2006); (b) P.Q. Zheng, Y.P. Ren, L.S. Long, R.B. Huang, L.S. Zheng. *Inorg. Chem.*, **44**, 1190 (2005); (c) X.-J. Kong, Y.-P. Ren, P.-Q. Zheng, Y.-X. Long, L.-S. Long, R.-B. Huang, L.-S. Zheng. *Inorg. Chem.*, **45**, 10702 (2006).

[11] (a) M.-L. Wei, C. He, W.-J. Hua, C.-Y. Duan, S.-H. Li, Q.-J. Meng. *J. Am. Chem. Soc.*, **128**, 13318 (2006); (b) M.-L. Wei, C. He, Q.-Z. Sun, Q.-J. Meng, C.-Y. Duan. *Inorg. Chem.*, **46**, 5957 (2007); (c) M.-L. Wei, R.-P. Sun, K. Jiang, L. Yang. *J. Coord. Chem.*, **61**, 3800 (2008); (d) M.-L. Wei, R.-P. Sun, K. Jiang. *Z. Naturforsch.*, **63b**, 255 (2008).

[12] (a) J.-Y. Niu, M.-L. Wei, J.-P. Wang, D.-B. Dang. *Eur. J. Inorg. Chem.*, **1**, 160 (2004); (b) J.-P. Wang, M.-L. Wei, J.-W. Zhao, J.-Y. Niu. *J. Coord. Chem.*, **59**, 1261 (2006).

[13] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot. *Inorg. Chem.*, **22**, 207 (1983).

[14] SMART and SAINT, Area Detector Control and Integration Software, Siemens Analytical X-ray Systems, Inc., Madison, WI (1996).

[15] G.M. Sheldrick. SHELXTL V5.1, Software Reference Manual, Bruker AXS, Inc., Madison, WI (1997).

[16] Y. Kanda, K.Y. Lee, S. Nakata, S. Asaoka, M. Misono. *Chem. Lett.*, **17**, 139 (1988).

[17] J. Yang, M.J. Janik, D. Ma, A. Zheng, M. Zhang, M. Neurock, R.J. Davis, C. Ye, F. Deng. *J. Am. Chem. Soc.*, **127**, 18274 (2005).

[18] A.L. Spek. *Acta Crystallogr., Sect. A*, **46**, C43 (1990).