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Influence of Steric Hindrance of Organic Ligand on the Structure of Keggin-Based Coordination Polymer

Yan-Ping Ren, Xiang-Jian Kong, Xiang-Yang Hu, Meng Sun, La-Sheng Long,* Rong-Bin Huang, and Lan-Sun Zheng

State Key Laboratory of Physical Chemistry of Solid Surface, Key Laboratory of Analytical Sciences, Ministry of Education, and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

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Five Keggin-based 3D coordination polymers, namely, $[Cu_3(pz)_3(PW_{12}O_{40})]$ (pz = pyrazine) (**1**), $[Cu_3(2,3\text{-}Me_2pz)_3(PW_{12}O_{40})]$ (2,3-Me_2pz = 2,3-dimethylpyrazine) (**2**), $[Cu_2(2,5\text{-}Me_2pz)_{1.5}(2,5\text{-}HMe_2pz)(PW_{12}O_{40})]$ (2,5-Me_2pz = 2,5-dimethylpyrazine) (**3**), $[Cu_3(2,3\text{-}Me_2pz)_3(PMo_{12}O_{40})]$ (**4**), and $[Ag_3(pz)_3(PW_{12}O_{40})]\cdot 0.5H_2O$ (**5**), were synthesized and structurally characterized. Crystal data are as follows: trigonal, space group $R\bar{3}c$, $a = 18.4070(14)$ Å, $c = 22.544(3)$ Å, $\gamma = 120°$, and $Z = 6$ for **1**; orthorhombic, space group *Pccn*, $a = 16.599(2)$ Å, $b = 20.470(3)$ Å, $c = 14.3757(18)$ Å, and $Z = 4$ for **2**; triclinic, space group $P\bar{1}$, $a = 10.667(2)$ Å, $b = 11.147(2)$ Å, $c = 20.207(4)$ Å, $\alpha = 90.983(4)°$, $\beta = 108.128(3)°$, $\gamma = 92.150(4)°$, and $Z = 2$ for **3**; orthorhombic, space group *Pccn*, $a = 16.450(3)$ Å, $b = 20.170(4)$ Å, $c = 14.244(3)$ Å, and $Z = 4$ for **4**; and rhombohedral, space group *R*32, $a = 18.2047(13)$ Å, $c = 23.637(3)$ Å, $\gamma = 120°$, and $Z = 6$ for **5**. Their structural differences were investigated using crystal structure analysis, revealing that the influence of steric hindrance of organic ligand on the structures of Keggin-based coordination polymers is realized through changing the number of metal–organic units surrounding the POM anion.

Introduction

The construction of inorganic−organic networks through crystal engineering has been the subject of much interest in recent years because of their structural diversity and potential applications as functional materials.[1,2] Keggin-type polyoxometalate (POM), because its diverse electronic, magnetic, photochemical, and catalytic properties,[3,4] has widely been regarded as an important molecular building unit for inorganic−organic coordination polymers.[3−8] Many efforts have focused on the construction of such coordination polymers in the past decades,[3−8] and so far, a variety of POM-based coordination polymers have successfully been

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* To whom correspondence should be addressed. E-mail: lslong@jingxian.xmu.edu.cn. Fax: 86-591-2183047.

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assembled through POM covalently linked with metal−organic units.[3−9] However, in comparison with other inorganic−organic coordination polymers, the rational design and assembly of POM-based coordination polymers remains an arduous task for coordination chemists. The obstacle to rationally construct POM-based coordination polymers is mainly the structural character of POM itself. First, it has a large number of terminal and bridge oxygen atoms that have the potential to combine with metal ions, therefore not only could POM anion coordinate with metal ion through its different terminal and bridge atoms but also the number of metal ion combined often changes on a case by case basis as demonstrated in this work. Second, compared to the organic ligand, the relatively weak coordination ability of the POM anion often makes the assembly of POM-based coordination polymers very sensitive to synthesis condition, such as temperature[10] and pH.[11] Third, the structure of POM-based coordination polymer is easily affected by the spacer and the steric hindrance of organic ligand in metal-organic units[12] because of its relatively large volume. Hence, as a modular building block, the structural information of the POM anion seldom guides the self-assembly reaction, in contrast to those of organic ligands.[12] In the previous work, we have respectively shown the pH[10c] and anion[10d] effects on the structure of a POM-based coordination polymer. As a continuation of our research on the POM-based coordination polymer, in this work, we, using copper(I) or silver(I) ions, $PM_{12}O_{40}^{3-}$ anion (M = W, Mo), pyrazine (pz), and its derivatives, 2,3-dimethylpyrazine (2,3-Me_2pz), and 2,5-dimethylpyrazine (2,5-Me_2pz), systematically investigate the steric effect of an organic ligand on the structure of POM-based coordination polymers and report herein the syntheses and crystal structures of $[Cu_3(pz)_3(PW_{12}O_{40})]$ (**1**), $[Cu_3(2,3\text{-}Me_2pz)_3(PW_{12}O_{40})]$ (**2**), $[Cu_2(2,5\text{-}Me_2pz)_{1.5}(2,5\text{-}HMe_2pz)(PW_{12}O_{40})]$ (**3**), $[Cu_3(2,3\text{-}Me_2pz)_3(PMo_{12}O_{40})]$ (**4**), and $[Ag_3(pz)_3(PW_{12}O_{40})]\cdot 0.5H_2O$ (**5**).

Experimental Section

Materials and Methods. All the reagents and solvents employed were commercially available and were used as received without further purification. The C, H, and N microanalyses were carried out with a CE instruments EA 1110 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 4000−400 cm^{-1} with a Nicolet AVATAR FT-IR360 spectrometer.

Syntheses. $[Cu_3(pz)_3(PW_{12}O_{40})]$ (1). $H_3PW_{12}O_{40}$ (0.36 g, 0.125 mmol), pz (0.08 g, 1.0 mmol), and $Cu(NO_3)_2\cdot 3H_2O$ (0.12 g, 0.5 mmol) were dissolved in 16 mL of distilled water at room temperature. When the pH value of the mixture was adjusted to about 3.5 with 1.0 mol L^{-1} NaOH, the solution was put into a Teflon-lined Parr vessel, heated to 200 °C for 50 h, and then cooled to 100 °C at a rate of 10 °C h^{-1}. After it was kept at 100 °C for 16 h, the mixture was cooled to room temperature at a rate of 3 °C h^{-1}. The red block crystals were obtained in a 14.3% yield (based on pz). Anal. Calcd (Found) for $C_{12}H_{12}Cu_3N_6O_{40}PW_{12}$ (**1**): C, 4.36 (4.17); H, 0.37 (0.38); N, 2.54 (2.59). IR (KBr, cm^{-1}): 3446s, 2925m, 2360w, 1635s, 1433w, 1161w, 1079s, 982s, 891s, 816s, 595w, 519m, 473m.

$[Cu_3(2,3\text{-}Me_2pz)_3(PW_{12}O_{40})]$ (2). Complex **2** was prepared in a manner similar to that described for **1**, except 2,3-Me_2pz replaced the pz ligand. The yield is 35.3% (based on 2,3-Me_2pz). Anal. Calcd (Found) for $C_{18}H_{24}Cu_3N_6O_{40}PW_{12}$ (**2**): C, 6.37 (6.30); H, 0.71 (0.78); N, 2.48 (2.52). IR (KBr, cm^{-1}): 3446s, 2928m, 2859w, 2346w, 1630s, 1384m, 1082s, 1051w, 981m, 896w, 811s, 778w, 474m.

$[Cu_2(2,5\text{-}Me_2pz)_{1.5}(2,5\text{-}HMe_2pz)(PW_{12}O_{40})]$ (3). $H_3PW_{12}O_{40}$ (0.36 g, 0.125 mmol), 2,5-Me_2pz (0.11 g, 1.0 mmol), and $Cu(NO_3)_2\cdot 3H_2O$ (0.12 g, 0.5 mmol) were dissolved in 16 mL of distilled water at room temperature. When the pH value of the mixture was adjusted to about 3.5 with 1.0 mol L^{-1} NaOH, the solution was put into a Teflon-lined Parr vessel, heated to 180 °C for 32 h, and then cooled to 100 °C at a rate of 10 °C h^{-1}. After it was kept at 100 °C for 16 h, the mixture was cooled to room temperature at a rate of 3 °C h^{-1}. The red block crystals were obtained in an 18.8% yield (based on 2,5-Me_2pz). Anal. Calcd (Found) for $C_{15}H_{21}Cu_2N_5O_{40}PW_{12}$ (**3**): C, 5.51 (5.32); H, 0.64 (0.75); N, 2.14 (2.31). IR (KBr, cm^{-1}): 3446s, 2360m, 2342w, 1636s, 1385w, 1079m, 982m, 894m, 814s, 668w, 518w.

$[Cu_3(2,3\text{-}Me_2pz)_3(PMo_{12}O_{40})]$ (4). $H_3PMo_{12}O_{40}$ (0.304 g, 0.167 mmol), 2,3-Me_2pz (0.11 g, 1.0 mmol), and $Cu(NO_3)_2\cdot 3H_2O$ (0.12 g, 0.5 mmol) were dissolved in 16 mL of distilled water at room temperature. When the pH value of the mixture was adjusted to about 3.5 with 1.0 mol L^{-1} NaOH, the solution was put into a Teflon-lined Parr vessel, heated to 180 °C for 50 h, and then cooled to 100 °C at a rate of 5 °C h^{-1}. After it was kept at 100 °C for 16 h, the mixture was cooled to room temperature at a rate of 3 °C h^{-1}.The black block crystals were obtained in a 39.8% yield (based on 2,3-Me_2pz). Anal. Calcd (Found) for $C_{18}H_{24}Cu_3N_6O_{40}PMo_{12}$ (**4**): C, 9.25 (9.11); H, 1.04 (1.12); N, 3.60 (3.43). IR (KBr,cm^{-1}): 3434s, 2925m, 2855w, 1629m, 1406m, 1058s, 953s, 786s, 472s.

$[Ag_3(pz)_3(PW_{12}O_{40})]\cdot 0.5H_2O$ (5). $H_3PW_{12}O_{40}$ (0.43 g, 0.15 mmol), pz (0.08 g, 1.0 mmol), $AgNO_3$ (0.17 g, 1.0 mmol), and NH_4F(0.037 g, 1 mmol) were dissolved in 13 mL of distilled water at room temperature. When the pH value of the mixture was adjusted to about 2.5 with 1.0 mol L^{-1} NaOH, the solution was put into a Teflon-lined Parr vessel, heated to 200 °C for 100 hours, and then cooled to 100 °C at a rate of 3 °C h^{-1}. After it was kept at 100 °C for 16 h, the mixture was cooled to room temperature at a rate of 3 °C h^{-1}. The colorless block crystals were obtained in a 12.2% yield (based on pz). Anal. Calcd (Found) for $C_{12}H_{13}Ag_3N_6O_{40.5}PW_{12}$ (**5**): C, 4.17 (4.37); H, 0.37 (0.45); N, 2.43 (2.21). IR (KBr, cm^{-1}): 3463m, 2976w, 2922w, 1624m, 1415w, 1086s, 984s, 891s, 814s, 596w, 526m.

In the synthesis of complexes **1**−**4**, the oxidation state of copper was changed from the reactant copper(II) ion to the resultant copper-

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Table 1. Crystal Data and Details of the Data Collection and Refinement for Complexes **1**−**5**

	1	**2**	**3**	**4**	**5**
formula	$C_{12}H_{12}Cu_3N_6O_{40}PW_{12}$	$C_{18}H_{24}Cu_3N_6O_{40}PW_{12}$	$C_{15}H_{21}Cu_2N_5O_{40}PW_{12}$	$C_{18}H_{24}Cu_3N_6O_{40}PMo_{12}$	$C_{12}H_{13}Ag_3N_6O_{40.5}PW_{12}$
M_r	3308.07	3392.22	3275.62	2337.30	3450.06
cryst syst	trigonal	orthorhombic	triclinic	orthorhombic	rhombohedral
space group	*R*-3*c*	*Pccn*	$P\bar{1}$	*Pccn*	*R*32
a (Å)	18.4070(14)	16.599(2)	10.667(2)	16.450(3)	18.2047(13)
b (Å)		20.470(3)	11.147(2)	20.170(4)	
c (Å)	22.544(3)	14.3757(18)	20.207(4)	14.244(3)	23.637(3)
α (deg)			90.983(4)		
β (deg)			92.150(4)		
γ (deg)	120.0		108.128(3)		120.0
V ($Å^3$)	6614.9(11)	4884.5(11)	2280.6(7)	4726.0(15)	6784.1(12)
Z	6	4	2	4	6
D_c (g cm^{-3})	4.983	4.613	4.770	3.285	5.067
μ (mm^{-1})	32.718	29.546	31.181	4.536	31.792
data/params	1781/113	4790/363	8768/676	4651/472	3617/226
θ (deg)	2.21−28.32	1.58−26.00	2.01−26.00	1.60−26.00	1.55−28.39
obsd reflns	1757	4581	7693	3814	3543
R1 [$I > 2\sigma(I)$]	0.0582	0.0638	0.0670	0.0588	0.0442
wR2 (all data)	0.1297	0.1457	0.1561	0.1313	0.1092

(I) ion. Such a phenomena was often observed in the reaction of a nitrogen-containing ligand with the copper(II) ion under hydrothermal conditions, and the pH and temperature of the reaction were found to be important factors influencing the oxidation state of the copper ion.[13]

X-ray Crystallography. Data were collected on a Bruker SMART Apex CCD diffractometer at 123 K for **1** and **5** and 173 K for **2** to **4**. Absorption corrections were applied using the multiscan program SADABS.[14] The structures were solved by direct methods, and the non-hydrogen atoms were refined anisotropically by the least-squares method on F^2 using the SHELXTL program.[15] The hydrogen atoms of organic ligand were generated geometrically (C−H = 0.96 Å, N−H = 0.90 Å). Crystal data, as well as details of the data collection and refinement, for the complexes are summarized in Table 1. Selected bond distances and angles are shown in Table 2.

Results and Discussion

Description of Crystal Structures. Crystal structure analysis reveals that complex **1** consists of three copper(I) ions, three pz ligands, and one $PW_{12}O_{40}^{3-}$ anion. Each copper(I) ion is four-coordinated by two nitrogen atoms and two oxygen atoms from two pz ligands and two $PW_{12}O_{40}^{3-}$ anions, respectively, as shown in Figure 1. The bond distances and angles around copper(I) ion are 1.896(13) Å (Cu−N), 2.422(14) Å (Cu−O), 178.3(9)° (N−Cu−N), 88.9(6)−92.3(5)° (N−Cu−O), and 85.7(8)° (O−Cu−O), which are different from those in the four-coordinated copper(I) complex $[\{Cu_2(2,4'\text{-}Hbpy)_4\}Mo_{18}As_2O_{62}]\cdot 2H_2O$ of 1.913−1.920 Å (Cu−N), 2.201−2.625 Å (Cu−O), 151.27(15)° (N−Cu−N), 83.62(11)−108.80(13)° (N−Cu−O), and 90.85(10)° (O−Cu−O).[16] Notably, the bond angle of N−Cu−N being very close to 180° (178.3(9)°) indicates that copper(I) ion in complex **1** is located in a unique four-coordinated geometry. Indeed, a survey of the Cambridge Crystallographic Database (CSD)[17] revealed that only one copper(I) complex with tetrahedral geometry and a bond angle around the copper(I) ion larger than 170° (171.85(5)°) has been reported so far:[18] this value is even 6.4° smaller than that in complex **1**.

The 3D structure of **1** can be viewed as a set of parallel 2D structures of $[Cu_2(pz)_2(PW_{12}O_{40})]_n^{n-}$ (Figure 2a) vertically linked by two sets of such 2D structures via sharing of the $PW_{12}O_{40}^{3-}$ anion as illustrated in Figure 2b. This arrangement not only makes each $PW_{12}O_{40}^{3-}$ anion a six-connected linkage coordinated to six copper(I) ions from six adjacent 1D chains of $[Cu(pz)]_n^{n+}$ in **1** (Figure 3a) but also makes each 1D chain of $[Cu(pz)]_n^{n+}$ be surrounded by four sets of the 1D chains as shown in Figure 3b. It was noted that, even though the six-connected $PV_2Mo_{10}O_{40}^{5-}$ anion was known in the inorganic coordination polymer of $\{[(Cu^{II}(OH_2)_4)_3(OH)]PV_2Mo_{10}O_{40}\}_n$,[19] complex **1** is the first example of a Keggin-based inorganic−organic coordination polymer in which the $PW_{12}O_{40}^{3-}$ anion acts as a six-connected linkage.[20]

Complex **2** consists of three copper(I) ions, three 2,3-Me_2pz ligands and one $PW_{12}O_{40}^{3-}$ anion. Crystal structure analysis reveals that there are two independent copper(I) centers in **2**, in which, one is two-coordinated by two nitrogen atoms of the 2,3-Me_2pz ligand in linear coordination geometry, and the other is four-coordinated by two nitrogen atoms of the 2,3-Me_2pz ligand and two oxygen atoms from two $PW_{12}O_{40}^{3-}$ anions in tetrahedral coordination geometry as shown in Figure 4. The 3D structure of **2** (Figure 5a) can

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Table 2. Selected Bond Distances (Å) and Angles (deg°) for Complexes **1**−**5**[a]

			complex 1				
Cu1−N1	1.896(13)	Cu1−N1b	1.896(13)	Cu1−O9	2.422(14)	Cu1−O9f	2.422(14)
N1−Cu1−N1b	178.3(9)	N1−Cu1−O9f	92.3(5)	N1−Cu1−O9	88.9(6)	N1b−Cu1−O9f	88.9(6)
N1b-Cu1−O9	92.3(5)	O9−Cu1−O9f	85.7(8)				
			complex **2**				
Cu1−N1	1.914(19)	Cu1−N1a	1.914(19)	Cu2−N2	1.965(17)	Cu2−N3	1.995(18)
Cu2−O13b	2.424(19)	Cu2−O19	2.107(15)				
N1−Cu1−N1a	175.7(11)	N2−Cu2−N3	125.5(8)	N2−Cu2−O19	134.9(7)	N3−Cu2−O19	96.8(7)
N2−Cu2−O13b	108.9(7)	N3−Cu2−O13b	94.3(7)	O19−Cu2−O13b	78.9(6)		
			complex **3**				
Cu1−N3	1.880(16)	Cu1−N5	1.903(16)	Cu2−N4	1.901(19)	Cu2−N1	1.938(18)
Cu1−O6b	2.346(14)	Cu1−O37	2.283(14)	Cu2−O34	2.237(15)	Cu2−O27a	2.694(18)
N3−Cu1−N5	158.8(7)	N3−Cu1−O37	109.4(6)	N5−Cu1−O37	89.6(6)	N3−Cu1−O6b	101.2(7)
N5−Cu1−O6b	85.9(6)	O37−Cu1−O6b	94.9(5)	N4−Cu2−N1	163.2(8)	N4−Cu2−O34	102.3(7)
N1−Cu2−O34	93.1(7)	N4−Cu2−O27a	98.0(8)	N1−Cu2−O27a	92.6(7)	O34−Cu2−O27a	74.2(5)
			complex **4**				
Cu1−N1	1.906(8)	Cu1−N1b	1.906(8)	Cu2−N2	1.949(8)	Cu2−N3	1.986(8)
Cu2−O13c	2.327(8)	O13−Cu2a	2.327(8)				
N1−Cu1−N1b	174.8(5)	N2−Cu2−N3	123.9(3)	N2−Cu2−O19	134.8(3)	N3−Cu2−O19	98.5(3)
N2−Cu2−O13c	108.1(3)	N3−Cu2−O13c	94.5(3)	O19−Cu2−O13c	80.7(3)		
			complex **5**				
Ag1−N1	2.161(18)	Ag1−N1a	2.161(19)	Ag1−O13	2.868(15)	Ag1−O13a	2.868(15)
Ag2−N2	2.158(18)	Ag2−N2b	2.158(18)	Ag2−O5c	3.011(14)	Ag2−O5d	3.011(14)
Ag2−O16c	3.073(15)	Ag2−O16d	3.073(15)				
N1−Ag1−N1a	141.9(10)	N1−Ag1−O13	87.9(6)	N1−Ag1−O13a	107.9(5)	O13−Ag1−O13a	130.8(6)
N2−Ag2−N2b	150.6(9)	N2−Ag2−O16d	80.4(6)	N2−Ag2−O16c	112.5(5)	N2b−Ag2−O5c	133.5(6)
N2−Ag2−O5c	69.8(5)	N2b−Ag2−O5c	133.5(6)	O5c−Ag2−O16d	89.7(4)	O5c−Ag2−O5d	94.9(5)
O16c−Ag2−O16d	129.7(6)						

[a] Symmetry transformations: b $x - y + 2/3, -y + 4/3, -z - 1/6$, f $-x + 1/3, -y + 5/3, -z - 1/3$ for **1**; a $-x + 1/2, -y + 3/2, z$, b $-x - 1/2, y, z + 1/2$ for **2**; a $x, y + 1, z$, b $-x + 1, -y + 1, -z + 1$ for **3**; a $-x - 1/2, y, z - 1/2$, b $-x + 1/2, -y + 3/2, z$, c $-x - 1/2, y, z + 1/2$ for **4**; a $-x + 2/3, -x + y + 1/3, -z + 7/3$, b $-x + 4/3, -x + y + 2/3, -z + 8/3$, c $y, x, -z + 2$, d $-y + 4/3, x - y + 2/3, z + 2/3$ for **5**.

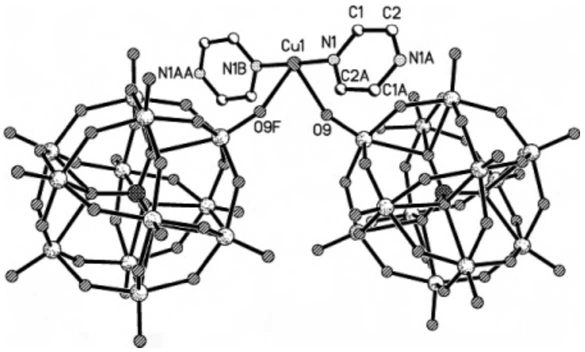

Figure 1. ORTEP plot showing the coordination environment of copper(I) ion in $[Cu_3(pz)_3(PW_{12}O_{40})]$ (**1**).

be viewed as a 2D layer of $[Cu_3(2,3\text{-}Me_2pz)_3(PW_{12}O_{40})]_n$ with its three-coordinated copper(I) ion covalently linked by the $PW_{12}O_{40}^{3-}$ anions from adjacent layers, while the 2D layer (Figure 5b) in **2** can be viewed as adjacent 1D chains of $[Cu(2,3\text{-}Me_2pz)]_n^{n+}$ linked by $PW_{12}O_{40}^{3-}$ anions. Such a linking mode results in the $PW_{12}O_{40}^{3-}$ anion being a four-connected linkage surrounded by four $[Cu(2,3\text{-}Me_2pz)]_n^{n+}$ chains, a rare linking mode in Keggin-based coordination polymers (Figure 6). The Cu−N bond distance and the N−Cu−N bond angle in linear coordination geometry are 1.914(19) Å and 175.7(11)°, respectively, compared to 1.907(19)−1.948(17) Å and 174.5(8)°, respectively, in the two-coordinated copper(I) complex of $[Cu_4(2,4'\text{-}bipy)_4SiW_{12}O_{40}]$.[10d] The bond distances and angles around the copper(I) ion in tetrahedral coordination geometry are 1.965(17)−1.995(18) Å (Cu−N), 2.107(15)−2.424(19) Å (Cu−O), 125.5(8)° (N−Cu−N), 94.3(7)−134.9(7)° (N−Cu−O), and 78.9(6)° (O−Cu−O), which are significantly different those in tetrahedral coordination geometry of **1**.

Complex **3** consists of two copper(I) ions, one and half 2,5-Me_2pz ligands, one monoprotonated 2,5-HMe_2pz ligand, and one $PW_{12}O_{40}^{3-}$ anion. Of the two independent copper(I) centers, one is four-coordinated by two nitrogen atoms from 2,5-HMe_2pz and 2,5-Me_2pz and two oxygen atoms from two $PW_{12}O_{40}^{3-}$ anions, and the other is four-coordinated by two nitrogen atoms of 2,5-Me_2pz and two oxygen atoms from two $PW_{12}O_{40}^{3-}$ anions (Figure 7). The 3D structure of **3** (Figure 8a) can be viewed as adjacent layers of $[Cu_2(2,5\text{-}Me_2pz)_{1.5}(2,5\text{-}HMe_2pz)PW_{12}O_{40}]_n$ connected through the coordination of the copper(I) ion from one layer to the $PW_{12}O_{40}^{3-}$ anion from another layer, while the 2D layer can be viewed as a 1D chain of $[Cu(2,5\text{-}Me_2pz)(PW_{12}O_{40})]_n^{2n-}$ linked by $[Cu_2(2,5\text{-}Me_2pz)(2,5\text{-}HMe_2pz)_2]^{4+}$ units (Figure 8b). The $PW_{12}O_{40}^{3-}$ anion in **3** functionalizes a four-connected linkage (Figure 9). Bond distances and angles around Cu1 are 1.880(16)−1.903(16) Å (Cu−N), 2.283(14)−2.346(14) Å (Cu−O), 158.8(7)° (N−Cu−N), 85.9(6)−109.4(6)° (N−Cu−O), and 94.9(5)° (O−Cu−O), while those around Cu2 are 1.901(19)−1.938(18) Å (Cu−N), 2.237(15)−2.694(18) Å (Cu−O), 163.2(8)° (N−Cu−N), 92.6(7)−102.3(7)° (N−Cu−O), and 74.2(5)° (O−Cu−O). They are very different from those in **1** and **2**.

Complex **4** consists of three copper(I) ions, three 2,3-Me_2pz ligands, and one $PMo_{12}O_{40}^{3-}$ anion. Each

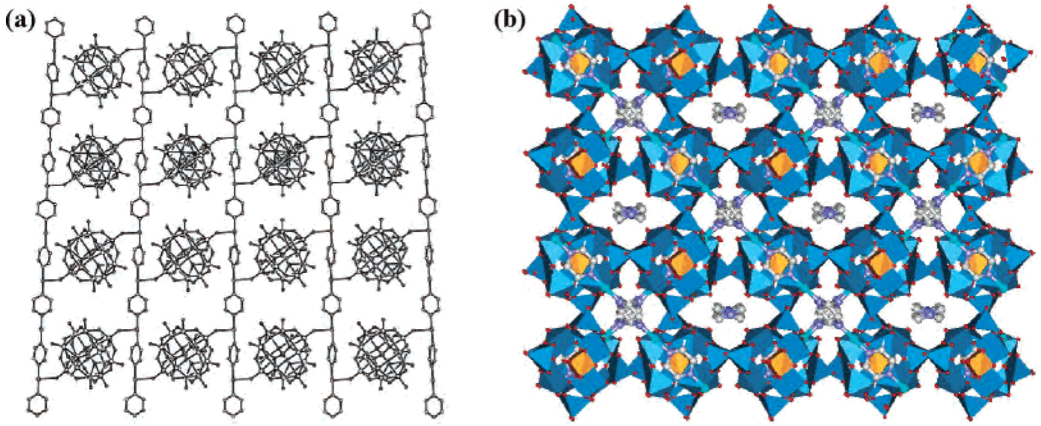

Figure 2. (a) ORTEP plot showing the 2D structure in $[Cu_3(pz)_3(PW_{12}O_{40})]$ and (b) a polyhedral view of the 3D structure of $[Cu_3(pz)_3(PW_{12}O_{40})]$ viewed along 101 plane (Cu, cyan; O, red; W, blue; P, orange; C, gray; N, Cambridge blue).

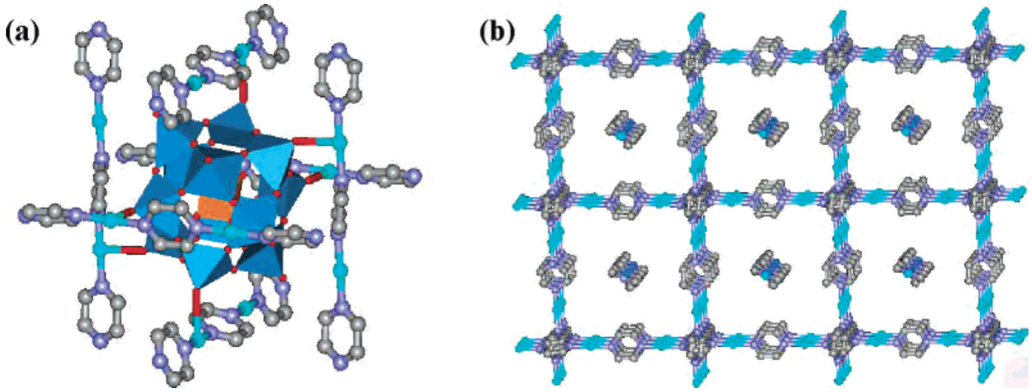

Figure 3. (a) Polyhedral view of the coordination environment of $PW_{12}O_{40}^{3-}$ anion in $[Cu_3(pz)_3(PW_{12}O_{40})]$ and (b) a ball and stick plot of the arrangement of 1D chain of $[Cu(pz)]_n^{n+}$ in $[Cu_3(pz)_3(PW_{12}O_{40})]$ (Cu, cyan; O, red; W, blue; P, orange; C, gray; N, Cambridge blue).

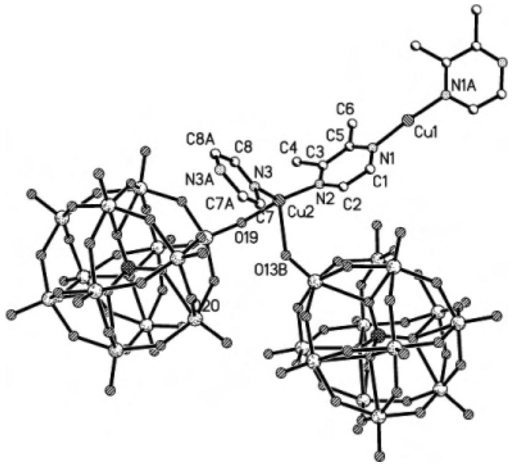

Figure 4. ORTEP plot showing the coordination environment of copper(I) ion in $[Cu_3(2,3\text{-}Me_2pz)_3(PW_{12}O_{40})]$.

$PMo_{12}O_{40}^{3-}$ anion in **4** acts as a four-connected linkage, connects with four chains of $[Cu(2,3\text{-}Me_2pz)]_n^{n+}$, and generates a 3D structure very similar to that of **2**. In fact, complex **4** is an isomer of **2**. Cu−N bond distances and N−Cu−N bond angles in linear geometry are 1.906(8) Å and 174.8(5)° respectively, while the bond distances and angles around copper(I) ion in tetrahedral coordination geometry are 1.949(8)−1.986(8) Å (Cu−N), 2.042(6)−2.327(8) Å (Cu−O), 123.9(3)° (N−Cu−N), 94.5(3)−134.8(3)° (N−Cu−O), and 80.7(3)° (O−Cu−O). Both the bond distances and angles in **4** are comparable to those in **2**.

Complex **5** consists of three silver(I) ions, three pz ligands, one $PW_{12}O_{40}^{3-}$ anion, and half a water molecule. Crystal structure analysis reveals that there are two independent silver(I) centers in **5**, in which, one is four-coordinated by two nitrogen atoms of two pz ligands and two oxygen atoms from two $PW_{12}O_{40}^{3-}$ anions in distorted tetrahedral geometry, and the other is six-coordinated by two nitrogen atoms from two pz ligands and four oxygen atoms from two $PW_{12}O_{40}^{3-}$ anions in distorted octahedral geometry as shown in Figure 10. Bond distances around Ag1 are 2.161(18) (Ag−N) and 2.868(15) Å (Ag−O), while those around Ag2 are 2.158(18) (Ag−N) and 3.011(14)−3.073(15) Å (Ag−O). Each $PW_{12}O_{40}^{3-}$ anion coordinates with six silver(I) ions from six adjacent 1D chains of $[Ag(pz)]_n^{n+}$, and each 1D chain surrounded by four sets of 1D chains (Figure 11a) generates a 3D structure very similar to that of **1** (Figure 11b). Previous investigation shows that, when combined with 1D $[Ag(pz)]_n^{n+}$ chains, the anion was often surrounded by four 1D $[Ag(pz)]_n^{n+}$ chains, as demonstrated in the complexes of $[Ag(pz)]_n{\cdot}nNO_3$,[21] $[Ag(pz)]_n{\cdot}nBF_4$,[22] $[Ag(pz)]_n{\cdot}0.5n(OH){\cdot}0.5n(PF_6)$,[23] and $[Ag(pz)]_n{\cdot}nPF_6$.[24] Clearly, POM anion being

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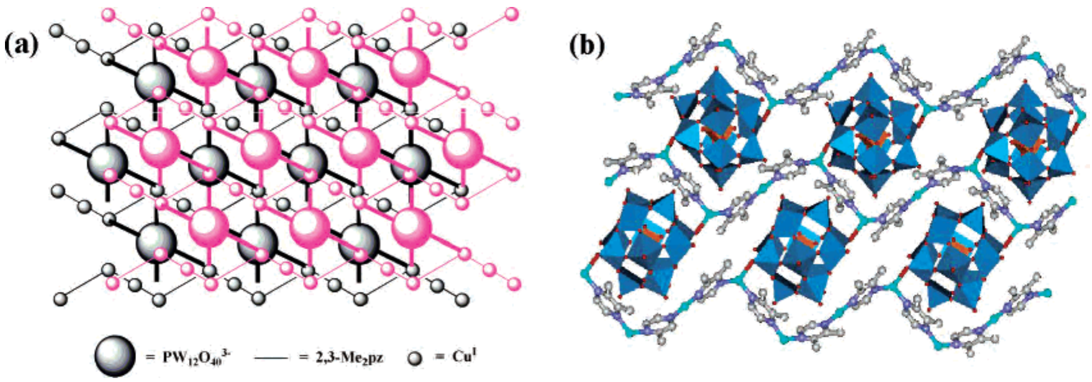

Figure 5. (a) Schematic view of the 3D structure of [Cu_3(2,3-Me_2pz$)_3$($PW_{12}O_{40}$)] and (b) a polyhedral view of the 2D structure in [Cu_3(2,3-Me_2pz$)_3$-($PW_{12}O_{40}$)] (Cu, cyan; O, red; W, blue; P, orange; C, gray; N, Cambridge blue).

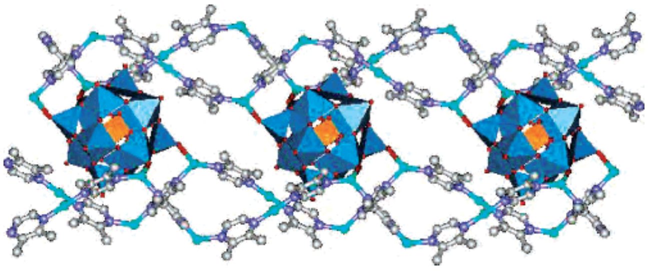

Figure 6. Polyhedral view of the linking mode of $PW_{12}O_{40}^{3-}$ in [Cu_3(2,3-Me_2pz$)_3$($PW_{12}O_{40}$)] (Cu, cyan; O, red; W, blue; P, orange; C, gray; N, Cambridge blue).

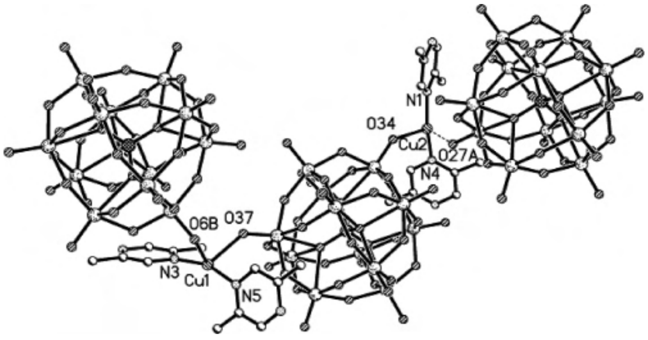

Figure 7. ORTEP plot showing the coordination environment of copper-(I) ion in [Cu_2(2,5-Me_2pz$)_{1.5}$(2,5-HMe_2pz)($PW_{12}O_{40}$)].

surrounded by six 1D $[Ag(pz)]_n^{n+}$ chains is attributed to its larger volume. It was noted that, even though coordination environment of the cation in **5** is different from that in **1**, the topology of **5** is very similar to that in **1**, indicating that the steric hindrance of organic ligand is an important factor influencing on the topology of coordination polymers.

Influence of the Steric Hindrance of the Organic Ligand on the Structure of Keggin-Based Coordination Polymers. On the basis of the structures of **1**−**5**, especially the structural similarity between **1** and **5** and **2** and **4**, it is clear that the steric hindrance of the organic ligand is of key importance for the topology of POM-based coordination polymer. Investigation of their structural differences shows that the steric effect of the organic ligand on the structure of POM-based coordination polymer is realized through changing the number of metal−organic units surrounding or linking to POM anion, for example, the six-connected POM anion in **1** and **5** and the four-connected POM anion in **2**, **3**, and **4**. Because a similar effect has not been observed in other previously reported pz-related copper(I) coordination polymers,[25] we attributed it to the POM anion, which is understandable because of its larger volume. As we know, when combined with metal−organic units, because of its larger volume, the POM anion has a potential to function as a high-connected linkage. However, the ability of POM anion to function as a high-connected linkage in coordination polymers depends on the organic ligand used in metal−organic units. If the steric hindrance of organic ligand in the metal−organic unit were larger, the volume of the metal-organic unit would be larger. In this case, the POM anion functioning as a high-connected linkage would result in separation among metal−organic units, the metal−organic unit and POM anion being too close, and the coordination polymer formed being instable. To effectively form the coordination polymer with such a metal−organic unit, POM has to decrease the number of metal−organic units it combines and function as a low-connected linkage. Only when the steric hindrance of the organic ligand in the metal−organic unit is smaller could the POM anion effectively function as a high-connected linkage. Indeed, the shortest separation among the $[Cu(pz)]_n^{n+}$ chains (C···C interaction) and between POM anion and the $[Cu(pz)]_n^{n+}$ chain (C···O interaction) in **1** are 4.440 and 3.104 Å, respectively. If the POM anion in complex **2** and **3** functioned as a six-connected linkage to form a structure similar to that of **1**, the corresponding values would be 2.231 and 1.686 Å for **2** and

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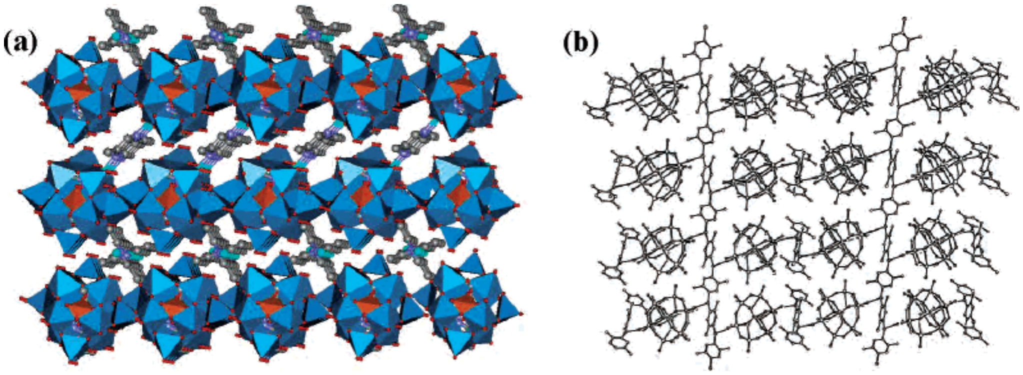

Figure 8. (a) Polyhedral view of the 3D structure of $[Cu_2(2,5\text{-}Me_2pz)_{1.5}(2,5\text{-}HMe_2pz)(PW_{12}O_{40})]$ (Cu, cyan; O, red; W, blue; P, orange; C, gray; N, Cambridge blue) and (b) an ORTEP plot showing the 2D layer in $[Cu_2(2,5\text{-}Me_2pz)_{1.5}(2,5\text{-}HMe_2pz)(PW_{12}O_{40})]$.

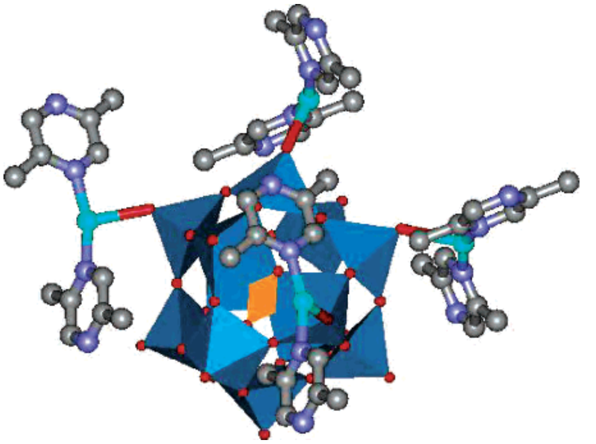

Figure 9. Coordination environment of the $PW_{12}O_{40}{}^{3-}$ anion in $[Cu_2(2,5\text{-}Me_2pz)_{1.5}(2,5\text{-}HMe_2pz)(PW_{12}O_{40})]$ (Cu, cyan; O, red; W, blue; P, orange; C, gray; N, Cambridge blue).

3.668 and 1.686 Å for **3** (the separation was obtained on the basis of C−C = 1.5 Å), which are significantly shorter than those of 3.958 and 3.047 Å in **2** and 3.739 and 3.120 Å in **3**, when the POM anion in these two complexes functionalized a four-connected linkage. Similarly, if complex **3** formed a structure similar to that of **2**, the shortest separation among $[Cu(2,5\text{-}Me_2pz)]_n{}^{n+}$ chains (C⋯C interaction) and between POM anion and the $[Cu(2,5\text{-}Me_2pz)]_n{}^{n+}$ chain (C⋯O interaction) would be 3.052 and 2.29 Å (C−C = 1.5 Å), respectively, which are much shorter than those in **3**. It was noted that, although the POM anion both in **2** and **3** functions as a four-connected linkage, the ratio of POM to metal ion to organic ligand in **3** is much different from that in **2**. The POM/copper(I)/organic ligand ratio in **2** is 1:3:3, while that in **3** is 1:2:2.5. The POM/metal ion/organic ligand ration, in fact, represents the number of metal−organic units surrounding POM anion in the coordination polymer, and this indicates that the steric effect of the organic ligand on the structural differences between **2** and **3** is also realized through changing the number of metal−organic units surrounding or linking to POM anion.

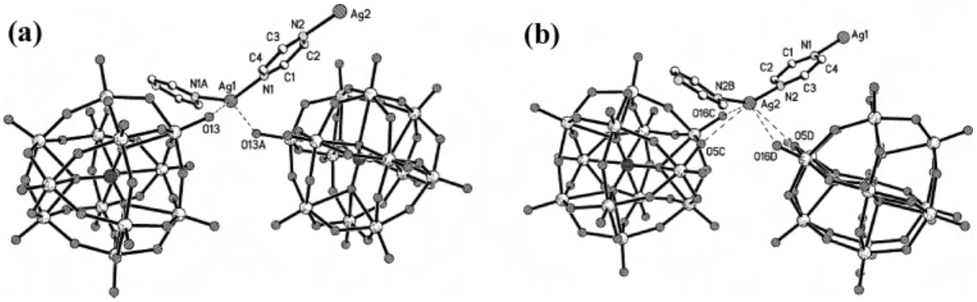

Figure 10. ORTEP plot showing the coordination environment of the silver(I) ion in $[Ag_3(pz)_3(PW_{12}O_{40})]\cdot 0.5H_2O$.

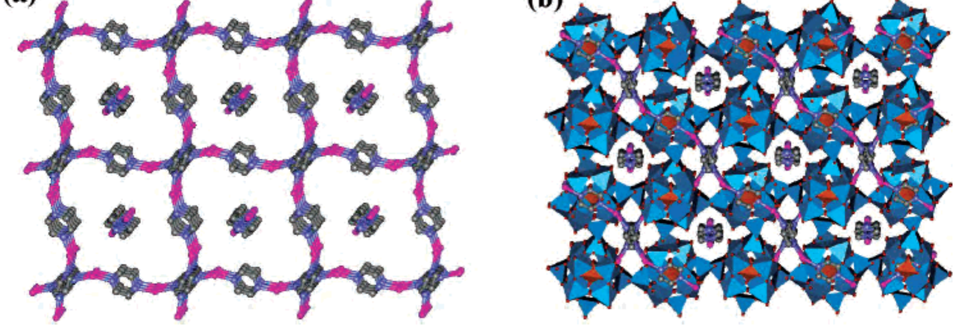

Figure 11. (a) Ball and stick plot showing the arrangement of 1D chain of $[Ag(pz)]_n{}^{n+}$ in $[Ag_3(pz)_3(PW_{12}O_{40})]\cdot 0.5H_2O$ and (b) a polyhedral view of the 3D structure of $[Ag_3(pz)_3(PW_{12}O_{40})]\cdot 0.5H_2O$ (Ag, purple; O, red; W, blue; P, orange; C, gray; N, Cambridge blue).

Conclusion

The steric effect of an organic ligand is known to be an important factor in the modification of the structure of a coordination polymer.[26−28] For example, interpenetration of the metal−organic framework could be effectively prevented by the steric effects of the organic ligand.[26] However, such an effect is seldom considered in the assembly of POM-based coordination polymers. In this work, we have synthesized and structurally characterized a series of POM-based coordination polymers showing the contribution of the steric hindrance of the organic ligand to the structure of POM-based coordination polymers. Investigation of their structural differences reveals that the steric effect of an organic ligand on the structure of a POM-based coordination polymer is closely related to the larger volume of POM anion and a smaller steric hindrance of the organic ligand favors the POM anion functioning as a high-connected linkage in the coordination polymer and vice versa. Hence our present work would help in the rational design and assembly of POM-based coordination polymers.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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