

# Hydrothermal syntheses, structures and characterizations of three one-dimensional polyoxomolybdates with 4,4'-dimethylenebiphenyl diphosphonic acid as bridge

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## Abstract

Three heterometallic 1-D polymers,  $[\{\text{Ni}(1,10\text{-phen})_2(\text{H}_2\text{O})\}_2 \{(\text{Mo}_5\text{O}_{15})(4,4'\text{-dbp})\} \cdot (5.75\text{H}_2\text{O})]$  ( $4,4'\text{-dbp} = \text{O}_3\text{PCH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_2\text{PO}_3$ ) (**1**),  $[\{\text{Co}(1,10\text{-phen})_2(\text{H}_2\text{O})\}_2 \{(\text{Mo}_5\text{O}_{15})(4,4'\text{-dbp})\} \cdot (5.5\text{H}_2\text{O})]$  (**2**) and  $[\{\text{Ni}(2,2'\text{-bpy})_3\} \{\text{Ni}(2,2'\text{-bpy})_2(\text{H}_2\text{O})\} \{(\text{Mo}_5\text{O}_{15})(4,4'\text{-dbp})\} \cdot (4.75\text{H}_2\text{O})]$  (**3**), have been synthesized under hydrothermal conditions. Their structures were determined by single crystal X-ray diffraction. The 1-D chains is constructed of  $[\text{Mo}_5\text{O}_{15}(4,4'\text{-dbp})]^{4-}$  units, which are further decorated and charge compensated by  $[\text{M}(1,10\text{-phen})_2]$  ( $\text{M} = \text{Ni}, \text{Co}$ ) or  $[\text{Ni}(2,2'\text{-bpy})_2]$  subunits. The thermogravimetric analyses and magnetic properties of **1** and **2** were studied.

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**Keywords:** Hydrothermal synthesis; Crystal structure; Metal-organic subunit; One-dimensional; Polyoxomolybdate; 4,4'-dimethylenebiphenyldiphosphonic acid

## 1. Introduction

Being an important class of inorganic–organic hybrid materials, metal phosphonates have gained much attention in recent years owing to their structural diversities and potential applications in catalysis, ion exchange, and intercalation chemistry [1–4]. An important subclass of metal phosphonates is oxomolybdenum-organophosphonates, which exhibit a remarkable range of structure type: complex molecular anion [5], 1-D chain [6], 2-D layered materials [7], and net-work [8b,d,f,g]. Recently, one of the important trends in this system is the introduction of metal-organic subunits and many new compounds have been synthesized [8,9]. These subunits play an important role as charging-compensator, structure-director, and

space-filler, which further decorate inorganic clusters. The use of organodiphosphonic acids as ligands can provide poly dimensional polymers whose structures are affected greatly by the length of the ligands. Furthermore, the structures are also influenced by different metal ions and shapes of organics. Zubietta and co-workers have done much work in this aspect. They obtained crystalline materials using copper-organonitrogen or nickel-organonitrogen subunits and short length organodiphosphonic acids ( $\text{H}_2\text{O}_3\text{P}(\text{CH}_2)_n\text{PO}_3\text{H}_2$ ,  $n = 1, 2, 3, 4, 5$ ) [8]. With these organodiphosphonic acids as ligands, we also synthesized five compounds involving cobalt or copper ions chelated by organoamine as subunits [9]. In an attempt to extend the chemistry of oxomolybdenum organophosphonates, a much longer diphosphonate ligand, 4,4'-dbp ( $4,4'\text{-dbp} = \text{O}_3\text{PCH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_2\text{PO}_3$ ) was synthesized. Using 4,4'-dbp as a linker, and  $[\{\text{Ni}(1,10\text{-phen})_2\}^{2+}]$ ,  $[\{\text{Co}(1,10\text{-phen})_2\}^{2+}]$ , and  $[\{\text{Ni}(2,2'\text{-bpy})_2\}^{2+}]$

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as metal-organic subunits, three one-dimensional compounds:  $[\{Ni(1,10\text{-phen})_2(H_2O)\}_2\{Mo_5O_{15}(4,4'\text{-dbp})\} \cdot (5.75H_2O)]$  (**1**),  $[\{Co(1,10\text{-phen})_2(H_2O)\}_2\{Mo_5O_{15}(4,4'\text{-dbp})\} \cdot (5.5H_2O)]$  (**2**) and  $[\{Ni(2,2'\text{-bpy})_3\}\{Ni(2,2'\text{-bpy})_2(H_2O)\}\{Mo_5O_{15}(4,4'\text{-dbp})\} \cdot (4.75H_2O)]$  (**3**) were synthesized. Their structures were determined by single crystal X-ray diffraction. The thermogravimetric analyses and magnetic properties were studied.

## 2. Experiment section

### 2.1. Materials and instruments

4,4'-dimethylenebiphenyldiphosphonic acid was prepared by hydrolyzing 4,4'-bis-(diethoxyphosphonomethyl)-diphenyl with concentrated hydrochloric acid for 96 h under refluxing. The product was washed with ether and distilled water and used without characterization. Other chemicals are of reagent grade and used without further purification. Elemental analyses were carried out by the Elemental Analyses lab of our institute on Vario EL III element analyzer. Infrared spectra were obtained on a PerkinElmer Spectrum One. Thermogravimetric analysis (TGA) was performed on METTLER TGA/SDTA851<sup>c</sup> thermal analyzer under air at a heating rate of 10 °C min<sup>-1</sup> from room temperature to 1000 °C. Magnetic Properties were measured on a PPMS-9.

### 2.2. Syntheses

#### 2.2.1. $[\{Ni(1,10\text{-phen})_2(H_2O)\}_2\{Mo_5O_{15}(4,4'\text{-dbp})\} \cdot (5.75H_2O)]$ (**1**)

A mixture of 0.5 mmol  $Ni(CH_3COO)_2 \cdot 4H_2O$ , 1 mmol  $Na_2MoO_4 \cdot 2H_2O$ , 1 mmol  $MoO_3$ , 1 mmol 1,10-phenanthroline  $\cdot H_2O$ , and 1 mmol 4,4'-dimethylenebiphenyldiphosphonic acid in 10 ml distilled water was sealed in a Parr Teflon-lined stainless steel vessel (25 ml), and then heated at 180 °C for 72 h. After cooled to room temperature, green block-like crystals of complex **1** were obtained. The yield is about 68% based on Ni (found: C, 36.87; H, 2.91; N, 5.52. Calc. for  $C_{62}H_{59.5}N_8O_{28.75}P_2Ni_2Mo_5$ : C, 36.58; H, 2.95; N, 5.50%) IR (KBr pellet, 400–4000 cm<sup>-1</sup>) 3425vs, 2916m, 2850w, 1627m, 1514m, 1427vs, 1114m( $\nu_{P-O}$ ), 1042m( $\nu_{P-O}$ ), 975vs( $\nu_{Mo=O}$ ), 914vs( $\nu_{Mo=O}$ ), 729vs( $\nu_{P-C}$ ), 703vs( $\nu_{Mo-O-Mo}$ ), 600w( $\nu_{Mo-O-Mo}$ ), 534w.

#### 2.2.2. $[\{Co(1,10\text{-phen})_2(H_2O)\}_2\{Mo_5O_{15}(4,4'\text{-dbp})\} \cdot (5.5H_2O)]$ (**2**)

Compound **2** was synthesized by the same procedure as **1** except for replacement of  $Ni(CH_3COO)_2 \cdot 4H_2O$  with  $Co(CH_3COO)_2 \cdot 4H_2O$ . The yield is about 55% based on Co. (found: C, 36.66; H, 2.82; N, 5.39. Calc. for  $C_{62}H_{59}N_8O_{28.50}P_2Co_2Mo_5$ : C, 36.65; H, 2.93; N, 5.52%)

IR (KBr pellet, 400–4000 cm<sup>-1</sup>): 3430vs, 2914w, 1622m, 1514m, 1427vs, 1380m, 1108m ( $\nu_{P-O}$ ), 1043m ( $\nu_{P-O}$ ), 981vs ( $\nu_{Mo=O}$ ), 920vs ( $\nu_{Mo=O}$ ), 894vs, 735vs( $\nu_{P-C}$ ), 690vs( $\nu_{Mo-O-Mo}$ ), 606w( $\nu_{Mo-O-Mo}$ ), 535w.

#### 2.2.3. $[\{Ni(2,2'\text{-bpy})_3\}\{Ni(2,2'\text{-bpy})_2(H_2O)\}\{Mo_5O_{15}(4,4'\text{-dbp})\} \cdot (4.75H_2O)]$ (**3**)

Compound **3** was synthesized by the same procedure as **1** except for replacement of 1,10-phen with 2,2'-bpy. The yield is only about 9% based on Ni. The yield of **3** is much lower than **1** and **2**. We changed the ratio of the reactants and the reaction temperature, but failed to find a more efficient way to synthesize **3** (found: C, 37.32; H, 3.11; N, 6.80. Calc. for  $C_{64}H_{63.5}N_{10}O_{26.75}P_2Ni_2Mo_5$ : C, 37.32; H, 3.11; N, 6.80%) IR (KBr pellet, 400–4000 cm<sup>-1</sup>) 3409vs, 3606m, 2947w, 1632m, 1586vs, 1124m( $\nu_{P-O}$ ), 1042m( $\nu_{P-O}$ ), 975vs( $\nu_{Mo=O}$ ), 934vs( $\nu_{Mo=O}$ ), 893vs( $\nu_{P-C}$ ), 704v( $\nu_{Mo-O-Mo}$ ), 618m( $\nu_{Mo-O-Mo}$ ), 545w.

### 2.3. X-ray crystallography

X-ray data were collected at 130.15k on a Rigaku Mercury CCD/AFC diffractometer with  $MoK\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Lorentz and polarization corrections as well as empirical absorption correction were carried out for the net intensities [11]. The structures were solved by direct methods and refined by full-matrix least-squares techniques using SHELXTL-97 [12]. All non-hydrogen atoms were treated anisotropically in the three complexes. No attempt was made to locate the hydrogen atoms of water. The crystallographic data are summarized in Table 1. Selected bond lengths and angles are listed in Table S-1, S-2 and S-3. CCDC 252520–252522 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

## 3. Result and discussion

### 3.1. Description of the structure

Compounds **1** and **2** are isomorphous. So **1** was used as an example to describe their structures in detail. **1** is a neutral 1-D chain built up from  $[Ni(1,10\text{-phen})_2(H_2O)]^{2+}$  cationic fragments and  $[(Mo_5O_{15})(4,4'\text{-dbp})]^{4-}$  anionic chain (Fig. 1a). All Ni<sup>II</sup> atoms are in distorted octahedral coordination geometries and each coordinates to four nitrogen atoms from two 1,10-phen ligands and two oxygen atoms. The  $\{NiN_4O_2\}$  moiety shares an oxo group with  $\{Mo_2O_6\}$  octahedron

Table 1  
Crystallographic data for 1–3

	1	2	3
Empirical formula	$C_{62}H_{59.50}N_8O_{28.75}P_2Ni_2Mo_5$	$C_{62}H_{59}N_8O_{28.5}P_2Co_2Mo_5$	$C_{64}H_{63.50}N_{10}O_{26.75}P_2Ni_2Mo_5$
Formula weight	2035.74	2031.67	2059.81
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P2(1)/c
<i>a</i> (Å)	13.677(1)	13.756(2)	20.935(2)
<i>b</i> (Å)	15.269(2)	15.289(2)	15.168(7)
<i>c</i> (Å)	19.481(2)	19.455(3)	23.822(2)
$\alpha$ (deg)	70.246(4)	70.541(6)	90
$\beta$ (deg)	76.120(4)	76.102(6)	103.077(3)
$\gamma$ (deg)	68.743(4)	68.662(5)	90
<i>V</i> (Å <sup>3</sup> )	3536.3(6)	3560.6(8)	7368.1(8)
<i>Z</i>	2	2	4
<i>D</i> <sub>calc.</sub> (g cm <sup>-3</sup> )	1.912	1.913	1.857
$\mu$ (mm <sup>-1</sup> )	1.516	1.445	1.455
<i>F</i> (000)	2027	2032	4110
<i>R</i> (int)	0.0158	0.0275	0.0240
<i>R</i> <sup>a</sup>	0.0284	0.0469	0.0287
<i>R</i> <sub>w</sub> <sup>b</sup>	0.0693	0.0878	0.0778

<sup>a</sup> $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$ .

<sup>b</sup> $R_w = \{\Sigma w[(F_o^2 - F_c^2)^2] / \Sigma w[(F_o^2)^2]\}^{1/2}$ ,  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ,  $P = (F_o^2 + 2F_c^2)/3$ . **1**,  $a = 0.0297$ ,  $b = 6.6450$ ; **2**,  $a = 0.0255$ ,  $b = 7.6677$ ; **3**,  $a = 0.0490$ ,  $b = 10.4337$ .

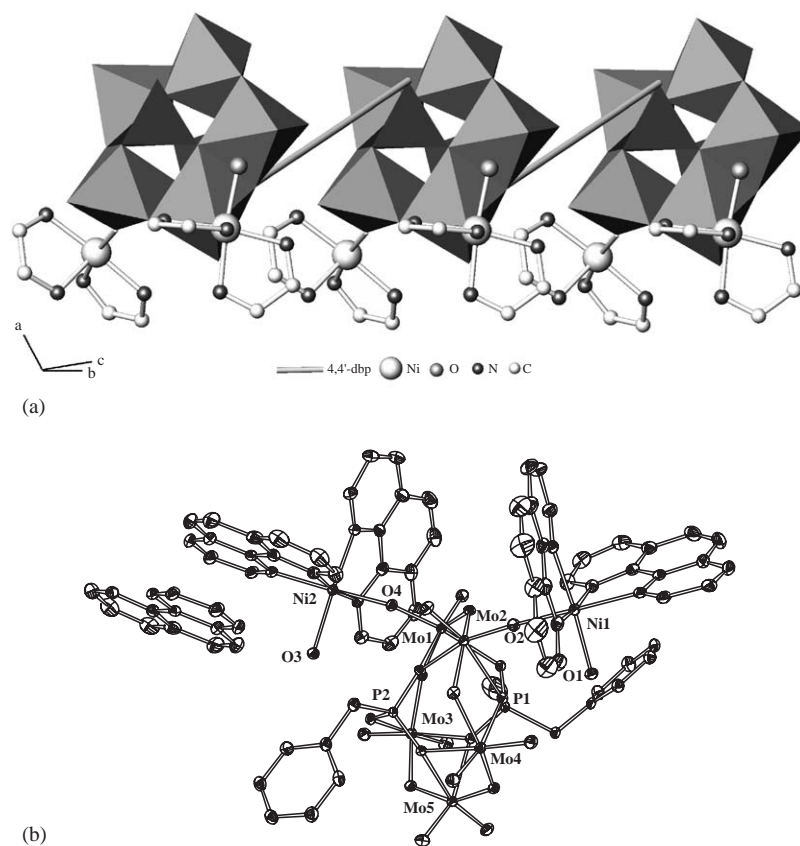


Fig. 1. (a) The neutral 1-D chain built up from  $[Ni(1,10\text{-phen})_2]^{2+}$  cationic fragments and  $[(Mo_5O_{15})(4,4'\text{-dbp})]^{4-}$  anionic chain of **1**. Free water molecules and hydrogen atoms are omitted for clarity. (b) ORTEP view of **1** showing the coordination geometries of the nickel, molybdenum and phosphorus atoms (ellipsoids at 50%). Free water molecules and hydrogen atoms are omitted for clarity.

(Ni1–O2 = 2.025 Å, Mo2–O2 = 1.732 Å, Ni1–O2–Mo2 = 175.83°). {Ni2N<sub>4</sub>O<sub>2</sub>} subunit is also adjoined to the {Mo<sub>5</sub>O<sub>15</sub>} cluster in the same manner (Ni2–O4 = 2.121 Å, Mo1–O4 = 1.741 Å, Ni2–O4–Mo1 = 151.15°), as shown in (Fig. 1b). The Ni–O and Ni–N distances are in range of 2.03–2.12 Å. The framework of this compound is obviously different from that of [{Co(1,10-phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>}{Co(1,10-phen)<sub>2</sub>(H<sub>2</sub>O)}{(Mo<sub>5</sub>O<sub>15</sub>)(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PO<sub>3</sub>)}·(6H<sub>2</sub>O)] reported by our group [9a], in which there is only one {CoN<sub>4</sub>O<sub>2</sub>} moiety linked to the {Mo<sub>5</sub>O<sub>15</sub>} cluster through an oxygen atom and the other {CoN<sub>4</sub>O<sub>2</sub>} moiety interacts with the anionic chain through hydrogen bonding.

Compound **3** is constructed from isolated {Ni(2,2'-bpy)<sub>3</sub>}<sup>2+</sup> cations, [Ni(2,2'-bpy)<sub>2</sub>(H<sub>2</sub>O)]<sup>2+</sup> cationic fragments and [(Mo<sub>5</sub>O<sub>15</sub>)(4,4'-dbp)]<sup>4-</sup> anionic chain (Fig. 2a). To Ni(1) of the {Ni(2,2'-bpy)<sub>3</sub>}<sup>2+</sup>, small deviations of bond angles from 180° of the idealized octahedral geometry are found for angles N1–Ni1–N6 [172.8°], N3–Ni1–N5 [171.6°] and N2–Ni1–N4 [170.0°], implying it has a slightly distorted octahedral configuration. The Ni–N distances vary from 2.048 to 2.104 Å. The {Ni2N<sub>4</sub>O<sub>2</sub>} unit is defined by two unequal oxygen

atoms (one is from a coordinated water molecule and the other is from {Mo<sub>5</sub>O<sub>15</sub>} cluster) and four nitrogen atoms of two 2,2'-bpy ligands. The Ni2 ion is also in a distorted octahedral coordination geometry. It is connected to {Mo<sub>5</sub>O<sub>15</sub>} cluster by sharing an oxygen atom with {Mo<sub>2</sub>O<sub>6</sub>} octahedron (Ni2–O22 = 2.012 Å, Mo2–O22 = 1.744 Å, Ni2–O22–Mo2 = 154.92°), as shown in Fig. 2b.

The {Mo<sub>5</sub>O<sub>21</sub>P<sub>2</sub>} clusters in the three compounds are isostructural, exhibiting the characteristic structure based on pentanuclear ring of corner and edge sharing {MoO<sub>6</sub>} octahedrons, capped by three oxygen atoms of {PO<sub>3</sub>} on each side.

Similar {Mo<sub>5</sub>O<sub>21</sub>P<sub>2</sub>} cluster has also been observed in several other oxomolybdenum organodiphosphonates. Their structures can be divided into two types. In compounds [{Co(1,10-phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>}{Co(1,10-phen)<sub>2</sub>(H<sub>2</sub>O)}{(Mo<sub>5</sub>O<sub>15</sub>)(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PO<sub>3</sub>)}·(6H<sub>2</sub>O)] [9a], the oxygen atoms in {PO<sub>3</sub>} tetrahedron only coordinate to the Mo atoms. While in compounds [{Cu<sub>2</sub>(tetra(2-pyridyl)pyrazine)(H<sub>2</sub>O)<sub>2</sub>}(Mo<sub>5</sub>O<sub>15</sub>)(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PO<sub>3</sub>)}·5.5H<sub>2</sub>O] [8f] and [Ni<sub>4</sub>(tppy<sub>3</sub>)<sub>3</sub>]{Mo<sub>5</sub>O<sub>15</sub>}(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>PO<sub>3</sub>)<sub>2</sub>·23H<sub>2</sub>O] [8a], one of

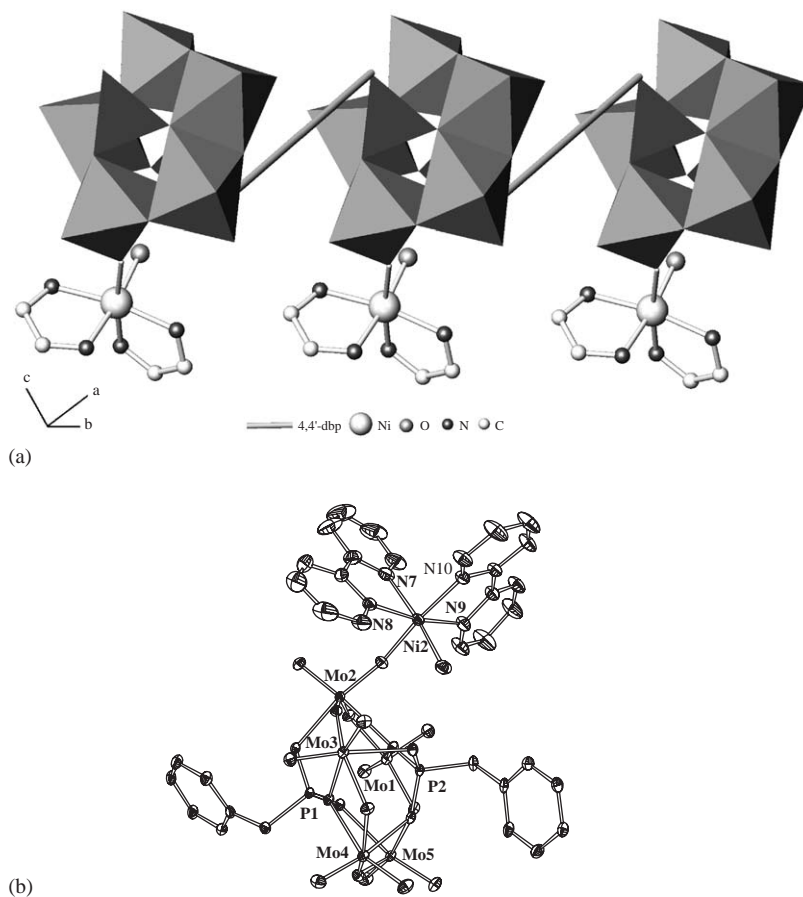


Fig. 2. (a) The 1-D anionic chain built up from [Ni(2,2'-bpy)<sub>2</sub>(H<sub>2</sub>O)]<sup>2+</sup> cationic fragments and [(Mo<sub>5</sub>O<sub>15</sub>)(4,4'-dbp)]<sup>4-</sup> anionic chain of **3**. (b) ORTEP view of **3** showing the coordination geometries of the nickel, molybdenum and phosphorus atoms (ellipsoids at 50%). Free water molecules and hydrogen atoms are omitted for clarity.

the oxygen atoms in  $\{\text{PO}_3\}$  tetrahedron also coordinates to the copper or nickel atoms of the metal-organic subunits. Our compounds fall into the first type. In addition, the structures of the three compound are obviously different from those containing shorter organodiphosphonate groups, including  $[\{\text{Co}(1,10\text{-phen})_2\}_2(\text{Mo}_4\text{O}_{12})(\text{O}_3\text{PCH}_2\text{CH}_2\text{PO}_3)\cdot(\text{H}_2\text{O})]$  and  $[\{\text{Co}(1,10\text{-phen})_2\}_2(\text{Mo}_4\text{O}_{12})(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{PO}_3)\cdot(1.5\text{H}_2\text{O})]$ , which are heterometallic hexanuclear clusters [9a].

In the three compounds, organodiphosphonate acid bridge  $\{\text{Mo}M\}$  ( $M = \text{Ni}, \text{Co}$ ) node. The periodic distance is about 15 Å. The adjacent chains act with each other through strong offset face-to-face  $\pi$ - $\pi$  stacking of neighboring parallel 1,10-phen groups at a distance of 3.2–3.6 Å in **1** and **2**. No obvious  $\pi$ - $\pi$  stacking was observed in the crystal structure of **3**.

### 3.2. IR spectroscopy

The IR spectra of compounds **1–3** all exhibit strong bands around 975–981 and 914–934  $\text{cm}^{-1}$ , characteristic of  $\nu(\text{Mo}=\text{O})$ . The bands around 690–704 and 600–608  $\text{cm}^{-1}$  originate from  $\nu(\text{Mo}-\text{O}-\text{Mo})$ . The bands around 1108–1124 and 1042–1043  $\text{cm}^{-1}$  can be attributed to the vibration of P–O.

### 3.3. TG analyses of **1** and **2**

The TGA diagram of **1** indicates that at about 33 °C, compound **1** begins to lose free water molecules and completes at about 149 °C with the weight loss of 4.2% (calcd. 5.1%). Between 149 and 272 °C, there is another weight loss of 2.4% (calcd. 1.8%), which is ascribed to coordinated water molecules (Fig. 3). For compound **2**, there are two obvious weight loss stages of water molecules 33–146 °C and 146–268 °C with weight loss 3.7% (calcd 4.9%) and 2.8% (calcd 1.8%), which is attributed to free water molecules and coordinated water molecules, respectively. The unusually high temperature needed for the release of water molecules may be due to the strong hydrogen bonds formed. The two compounds have a relatively high stability below 400 °C. The similar thermal behavior of **1** and **2** is based on their isomorphous structures.

### 3.4. Magnetic behavior of **1** and **2**

Temperature-dependent magnetic susceptibilities of complexes **1** and **2** were measured in the range 4–300 K at 10 kOe. Fig. 4 shows the temperature dependence of the molar susceptibility ( $\chi_m$ ), inverse molar susceptibility ( $\chi_m^{-1}$ ) and the effective magnetic moment ( $\mu_{\text{eff}}$ ). To a good approximation, high-temperature portion ( $T > 33$  K) of the susceptibility data of compound **1** can be well fitted to the Curie–Weiss law,  $\chi_m = C/(T-\theta)$ , where  $C$  ( $= 2.05 \text{ cm}^3 \text{ mol}^{-1}$ ) is the Curie

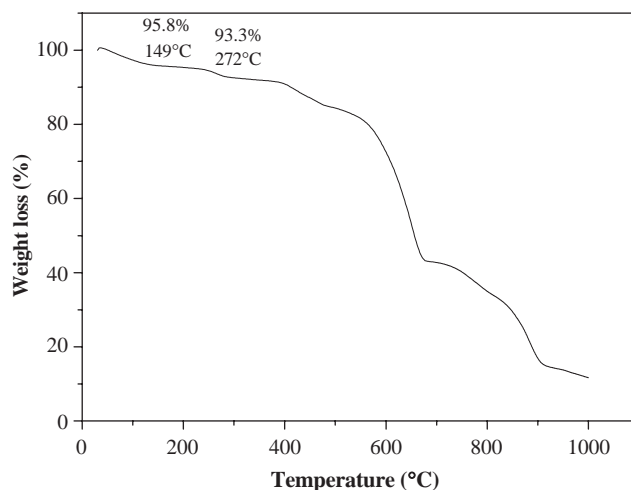


Fig. 3. TGA curves for compound **1**.

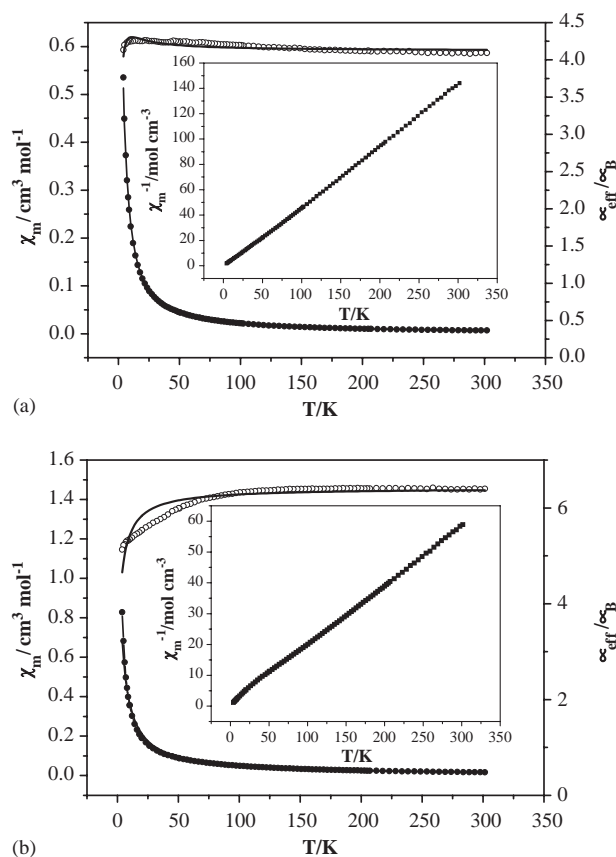


Fig. 4. Temperature dependence of  $\chi_m$  and the effective magnetic moment for compounds **1**(a) and **2**(b). Inset shows the  $\chi_m^{-1}$ - $T$  curve.

constant,  $\theta$  ( $= 5.20$  K) is the Weiss constant, and  $T$  is the temperature. Above 78 K, the susceptibility of **2** roughly obeys Curie–Weiss law with  $C = 5.19 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\theta = -3.23$  K. At room temperature, the effective magnetic moment of **1**,  $\mu_{\text{eff}} = 4.09 \mu_{\text{B}}$  (per two Ni(II) ions), which is close to the expected for spin-only ( $S_{\text{Ni}} = 1$ ,  $g = 2.0$ ) value of  $4.00 \mu_{\text{B}}$ . And the  $\mu_{\text{eff}}$  of **2** is  $6.39 \mu_{\text{B}}$ , which is higher than the expected



value of  $5.47\mu_B$  for two magnetically isolated high spin Co(II) ions ( $S_{Ni} = 3/2$ ,  $g = 2.0$ ). This larger value is the result of contributions to the susceptibility from orbital angular momentum at high temperatures. Upon cooling from 301.9 to 14 K, the  $\mu_{eff}$  of **1** increases very slightly and when the temperature is lowered to about 10 K, the  $\mu_{eff}$  begins to decrease very slightly. The margin between  $\mu_{eff(max.)}$  and  $\mu_{eff(min.)}$  is only  $0.1695\mu_B$ . The  $\mu_{eff}$  of **2** decreases slightly during being cooled from 301.5 to 100.4 K and at about 25 K, it begins to decrease relatively rapidly.

According to the structures described above, it is the two  $\{NiN_4O_2\}$  units that make the major contribution to the susceptibility of compound **1**. Assuming the magnetic exchange between the two Ni(II) ( $S = 1$ ) centers is isotropic,  $\hat{H} = -2J\hat{S}_1\hat{S}_2$  is introduced in. Still another possible origin of the magnetic behavior of **1** at low temperature is the zero-field splitting ( $D$ ) of Ni(II) ion in a distorted octahedral environment. Although there is no significant intermolecular interaction, a weak intermolecular antiferromagnetic interaction ( $\theta'$ ) cannot be neglected. Taking the three effects into account, a software named *Magnun* [10] was used to fit **1** and obtain a good result with the agreement factor  $R = \frac{\sum(\chi_{obsd.} - \chi_{calcd.})^2}{\sum\chi_{obsd.}^2} = 1.44 \times 10^{-4}$ ,  $J = 2.77 \text{ cm}^{-1}$ ,  $D = 5.0 \text{ cm}^{-1}$ ,  $\theta' = -2.1 \text{ K}$ . The positive Curie constant ( $\theta = 5.20 \text{ K}$ ) may arise from weak ferromagnetic interaction ( $J = 2.77 \text{ cm}^{-1}$ ) between the two Ni(II) ( $S = 1$ ) centers in **1**. When use the same method to fit **2**, the result is not good. The possible reason is the relatively strong spin-orbital coupling effects of Co(II) in octahedral symmetry crystal field.

#### 4. Conclusion

In summary, a much longer 4,4'-dimethylenebiphenyl-diphosphonic acid was introduced into polyoxomolybdates to synthesize three novel compounds under almost identical hydrothermal conditions using  $[Ni(1,10\text{-phen})_2(H_2O)]^{2+}$ ,  $[Co(1,10\text{-phen})_2(H_2O)]^{2+}$  and  $[Ni(2,2'\text{-bpy})_2(H_2O)]^{2+}$  as the metal-organic subunits. Our future work will focus on synthesizing novel compounds involving chiral organodiphosphonic acid and explore their applications in catalysis and absorption.

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