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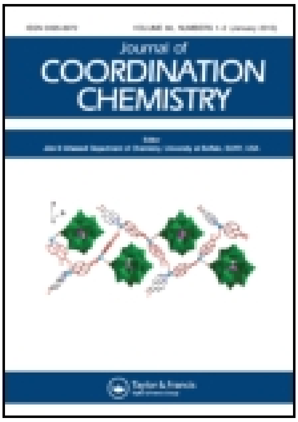

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Synthesis and structure of a one- and a three-dimensional material constructed from molybdenum phosphates and macrocyclic metal complexes

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Synthesis and structure of a one- and a three-dimensional material constructed from molybdenum phosphates and macrocyclic metal complexes

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Two new polyoxometalate-based materials, $[CuL]_2[H_2Mo_5P_2O_{23}]\cdot 2H_2O\cdot 2CH_3CN$ (**1**) and $[NiL]_2[H_2Mo_5P_2O_{23}]\cdot 10H_2O$ (**2**) ($L = 5,5,7,12,12,14$-hexamethyl-1,4,8,11-tetraaza-cyclotetradecane), have been isolated from the reactions of $[CuL](ClO_4)_2$ and $[NiL](ClO_4)_2$ with $(NH_4)_6Mo_7O_{24}$, respectively, and structurally characterized. Single-crystal X-ray diffraction analysis of **1** showed that clusters of $[H_2Mo_5P_2O_{23}]^{4-}$ bridge $[CuL]^{2+}$ to form 1-D chains, with O–H···O and N–H···O hydrogen bonding interactions forming a 3-D framework. The structure of **2** showed a 3-D network structure constructed from $[H_2Mo_5P_2O_{23}]^{4-}$ clusters bridging $[NiL]^{2+}$, generating 1-D channels occupied by guest water molecules.

Keywords: Macrocyclic metal complex; Molybdenum phosphate; Crystal structure

1. Introduction

The use of well-known polyoxometalates, such as Lindquist, Keggin and Dawson structures, to build novel materials has attracted much attention, not only because of structural esthetics but also for potential applications in different fields such as catalysis, medicine, ion exchange, gas storage, molecular electronics, and biological chemistry [1–5]. The construction of polyoxometalate-based materials with different extended dimensionalities and with controllable and desirable properties has become the focus of chemists [6–9]. Recently, molybdenum phosphates have been shown to be good candidates for building polyoxometalate-based materials, and many extended structures have been reported using molybdenum phosphates and transition metal complexes as building blocks [10–16].

The transition metal macrocyclic complexes $[ML]^{2+}$ ($L = 5,5,7,12,12,14$-hexamethyl-1,4,8,11-tetraazacyclotetradecane, M = Cu, Ni) can be utilized for construction of polyoxometalate-based materials (scheme 1), as four of the six coordination sites of the metal ions are blocked by the macrocyclic ligand; the two remaining coordination sites are accessible for coordination by the oxygens of a polyoxometalate to form 1- to 3-D structures. In our previous studies [17, 18], four different polyoxometalate materials with 1-D, 2-D, and 3-D

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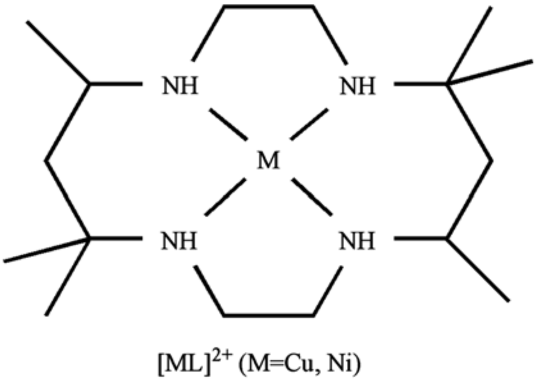

Scheme 1. The transition metal macrocyclic complexes $[ML]^{2+}$.

structures were obtained by reactions of $[ML](ClO_4)_2 \cdot (M = Ni$ and Cu) with NH_4VO_3 under different conditions. As a continuance of our research on the construction of polyoxometalate-based materials, we employed molybdenum phosphates and the transition metal macrocyclic complexes $[ML]^{2+}$ as building blocks. Herein, we report on the preparation and structures of two coordination polymers, $[CuL]_2[H_2Mo_5P_2O_{23}]$ and $[NiL]_2[H_2Mo_5P_2O_{23}]$, which are obtained by reactions of $[ML](ClO_4)_2$ (M = Cu, Ni) with $(NH_4)_6Mo_7O_{24}$. The former compound displays 1-D chains, which are formed through connection of $[H_2Mo_5P_2O_{23}]^{4-}$ clusters with $[CuL]^{2+}$, and the latter compound shows a 3-D structure, which is constructed through connection of $[H_2Mo_5P_2O_{23}]^{4-}$ clusters with $[NiL]^{2+}$ and generates 1-D channels.

2. Experimental

2.1. *Materials and measurements*

The macrocyclic ligand (*L*) and its Cu(II)/Ni(II) complexes were prepared according to literature methods [19–22]. All other chemicals were from commercial sources and used without purification. C, H, and N elemental analyses were determined using an Elementar Vario EL elemental analyzer. Cu, Ni, and Mo elemental analyses were determined by a TJA IRIS(HR) inductively coupled plasma-atomic emission spectrometer. IR spectra were recorded from 4000 to 400 cm^{-1} using KBr pellets on a Bruker EQUINOX 55 spectrometer. TG analyses were performed on a Perkin–Elmer TGS-2 instrument from 25 to 700 °C in flowing air with a heating rate of 10 °C min^{-1}. PXRD data were recorded on a Bruker D8 AVANCE X-ray powder diffractometer (Cu Kα, $\lambda = 1.5418$ Å).

2.2. *Synthesis of $[CuL]_2[H_2Mo_5P_2O_{23}] \cdot 2H_2O \cdot 2CH_3CN$ (1)*

An aqueous (20 ml) solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.617 g, 0.5 mmol) was adjusted to pH = 2.5 with 8 M H_3PO_4, and this solution was layered with a solution of $CuL(ClO_4)_2$ (0.813 g, 1.5 mmol) in acetonitrile (20 mL). After a few days, purple block-shaped crystals of **1** were isolated in 28% yield (based on Mo). Anal. Calcd for $C_{36}H_{84}Cu_2Mo_5N_{10}O_{25}P_2$

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(%): C, 25.05; H, 4.90; N, 8.12; Cu, 7.36; Mo, 27.80. Found: C, 25.08; H, 4.79; N, 8.12; Cu, 7.82; Mo, 28.18. IR (KBr, cm^{-1}): 3406(m), 3207(w), 3139(w), 2962(w), 1622(m), 1459(m), 1430(m), 1373(m), 1279(w), 1168(w), 1141(m), 1047(m), 1006(m), 916(m), 823 (w), 674(s), 603(w), 577(m), 552(w), 499(m).

2.3. *Synthesis of [NiL]$_2$[H$_2$Mo$_5$P$_2$O$_{23}$]·10H$_2$O (2)*

Use of NiL(ClO$_4$)$_2$ in a procedure analogous to that for **1** afforded yellow prismatic crystals of **2** in 32% yield (based on Mo). Anal. Calcd for $C_{32}H_{82}Mo_5Ni_2N_8O_{27}P_2$ ([NiL]$_2$[$H_2Mo_5P_2O_{23}\cdot 4H_2O$,%): C, 23.01; H, 4.95; N, 6.71; Ni, 7.03; Mo, 28.72. Found: C, 23.37; H, 4.93; N, 6.71; Ni, 7.39; Mo, 29.06. IR (KBr, cm^{-1}): 3433(m), 3229(w), 3163(w), 2966(w), 1636(m), 1461(m), 1426(m), 1375(m), 1285(w), 1184(w), 1159(m), 1047(m), 1007(m), 921(m), 820(w), 674(s), 600(w), 576(m), 551(w), 497(m).

2.4. *X-ray crystallography*

Single-crystal data for **1** and **2** were collected on a Bruker Smart 1000 CCD diffractometer with Mo-K radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied using SADABS [23]. Both structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All hydrogens of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL system of computer programs [24]. The crystallographic data and structure refinement parameters for **1** and **2** are summarized in table 1. Selected bond lengths and angles are listed in table 2. The hydrogen bond parameters for **1** are given in table 3.

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

Compound	1	2
Empirical formula	$C_{36}H_{84}Cu_2Mo_5N_{10}O_{25}P_2$	$C_{64}H_{188}Ni_4Mo_{10}N_{16}O_{66}P_4$
Formula weight	1725.85	3556.42
Temperature (K)	153(2)	173(2)
Crystal system	Triclinic	Monoclinic
Space group	*P-1*	*C2/c*
a/Å	12.410(4)	22.426(3)
b/Å	14.644(4)	25.220(4)
c/Å	17.947(5)	16.539(2)
α/°	102.071(2)	90
β/°	100.318(2)	112.953(2)
γ/°	103.847(2)	90
Volume /Å^3	3005.25(15)	8614(2)
Z	2	2
D_c/g cm^{-3}	1.907	1.371
μ/mm^{-1}	1.840	1.236
F(000)	1736	3608
θ Range for data collection	2.59–27.00	2.10–27.19
Reflections collected/unique	26371/12974 (0.0330)	21556/9378 (0.0568)
Completeness to $\theta = 28.35$	98.9%	97.7%
Goodness-of-fit on F^2	1.074	1.068
Final R indices ($I > 2\sigma(I)$)	0.0601, 0.1812	0.0709, 0.1955
R indices (all data)	0.0843, 0.1920	0.1272, 0.2334
Max. peak/hole (e.Å^{-3})	2.150/−4.087	1.845/−1.271

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

1					
Mo(1)–O(1)	1.726(5)	Mo(1)–O(2)	1.722(5)	Mo(1)–O(3)	1.927(5)
Mo(1)–O(15)	1.886(5)	Mo(1)–O(18)	2.221(5)	Mo(1)–O(21)	2.436(5)
Mo(2)–O(3)	1.922(5)	Mo(2)–O(4)	1.707(5)	Mo(2)–O(5)	1.722(5)
Mo(2)–O(6)	1.877(5)	Mo(2)–O(19)	2.286(5)	Mo(2)–O(21)	2.320(5)
Mo(3)–O(6)	1.938(5)	Mo(3)–O(7)	1.708(5)	Mo(3)–O(8)	1.700(6)
Mo(3)–O(9)	1.925(5)	Mo(3)–O(19)	2.400(5)	Mo(3)–O(22)	2.247(5)
Mo(4)–O(9)	1.924(5)	Mo(4)–O(10)	1.716(6)	Mo(4)–O(11)	1.705(5)
Mo(4)–O(12)	1.925(5)	Mo(4)–O(17)	2.250(5)	Mo(4)–O(22)	2.353(5)
Mo(5)–O(12)	1.902(5)	Mo(5)–O(13)	1.718(5)	Mo(5)–O(14)	1.700(5)
Mo(5)–O(15)	1.946(5)	Mo(5)–O(18)	2.372(5)	Mo(5)–O(20)	2.202(6)
Cu(1)–O(1)	2.357(6)	Cu(1)–N(1)	2.054(7)	Cu(1)–N(2)	1.985(6)
Cu(1)–N(3)	2.089(7)	Cu(1)–N(4)	2.005(7)	Cu(2)–O(5)	2.334(5)
Cu(2)–N(5)	2.061(6)	Cu(2)–N(6)	2.036(6)	Cu(3)–O(13)	2.398(5)
Cu(3)–N(7)	2.013(6)	Cu(3)–N(8)	2.062(6)	P(1)–O(16)	1.584(6)
P(1)–O(17)	1.510(5)	P(1)–O(18)	1.548(5)	P(1)–O(19)	1.533(5)
P(2)–O(20)	1.539(6)	P(2)–O(21)	1.538(5)	P(2)–O(22)	1.510(6)
P(2)–O(23)	1.528(6)				
N(2)–Cu(1)–N(4)	176.2(3)	N(3)–Cu(1)–O(1)	103.2(2)	N(6)–Cu(2)–O(5)[a]	92.0(2)
N(2)–Cu(1)–N(1)	88.2(3)	N(1)–Cu(1)–O(1)	86.6(2)	N(7)–Cu(3)–N(8)[b]	88.6(3)
N(4)–Cu(1)–N(1)	92.1(3)	O(5)[a]–Cu(2)–O(5)	180.00(19)	N(7)–Cu(3)–O(13)	92.2(2)
N(2)–Cu(1)–N(3)	90.5(3)	N(5)–Cu(2)–O(5)[a]	97.0(2)	N(8)–Cu(3)–O(13)	83.7(2)
N(4)–Cu(1)–N(3)	88.6(3)	N(6)–Cu(2)–O(5)	88.0(2)	N(7)–Cu(3)–O(13)[b]	87.8(2)
N(1)–Cu(1)–N(3)	170.2(3)	N(5)–Cu(2)–O(5)	83.0(2)	N(8)–Cu(3)–O(13)[b]	96.3(2)
N(2)–Cu(1)–O(1)	90.4(2)	N(6)–Cu(2)–N(5)[a]	86.2(3)	O(13)–Cu(3)–O(13)[b]	180.00(1)
N(4)–Cu(1)–O(1)	93.4(2)	N(6)–Cu(2)–N(5)	93.8(3)	N(7)–Cu(3)–N(8)	91.4(3)
O(17)–P(1)–O(19)	111.8(3)	O(19)–P(1)–O(18)	110.4(3)	O(19)–P(1)–O(16)	110.3(3)
O(17)–P(1)–O(18)	110.0(3)	O(17)–P(1)–O(16)	105.7(3)	O(18)–P(1)–O(16)	108.4(3)
O(22)–P(2)–O(23)	109.8(3)	O(23)–P(2)–O(21)	107.1(3)	O(23)–P(2)–O(20)	108.7(3)
O(22)–P(2)–O(21)	111.9(3)	O(22)–P(2)–O(20)	109.3(3)	O(21)–P(2)–O(20)	109.8(3)
Mo(1)–O(1)–Cu(1)	159.8(3)	Mo(2)–O(5)–Cu(2)	142.9(3)	Mo(5)–O(13)–Cu(3)	135.2(3)
2					
Mo(1)–O(1)	1.734(6)	Mo(1)–O(5)	1.704(6)	Mo(1)–O(9)	2.402(6)
Mo(1)–O(4)	1.914(2)	Mo(1)–O(8)	1.933(6)	Mo(1)–O(12)	2.163(6)
Mo(2)–O(2)	1.735(6)	Mo(2)–O(8)	1.915(6)	Mo(2)–O(10)	2.411(6)
Mo(2)–O(6)	1.707(6)	Mo(2)–O(9)	2.148(6)	Mo(2)–O(11)	1.914(6)
Mo(3)–O(3)	1.707(7)	Mo(3)–O(10)	2.331(6)	Mo(3)–O(11)	1.917(6)
Ni(1)–O(1)	2.086(6)	Ni(2)–O(2)	2.053(6)	P(1)–O(12)[c]	1.503(6)
Ni(1)–N(1)	2.086(9)	Ni(2)–N(3)	2.103(8)	P(1)–O(10)[c]	1.529(6)
Ni(1)–N(2)	2.108(9)	Ni(2)–N(4)	2.089(9)	P(1)–O(9)	1.556(6)
P(1)–O(7)	1.564(7)	Mo(2)–O(1)–Ni(1)	161.5(4)	Mo(2)–O(2)–Ni(2)	161.0(4)
O(5)–Mo(1)–O(1)	101.7(3)	O(4)–Mo(1)–O(8)	146.6(3)	O(1)–Mo(1)–O(8)	97.5(3)
O(5)–Mo(1)–O(4)	103.0(3)	O(5)–Mo(1)–O(12)	88.2(3)	O(8)–Mo(1)–O(12)	78.9(2)
O(1)–Mo(1)–O(4)	97.9(2)	O(1)–Mo(1)–O(12)	170.0(3)	O(5)–Mo(1)–O(9)	170.3(2)
O(5)–Mo(1)–O(8)	102.5(3)	O(8)–Mo(1)–O(9)	68.3(2)	O(1)–Mo(1)–O(9)	83.3(2)
O(6)–Mo(2)–O(2)	104.0(3)	O(11)–Mo(2)–O(8)	152.6(2)	O(4)–Mo(1)–O(9)	84.3(2)
O(6)–Mo(2)–O(11)	97.5(3)	O(6)–Mo(2)–O(9)	97.2(3)	O(4)–Mo(1)–O(12)	80.87(19)
O(2)–Mo(2)–O(11)	99.5(3)	O(2)–Mo(2)–O(9)	157.9(3)	O(12)–Mo(1)–O(9)	86.8(2)
O(6)–Mo(2)–O(8)	101.0(3)	O(11)–Mo(2)–O(9)	83.4(2)	O(8)–Mo(2)–O(9)	74.5(2)
O(2)–Mo(2)–O(8)	95.4(3)	O(3)–Mo(3)–O(11)	102.2(3)	O(6)–Mo(2)–O(10)	166.1(3)
O(11)–Mo(2)–O(10)	71.5(2)	O(3)–Mo(3)–O(11)[c]	99.3(3)	O(2)–Mo(2)–O(10)	86.5(2)
O(8)–Mo(2)–O(10)	86.7(2)	O(1)–Ni(1)–N(2)	85.5(3)	O(3)–Mo(3)–O(10)	88.1(3)
O(9)–Mo(2)–O(10)	73.6(2)	N(1)–Ni(1)–N(2)[d]	94.5(3)	O(11)–Mo(3)–O(10)	73.3(2)
O(3)[c]–Mo(3)–O(3)	102.4(5)	N(1)–Ni(1)–O(1)[d]	87.1(3)	O(11)–Mo(3)–O(11)[c]	145.3(4)
O(3)[c]–Mo(3)–O(11)	99.3(3)	N(1)–Ni(1)–O(1)	92.9(3)	O(3)[c]–Mo(3)–O(10)	168.5(3)
O(11)[c]–Mo(3)–O(10)	80.6(2)	N(1)–Ni(1)–N(2)	85.5(3)	O(10)–Mo(3)–O(10)[c]	82.0(3)
O(3)–Mo(3)–O(10)[c]	168.5(3)	O(2)–Ni(2)–N(3)[e]	93.7(3)	O(1)[d]–Ni(1)–O(1)	180.0(2)
O(11)–Mo(3)–O(10)[c]	80.6(2)	N(4)–Ni(2)–N(3)[e]	94.3(3)	O(1)–Ni(1)–N(2)[d]	94.5(3)

(*Continued*)

Table 2. (*Continued*)

O(10)[c]–P(1)–O(9)	111.2(3)	O(2)–Ni(2)–N(3)	86.3(3)	O(2)–Ni(2)–O(2)[e]	180.00(1)
O(12)[c]–P(1)–O(7)	106.9(3)	O(12)[c]–P(1)–O(9)	107.8(3)	O(2)–Ni(2)–N(4)	91.3(3)
O(10)[c]–P(1)–O(7)	110.2(4)	O(9)–P(1)–O(7)	108.3(3)	N(4)–Ni(2)–N(3)	85.7(3)

Symmetry codes: [a]$-x, -y+2, -z$; [b]$-x, -y+1, -z+1$; [c]$-x+1, y, -z+5/2$; [d]$-x+1, -y, -z+2$; [e]$-x+1/2, -y+1/2, -z+2$.

Table 3. Hydrogen bond parameters (Å, °) for **1**.

D–H…A	d(D–H)	d(H…A)	d(D…A)	<DHA
O(16)–H(16D)…O(1W)	0.862(10)	2.03(6)	2.627(8)	126(6)
O(23)–H(23D)…O(2W)	0.861(10)	1.948(7)	2.547(10)	125.5(15)
N(8)–H(8D)…O(13)	0.93	2.50	2.985(8)	112.9
N(5)–H(5C)…O(4)	0.93	2.09	3.018(8)	177.9
N(5)–H(5C)…O(5)	0.93	2.46	2.919(7)	110.6
N(2)–H(2C)…O(11)[a]	0.93	2.11	2.923(8)	145.1
N(3)–H(3A)…O(17)[b]	0.93	2.00	2.894(8)	160.0
N(7)–H(7D)…O(12)	0.93	2.08	3.003(8)	172.0
O(2W)–H(2WA)…O(10)	0.87(2)	2.202(10)	3.000(13)	153(5)
O(2W)–H(2WB)…O(8)[b]	0.864(19)	1.97(5)	2.801(10)	162(12)
O(1W)–H(1WA)…O(3)	0.86(2)	2.000(10)	2.700(7)	137(3)
O(1W)–H(1WB)…O(2)[c]	0.87(2)	1.90(3)	2.732(8)	161(5)

Symmetry codes: [a]$x+1, y, z$; [b]$-x, -y+2, -z+1$; [c]$-x, -y+1, -z$.

3. Results and discussion

3.1. *Structure of $[CuL]_2[H_2Mo_5P_2O_{23}]\cdot 2H_2O\cdot 2CH_3CN$ (1)*

X-ray crystal structural analysis revealed that **1** contains two $[CuL]^{2+}$ cations, one $[H_2Mo_5P_2O_{23}]^{4-}$ anion, and interstitial water and acetonitrile molecules (figure 1). There are three crystallographically independent Cu atoms in **1**; the Cu(2) and Cu(3) atoms are on inversion centers. Cu(1) is coordinated by four nitrogens (N(1), N(2), N(3), and N(4)) from *L* and an oxygen (O(1)) from $[H_2Mo_5P_2O_{23}]^{4-}$. Cu(2) is coordinated by four nitrogen donors (N(5), N(5A), N(6), and N(6A)) (symmetry code: A, $-x$, $2-y$, $-z$) from *L* and two oxygens (O(5) and O(5A)) from two adjacent $[H_2Mo_5P_2O_{23}]^{4-}$ clusters. Cu(3) is coordinated by four nitrogens (N(7), N(7B), N(8), and N(8B)) (symmetry code: B, $-x$, $1-y$, $1-z$) from *L* and two oxygens (O(13) and O(13B)) from two adjacent $[H_2Mo_5P_2O_{23}]^{4-}$ clusters. The axial Cu–O bonds (Cu(1)–O(1) 2.357(6) Å, Cu(2)–O(5) 2.334(5) Å, and Cu(3)–O(13) 2.398(5) Å) are considerably longer than the equatorial Cu–N bonds (Cu(1)–N 1.985(6)–2.089(7) Å, Cu(2)–N 2.037(6)–2.064(6) Å, and Cu(3)–N 2.015(6)–2.063(6) Å) owing to the Jahn-Teller distortion, and the Cu–O and Cu–N bond distances agree with those in previous reports [17, 18]. The structure of $[H_2Mo_5P_2O_{23}]^{4-}$ is different from that in reduced molybdenum phosphate $[Mo_6P_4O_{27}(OH)_4]^{8-}$ derivatives [15, 25, 26], which are made up of six MoO_6 octahedra and four PO_4 tetrahedra. The $[H_2Mo_5P_2O_{23}]^{4-}$ cluster can be described as a ring formed by five distorted edge- and corner-sharing MoO_6 octahedra capped on both poles by a phosphate tetrahedron sharing three vertices with the ring molybdenum centers. The two PO_4 groups provide three oxygens that bridge non-bonding Mo···Mo contacts (avg. distance, 3.44 Å). The Mo–O bond distances (2.202(6)–2.436(5) Å) involving O atoms which bridge Mo and P atoms (regardless if they are μ^2 or μ^3) are

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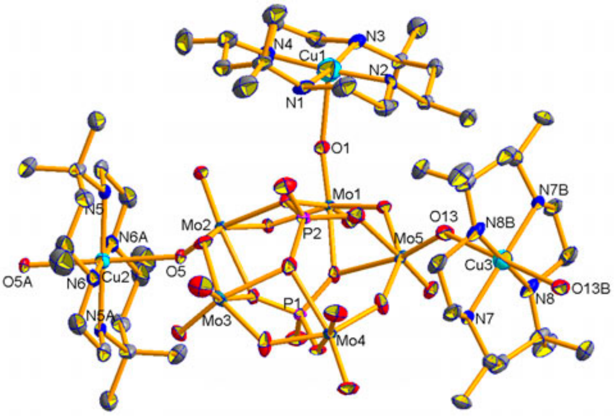

Figure 1. ORTEP diagram of **1** with 50% probability displacement ellipsoids (H atoms and water, and acetonitrile molecules are omitted for clarity). Symmetry codes for the generated atoms: A(–*x*, 2–*y*, –*z*), B(–*x*, 1–*y*, 1–*z*).

longer than the Mo–O bond distances (1.700(5)–1.946(5) Å) involving O atoms only bridging Mo atoms. The Mo–O bond distances agree with those in previous reports [26]. Based on valence sum calculations [27] ($S = \exp[(1.907 - r)/0.37]$, r = Mo–O distance), the values for the Mo atoms are 5.95–6.09, indicating that all are in the +6 oxidation state. The P–O bond lengths are 1.510(6)–1.584(6) Å and O–P–O bond angles 105.7(3) to 111.9 (3)°, in accord with the literature [15]. A 1-D chain is formed from connection of $[H_2Mo_5P_2O_{23}]^{4-}$ clusters and $[CuL]^{2+}$ units via Mo–O–Cu interactions (Mo(5)–O(13)–Cu (3) 135.2(3)° and Mo(2)–O(5)–Cu(2) 142.9(3)°) (figure 2). The remaining Cu(1) macrocycle not involved in creation of the 1-D chain has a larger bond angle, Mo(1)–O(1)–Cu(1), 159.8(3)°. The 1-D chains are connected through the N–H···O (2.894(8)–3.018(8) Å) (table 3) hydrogen bonds between the secondary (N(2) and N(3)) of *L* and oxygens (O(11) and O(17)) of $[H_2Mo_5P_2O_{23}]^{4-}$ to form 2-D sheets. The free water molecules are located between two adjacent sheets and link them through O–H···O (2.547(10)–3.000(13) Å) hydrogen bonds between the water molecules (O(1w) and O(2w)) and oxygen atoms (O (2), O(3), O(8) and O(10)) of $[H_2Mo_5P_2O_{23}]^{4-}$ to generate a 3-D structure (figure 3 and table 3).

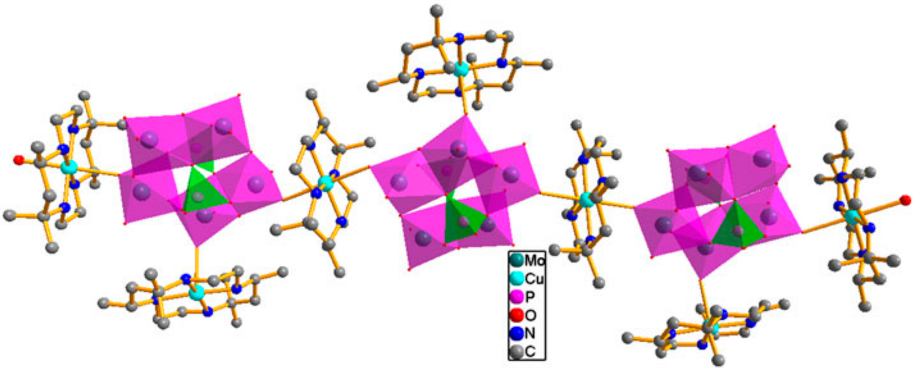

Figure 2. Structure of 1-D chains in **1**.

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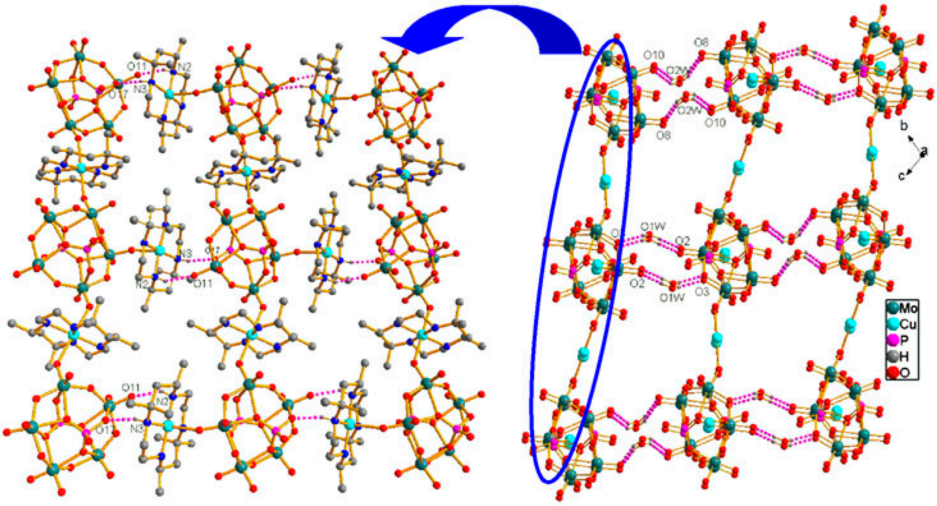

(a) (b)

Figure 3. (a) The 2-D sheet in **1**, formed through the N–H· · ·O hydrogen bonding interactions, and (b) the 3-D structure in **1** via the O–H· · ·O hydrogen bonding interactions (C and N atoms are omitted for clarity).

3.2. *Structure of $[NiL]_2[H_2Mo_5P_2O_{23}]\cdot 10H_2O$ (2)*

Interestingly, **1** and **2** show different structures although they were prepared by analogous procedures. The asymmetric unit of **2** consists of one $[NiL]^{2+}$ cation, half of $[H_2Mo_5P_2O_{23}]^{4-}$, and five waters (figure 4). Each Ni(II) lies on an inversion center and is coordinated by four nitrogens (N(1), N(1C), N(2) and N(2C) for Ni(1), N(3), N(3B), N(4), and N(4B) for Ni(2), symmetry codes: B, 0.5–*x*, 0.5–*y*, 2–*z*; C, 1–*x*, –*y*, 2–*z*) from *L* in the equatorial plane and two oxygens (O(1) and O(1C) for Ni(1), O(2) and O(2B) for Ni (2)) from $[H_2Mo_5P_2O_{23}]^{4-}$ in axial positions. The Ni–O distances (Ni(1)–O(1) 2.086(6), Ni(2)–O(2) 2.053(6) Å) are slightly shorter than the Ni–N distances (2.086(9)–2.108(9) Å), and both sets of bond distances agree with literature values [17, 18]. The Mo–O (2.148 (6)–2.411(6) Å) and P–O (1.503(6)–1.564(7) Å) bond distances and the O–P–O bond angles (106.9(3)–111.2(3)°) in **2** are within the same ranges and show the same patterns as those in **1**. Based on analogous valence sum calculations [27], all Mo atoms in **2** are also in the +6 oxidation state. Six adjacent $[H_2Mo_5P_2O_{23}]^{4-}$ clusters form a six-membered ring through connection with $[NiL]^{2+}$ and each six-membered ring adopts a chair conformation (figure 5). Each $[H_2Mo_5P_2O_{23}]^{4-}$ cluster is coordinated with four $[NiL]^{2+}$ along different directions via the corner-sharing interactions Mo–O–Ni (Mo(1)–O(1)–Ni(1) 161.5(4)°, Mo (2)–O(2)–Ni(2) 161.0(4)°), forming a 3-D porous framework structure with 1-D hydrophobic channels along the *c* axis and occupied by water molecules (figure 6). The channel size as measured by the C· · ·C distances is 10.72 × 10.96 Å and the solvent accessible volume of **2** is estimated by PLATON [28] to be 45.8% (3950.9 $Å^3$) of the total crystal volume. The pores are filled with water molecules, and some of the water molecules are easily lost at room temperature due to the hydrophobic environment of the channels. A difference of six waters between the structure of **2** and its elemental analysis was found and confirmed by the thermogravimetric analysis (vida infra).

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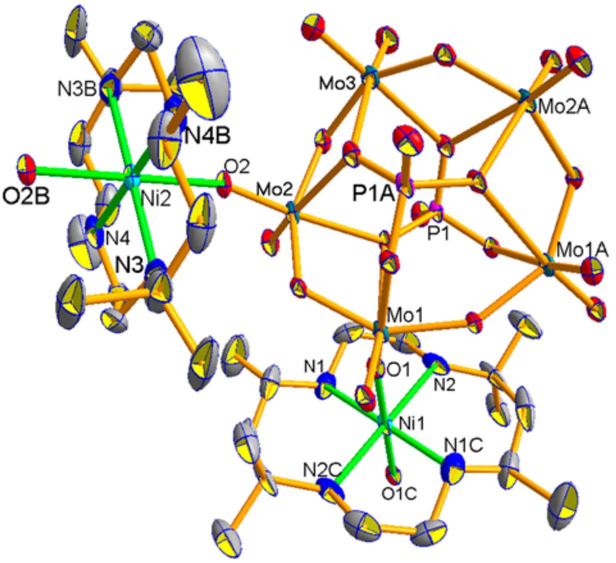

Figure 4. ORTEP diagram of **2** with 50% probability displacement ellipsoids (H atoms and water molecules are omitted for clarity). Symmetry codes for the generated atoms: A(1–*x*, *y*, 2.5–*z*), B(0.5–*x*, 0.5–*y*, 2–*z*), C(1–*x*, –*y*, 2–*z*).

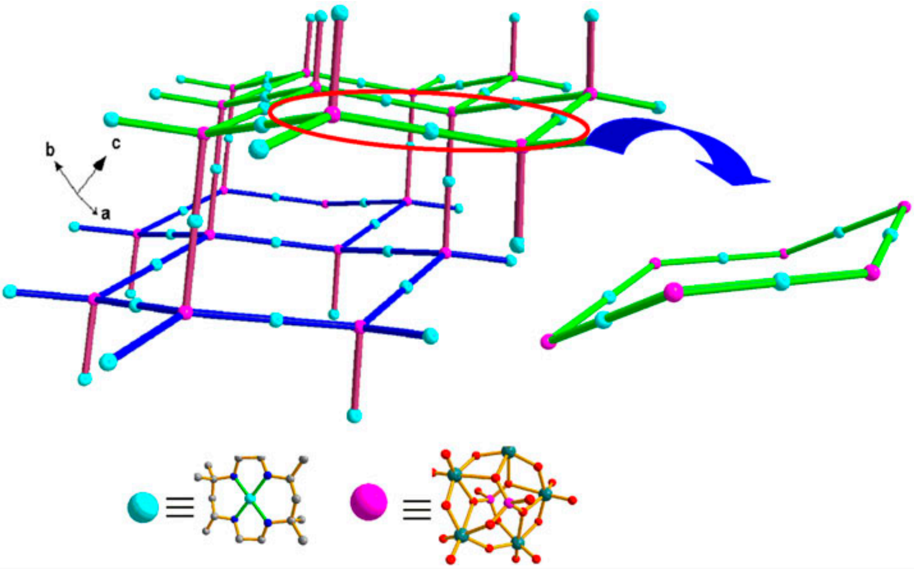

Figure 5. A skeleton drawing of **2** ($[H_2Mo_5P_2O_{23}]^{4-}$ clusters represented as pink balls, $[NiL]^{2+}$ as turquoise balls) showing the chair conformation formed by the six $[H_2Mo_5P_2O_{23}]^{4-}$ clusters.

In our previous report [17, 18], we used $[CuL](ClO_4)_2$ and $[NiL](ClO_4)_2$ with NH_4VO_3 as building blocks in similar procedures to construct two different 3-D structures. The Ni–N bond distances (2.086(9)–2.108(9) Å) in **2** are slightly longer than the Cu–N bond distances

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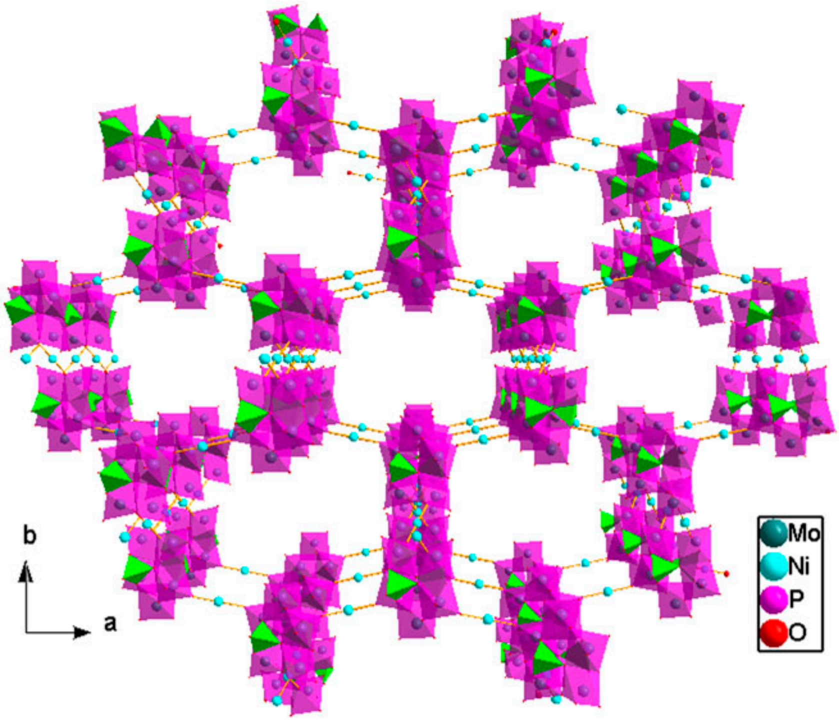

Figure 6. The 3-D porous framework of **2** with 1-D hydrophobic channels along the *c*-axis (*L* and water molecules are omitted for clarity).

(1.985(6)–2.089(7) Å) in **1**, but the Ni–O bond distances (2.053(6) Å, 2.086(6) Å) are much shorter than the Cu–O bond distances (2.334(5)–2.398(5) Å). The differences in the Ni–O and Cu–O bond distances may be the reason for the different structures.

3.3. *IR spectra*

The IR spectrum of **1** shows a characteristic band at 916 cm^{-1} attributed to the Mo–O group and bands between 674 and 499 cm^{-1} due to the bridging Mo–O–Mo group, between 1006 and 1279 cm^{-1} associated with the P–O bond [29, 30], and between 1622 and 1373 cm^{-1} assigned to the C–C and C–N stretching vibrations of the organic amines [31].

Similarly, the IR spectrum of **2** exhibits an intense band at 921 cm^{-1} attributed to the Mo–O group, features between 1636 and 1375 cm^{-1}, assigned to *L*, and bands at 674 and 1047 cm^{-1} attributed to the bridging Mo–O–Mo group and the P–O bond, respectively.

3.4. *PXRD and TG analyses*

The simulated and experimental PXRD patterns of **1** and **2** are shown in figure S1. The peak positions of the simulated and experimental patterns are in good agreement for both compounds, indicating the phase purity of the products.

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The thermogravimetric analyses are shown in figure S2. TG analysis of **1** showed that a weight loss of about 2.3% occurred below 200 °C, which is attributed to loss of water molecules in **1**. This is consistent with the calculated value for **12**H_2O (2.2%), indicating that the acetonitrile molecules were lost before TG data collection. The framework of **1** was stable up to 200 °C and then decomposed upon further heating. The TG curve for **2** revealed that the framework was stable up to 250 °C and then decomposed upon further heating. The observed weight loss (4.5% at 150 °C) is consistent with the elemental analysis with only four interstitial water molecules (4.4%) and smaller than the calculated value for **2** (10.1%), indicating that some water molecules were lost before TG data collection.

4. Conclusion

Using molybdenum phosphates and secondary transition metal complexes $[CuL]^{2+}$ and $[NiL]^{2+}$ as building blocks, we have assembled one- and 3-D compounds, **1** and **2**, respectively, under analogous reaction conditions. Compound **1** is a 1-D chain constructed through connections of $[H_2Mo_5P_2O_{23}]^{4-}$ with $[CuL]^{2+}$. Compound **2** shows a 3-D network structure constructed by connections of $[H_2Mo_5P_2O_{23}]^{4-}$ with $[NiL]^{2+}$. This work shows that the choice of transition metal can be crucial for driving the formation of a 3-D architecture. However, much research is needed to explore the synthetic approach of defined structure and discover their attractive properties.

Supplementary material

Figures of experimental and simulated PXRD patterns and TG data for **1** and **2**. Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Center as supplemental publication material numbers CCDC 903793 and 903794, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk.

Acknowledgments

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