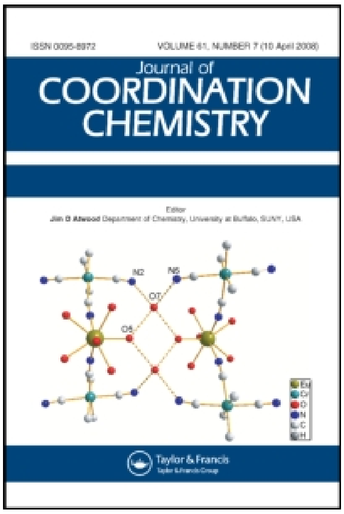

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Syntheses and crystal structures of two new heteropolyoxometalates consisting of octamolybdate anions

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Syntheses and crystal structures of two new heteropolyoxometalates consisting of octamolybdate anions

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Two new polyoxomolybdate compounds, $[\mathrm{Zn^{II}(Hppz)_3}]_2(\mathrm{Mo_8O_{26}})$ (**1**) and $[\mathrm{Ni^{II}(bpy_2}]_2$ $(\mathrm{Mo_8O_{26}})$ (**2**) (Hppz: 3-(2-pyridyl)pyrazole); bpy: 2,2′-bipyridine), were synthesized under hydrothermal conditions. X-ray diffraction analyses reveal that **1** consists of one β-octamolybdate and one $\mathrm{Zn^{II}}(H_{\mathrm{ppz}})_3^{2+}$. Compound **2** consists of one α-octamolybdate linked by two $\mathrm{Ni(bpy)_2^{2+}}$ complexes *via* terminal oxygen bridges. Crystal data of **1**: $\mathrm{C_{24}H_{21}Mo_4N_9O_{13}Zn}$, $M = 1092.63$, monoclinic, *P21/n*, $a = 12.4456(18)$, $b = 16.231(2)$, $c = 17.710(3)$ Å, $\beta = 109.883(2)^\circ$, $V = 3364.4(9)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 2.157\ \mathrm{g\,cm^{-3}}$, $F(000) = 2120$, $\mu = 2.229\ \mathrm{mm^{-1}}$, $R_1 = 0.0394$ and $wR_2 = 0.1139$ $(I > 2\sigma(I))$; Crystal data of **2**: $\mathrm{C_{40}H_{32}Mo_8N_8Ni_2O_{26}}$, $M = 1925.68$, triclinic, *P-1*, $a = 10.1608(5)$, $b = 11.6091(6)$, $c = 13.8789(7)$ Å, $\alpha = 114.2120(10)^\circ$, $\beta = 95.8650(10)^\circ$, $\gamma = 102.7460(10)^\circ$, $V = 1421.75(12)$ Å^3, $Z = 1$, $D_{\mathrm{calcd}} = 2.249\ \mathrm{g\,cm^{-3}}$, $F(000) = 928$, $\mu = 2.435\ \mathrm{mm^{-1}}$, $R_1 = 0.0220$ and $wR_2 = 0.0741$ $(I > 2\sigma(I))$.

Keywords: Polyoxomolybdate; Octamolybdate; Zinc; Nickel; X-ray analysis

1. Introduction

Synthesis of polyoxometalate clusters has attracted interest because of their appealing structural and topological novelty, and unusual optical, electronic, magnetic, and catalytic properties, as well as their potential medical application [1–6].

The construction of polyoxometalates is usually achieved by the connection of polyoxometalate-building subunits either *via* capping $\{\mathrm{MO_2}\}$ groups using the two bridging oxygens or by secondary transition metals [7, 8]. The use of well-defined molecular oxide clusters to construct topologies with more or less predictable connectivity in the crystal state is attractive because secondary metal/ligand bridges should provide sufficiently strong linkages to connect the clusters into stable crystalline

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architectures. During the past decade, the synthetic methodology of employing organic components to modify the crystallization of metal oxides in a hydrothermal medium has been especially researched [7]. The organic components in these examples usually play the roles of charge-compensating ions and space-filling structural subunits by linking directly to the metal oxide substructure or a secondary metal site as ligands. Two distinct subgroups of this family have emerged: (i) molecular structures comprised of polymeric molybdate substructures decorated by the secondary metal–ligand subunit [8] and (ii) crystal structures constructed from discrete molybdate clusters which were bridged by secondary metal–ligand components, forming chain, network, or framework structures [9, 10]. Consequently, the overall structure reflects both the geometric constraints of the ligand and relative dispositions of the donor groups, as well as the coordination preferences of the secondary metal site.

In this article, we describe the syntheses and structural characterizations of two new polyoxomolybdate compounds, $[Zn^{II}(Hppz)_3]_2(Mo_8O_{26})$ (**1**) and $[Ni^{II}(bpy_2]_2(Mo_8O_{26})$ (**2**).

2. Experimental

2.1. *General*

3-(2-Pyridyl)pyrazole) and 2,2′-bipyridine were purchased from Jinan Henghua Sci. & Tec. Co. and used without purification. Elemental analysis was conducted on a Perkin-Elmer 240C elemental analyzer; IR spectra were recorded (400–4000 cm^{-1}) on a Perkin-Elmer 2400LSII spectrometer.

2.2. *Synthesis*

2.2.1. Synthesis of 1. The synthesis is performed in 25 mL Teflon-lined stainless steel vessels. Ammonium molybdate tetrahydrate (0.08 mmol, 0.10 g), zinc acetate (0.27 mmol, 0.05 g), *p*-carboxyphenylboronic acid (0.30 mmol, 0.05 g), oxalic acid (1.00 mmol, 0.09 g), Hppz (0.34 mmol, 0.05 g), and water (14 mL) were mixed and heated to 170°C for 3 days. Anal. Calcd for $C_{24}H_{21}Mo_4N_9O_{13}Zn$ (%): C, 26.36; H, 1.92; N, 11.53. Found (%): C, 26.28; H, 1.82; N, 11.22. IR (KBr pellet, cm^{-1}): 3430, 3155, 2862, 2642, 1620, 1580, 1549, 1502, 1430, 930, 888, 863, 830, 627, 558, 520, 497, 431.

2.2.2. Synthesis of 2. The synthesis is performed in 25 mL Teflon-lined stainless steel vessels. Ammonium molybdate tetrahydrate (0.08 mmol, 0.10 g), nickel chloride hexahydrate (0.21 mmol, 0.05 g), 2-(4′-carboxyphenoxy)benzoic acid (0.20 mmol, 0.05 g), bpy (0.34 mmol, 0.05 g), and water (14 mL) were mixed and heated to 170°C for 3 days. Anal. Calcd for $C_{40}H_{32}Mo_8N_8Ni_2O_{26}$ (%): C, 20.26; H, 1.48; N, 8.88. Found (%): C, 20.18; H, 1.34; N, 8.72. IR (cm^{-1}): 3450, 2361, 1605, 1577, 1466, 1439, 1374, 1097, 950, 904, 802, 636, 544, 498, 406.

2.3. *Structure determination*

Intensity data collections were carried out on a Siemens SMART diffractometer equipped with a CCD detector using Mo-Kα monochromated radiation ($\lambda = 0.71073$ Å) at 293(2) K. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program based on the method of Blessing. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXTL package [11]. Crystallographic data for **1** and **2** are given in table 1. For further details on the crystal structure investigations of **1** and **2**, see the "Supplementary material".

3. Results and discussion

3.1. *Synthesis and general characterization*

Single crystal X-ray diffraction analyses revealed that **1** and **2** exhibit different structures, although similar synthetic methods, such as pH, temperature, and reaction

Table 1. Crystallographic data and details of diffraction experiments for **1** and **2**.

	1	**2**
Formula	$C_{16}H_{14}CoMo_4N_6O_{13}$	$C_{16}H_{14}Mo_4N_6NiO_{13}$
Color	Red	Green
Molecular mass ($g\,mol^{-1}$)	941.02	940.80
Crystal system	Triclinic	Triclinic
Space group	*P-1*	*P-1*
Unit cell dimensions (Å, °)		
a	10.065(3)	10.080(3)
b	11.583(3)	11.589(4)
c	11.583(3)	11.589(4)
α	88.79	88.57
β	74.772(2)	74.742(3)
γ	74.772(2)	74.742(3)
Volume (Å^3), Z	1255.4(6), 2	1258.7(7), 2
Calculated density ($g\,cm^{-3}$)	2.489	2.482
Absorption coefficient (mm^{-1})	2.667	2.749
Temperature (K)	298(2)	298(2)
Reflections collected	6818	6807
Independent reflection	4593	4593
Refined parameters	361	361
θ range for data collection (°)	1.82–25.49	1.82–25.50
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0360^a$, $wR_2 = 0.0992^b$	$R_1 = 0.0539^a$, $wR_2 = 0.1469^b$
R indices (all data)	$R_1 = 0.0389^a$, $wR_2 = 0.1018^b$	$R_1 = 0.0569^a$, $wR_2 = 0.1504^b$
Goodness-of-fit on F^2 [c]	0.998	1.006
Largest difference peak and hole (e Å^{-3})	0.957 and −1.246	0.983 and −1.090

[a] $R_1 = \Sigma||F_{obsd}| - |F_{calcd}||/\Sigma|F_{obsd}|$.
[b] $wR_2 = \{\Sigma[w(F^2_{obsd} - F^2_{calcd})^2]/\Sigma[w(F^2_{obsd})^2]\}^{1/2}$. $w = 1/[\sigma^2(F^2_o) + xP + (yP)^2]$; with $P = (F^2_o + 2F^2_c)/3$.
[c] Goodness-of-fit on $F^2 = [\Sigma w(F^2_{obsd} - F^2_{obsd})^2/(n-p)]^{1/2}$, where n = number of reflections, p = parameter used.

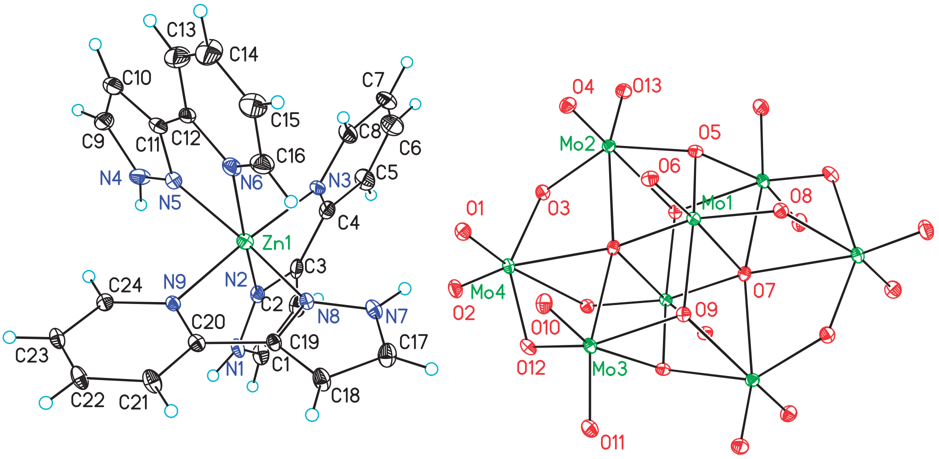

Figure 1. The molecular structure of **1**, drawn with 30% probability displacement ellipsoids for non-hydrogen atoms.

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

Bond	Distance	Bond	Distance
Mo(1)–O(6)	1.701(5)	Mo(3)–O(9)	1.997(5)
Mo(1)–O(8)	1.756(5)	Mo(4)–O(2)	1.694(5)
Mo(1)–O(5)	1.943(4)	Mo(4)–O(1)	1.718(5)
Mo(1)–O(9)	1.950(5)	Mo(4)–O(3)	1.911(5)
Mo(1)–O(7)	2.360(5)	Mo(4)–O(12)	1.924(5)
Mo(2)–O(13)	1.689(5)	N(2)–Zn(1)	2.067(7)
Mo(2)–O(4)	1.709(5)	N(3)–Zn(1)	2.137(7)
Mo(2)–O(3)	1.889(5)	N(5)–Zn(1)	2.085(7)
Mo(2)–O(5)	1.998(5)	N(6)–Zn(1)	2.118(7)
Mo(3)–O(11)	1.685(5)	N(8)–Zn(1)	2.051(6)
Mo(3)–O(10)	1.691(5)	N(9)–Zn(1)	2.088(6)
Mo(3)–O(12)	1.889(5)		
Angle	(°)	Angle	(°)
O(6)–Mo(1)–O(8)	103.3(2)	O(2)–Mo(4)–O(1)	104.9(3)
O(6)–Mo(1)–O(5)	102.5(2)	O(2)–Mo(4)–O(3)	101.7(3)
O(8)–Mo(1)–O(5)	96.2(2)	O(1)–Mo(4)–O(3)	100.4(2)
O(6)–Mo(1)–O(9)	100.4(2)	O(2)–Mo(4)–O(12)	102.2(2)
O(8)–Mo(1)–O(9)	96.2(2)	O(1)–Mo(4)–O(12)	97.1(2)
O(5)–Mo(1)–O(9)	150.56(19)	O(3)–Mo(4)–O(12)	145.5(2)
O(6)–Mo(1)–O(7)	176.6(2)	N(8)–Zn(1)–N(2)	95.5(2)
O(8)–Mo(1)–O(7)	79.87(18)	N(8)–Zn(1)–N(9)	78.4(2)
O(5)–Mo(1)–O(7)	78.06(18)	N(2)–Zn(1)–N(9)	98.8(2)
O(9)–Mo(1)–O(7)	78.00(17)	N(8)–Zn(1)–N(5)	167.9(3)
O(13)–Mo(2)–O(4)	105.1(3)	N(2)–Zn(1)–N(5)	94.6(3)
O(13)–Mo(2)–O(3)	101.9(2)	N(9)–Zn(1)–N(5)	93.5(3)
O(4)–Mo(2)–O(3)	101.5(2)	N(8)–Zn(1)–N(6)	93.0(3)
O(13)–Mo(2)–O(5)	101.8(2)	N(2)–Zn(1)–N(6)	169.3(3)
O(4)–Mo(2)–O(5)	96.3(2)	N(9)–Zn(1)–N(6)	89.3(3)
O(3)–Mo(2)–O(5)	145.3(2)	N(5)–Zn(1)–N(6)	77.9(3)
O(11)–Mo(3)–O(10)	105.0(3)	N(8)–Zn(1)–N(3)	99.8(3)
O(11)–Mo(3)–O(12)	101.2(3)	N(2)–Zn(1)–N(3)	77.2(3)
O(10)–Mo(3)–O(12)	100.6(2)	N(9)–Zn(1)–N(3)	175.5(3)
O(11)–Mo(3)–O(9)	102.9(2)	N(5)–Zn(1)–N(3)	88.9(3)
O(10)–Mo(3)–O(9)	97.8(2)	N(6)–Zn(1)–N(3)	94.9(3)
O(12)–Mo(3)–O(9)	144.6(2)		

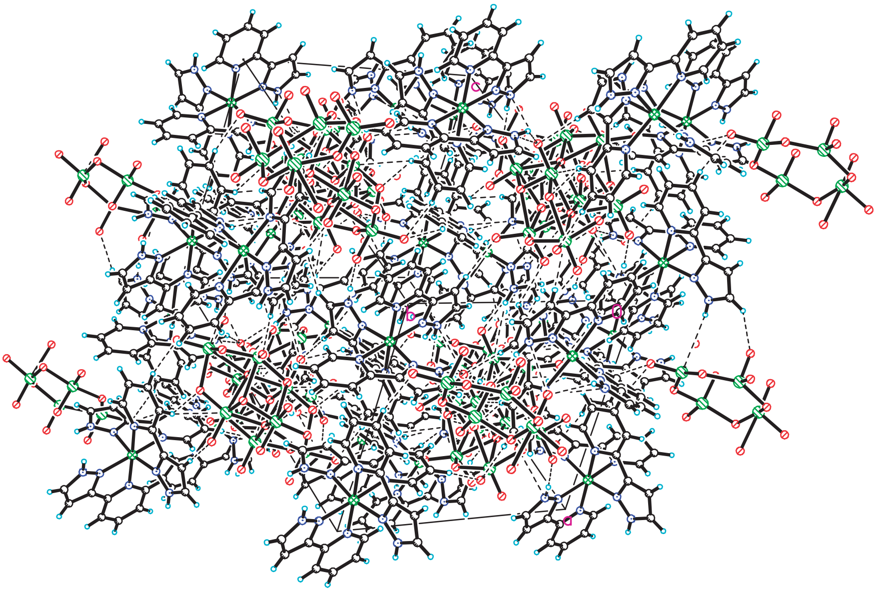

Figure 2. The molecular structure of **2**, drawn with 30% probability displacement ellipsoids for non-hydrogen atoms.

time, were employed during the synthetic procedure, except for the transitional metal salt.

3.2. *Structures of 1*

Single crystal X-ray diffraction analyses revealed that **1** consists of one-half of $Mo_8O_{26}(HL)_2^{4-}$ and one $Zn^{II}(HL)_3^{2+}$, shown in figure 1. The selected bond lengths and angles are given in table 2. The Zn^{II} is in a distorted octahedral environment, coordinated by six nitrogens from three chelating 3-(2-pyridyl)-1H-pyrazole ligands. The Zn–N bond distances and N–Zn–N angles are in normal range of 2.067(7)–2.118(7) Å and 77.9(3)°–175.5(3)°, respectively. Rms deviations of the three Hppz groups from planarity are 0.0410, 0.0270, and 0.0357 Å, respectively. The dihedral angles between the Hppz groups are 78.69(4) and 84.93(7) Å. The octamolybdate polyanion shows a β configuration with a center of symmetry, which can be bisected into two $[(\mu_5\text{-O})(Mo_4O_{12})]^{2-}$ planar subunits by breaking Mo–O bonds with the related lengths in the range of 2.26–2.39 Å, similar to previously reported isolated clusters [12, 10d]. The $[(\mu_5\text{-O})(Mo_4O_{12})]^{2-}$ plane could be considered as one Mo protruding outward from the plane of the other four Mo's. There are two types of Mo–O bonds in $[(M^{II}L_2)_2H_4Mo_8O_{26}]_n$, terminal Mo–O, and bridging μ_2-O–Mo, μ_3-O–Mo, and μ_5-O–Mo. The related bond distances vary from 1.690 Å for one of the terminal Mo–O bonds to 2.463 Å for one of the bonds to the unusual μ_5-O that sits in the four Mo plane near the center of each Mo–O moiety.

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

Bond	Distance	Bond	Distance
Mo(1)–O(9)	1.693(2)	Mo(3)–O(7)	2.0081(19)
Mo(1)–O(8)	1.748(2)	Mo(3)–O(3)	2.108(2)
Mo(1)–O(10)	1.880(2)	Mo(4)–O(2)	1.693(2)
Mo(1)–O(3)	1.887(2)	Mo(4)–O(1)	1.691(2)
Mo(1)–O(7)	2.188(2)	Mo(4)–O(4)	1.969(2)
Mo(2)–O(12)	1.690(2)	Mo(4)–O(3)	2.284(2)
Mo(2)–O(13)	1.730(2)	N(1)–Ni(1)	2.059(3)
Mo(2)–O(11)	1.869(2)	N(2)–Ni(1)	2.052(3)
Mo(2)–O(7)	2.010(2)	N(3)–Ni(1)	2.068(3)
Mo(2)–O(10)	2.112(2)	N(4)–Ni(1)	2.066(3)
Mo(3)–O(5)	1.679(2)	Ni(1)–O(6)	2.059(2)
Mo(3)–O(6)	1.726(2)	Ni(1)–O(13)	2.068(2)
Mo(3)–O(4)	1.866(2)		
Angle	(°)	Angle	(°)
O(9)–Mo(1)–O(8)	107.63(11)	O(5)–Mo(3)–O(3)	99.05(10)
O(9)–Mo(1)–O(10)	106.09(10)	O(6)–Mo(3)–O(3)	155.66(9)
O(8)–Mo(1)–O(10)	96.68(10)	O(4)–Mo(3)–O(3)	76.51(9)
O(9)–Mo(1)–O(3)	105.09(10)	O(7)–Mo(3)–O(3)	73.82(8)
O(8)–Mo(1)–O(3)	95.85(10)	O(2)–Mo(4)–O(1)	104.60(12)
O(10)–Mo(1)–O(3)	140.86(9)	O(2)–Mo(4)–O(4)	101.66(11)
O(9)–Mo(1)–O(7)	106.63(10)	O(1)–Mo(4)–O(4)	96.15(11)
O(8)–Mo(1)–O(7)	145.74(9)	O(2)–Mo(4)–O(3)	90.32(10)
O(10)–Mo(1)–O(7)	74.53(8)	O(1)–Mo(4)–O(3)	161.96(10)
O(3)–Mo(1)–O(7)	74.32(8)	O(4)–Mo(4)–O(3)	70.50(8)
O(12)–Mo(2)–O(13)	105.30(12)	N(2)–Ni(1)–O(6)	93.96(10)
O(12)–Mo(2)–O(11)	105.80(12)	N(2)–Ni(1)–N(1)	79.24(12)
O(13)–Mo(2)–O(11)	98.98(10)	O(6)–Ni(1)–N(1)	90.16(10)
O(12)–Mo(2)–O(7)	101.00(11)	N(2)–Ni(1)–N(4)	92.09(12)
O(13)–Mo(2)–O(7)	98.00(9)	O(6)–Ni(1)–N(4)	172.94(11)
O(11)–Mo(2)–O(7)	143.01(9)	N(1)–Ni(1)–N(4)	94.54(12)
O(12)–Mo(2)–O(10)	100.07(11)	N(2)–Ni(1)–N(3)	97.26(11)
O(13)–Mo(2)–O(10)	154.43(10)	O(6)–Ni(1)–N(3)	96.11(10)
O(11)–Mo(2)–O(10)	76.82(9)	N(1)–Ni(1)–N(3)	173.03(11)
O(7)–Mo(2)–O(10)	73.75(8)	N(4)–Ni(1)–N(3)	79.50(12)
O(5)–Mo(3)–O(6)	104.65(11)	N(2)–Ni(1)–O(13)	173.19(10)
O(5)–Mo(3)–O(4)	106.78(11)	O(6)–Ni(1)–O(13)	80.48(9)
O(6)–Mo(3)–O(4)	101.46(10)	N(1)–Ni(1)–O(13)	96.75(11)
O(5)–Mo(3)–O(7)	101.93(10)	N(4)–Ni(1)–O(13)	93.72(10)
O(6)–Mo(3)–O(7)	95.64(9)	N(3)–Ni(1)–O(13)	87.30(10)
O(4)–Mo(3)–O(7)	141.32(9)		

3.3. *Structures of 2*

Single crystal X-ray diffraction analysis revealed that **2** consists of one α-$Mo_8O_{26}^{4-}$ linked by two $Ni(bpy)_2^{2+}$ *via* terminal oxygen bridges, shown in figure 2. Selected bond lengths and angles are given in table 3. The Ni^{II} is in a distorted octahedral environment, coordinated by four nitrogens from two chelating bpy ligands and two terminal oxygens. The Ni–N and Ni–O bond distances are in the normal range of 2.049(3)–2.069(3) and 2.059(2)–2.069(3) Å, respectively. The N(O)–Ni–N(O) angles are in the range of 79.33(13)–172.95(12)°. Rms deviations of the two bipyridine groups from planarity are 0.0168 and 0.0661 Å. The dihedral angles between the two bipyridine groups are 84.03(9) Å. The molybdate has an approximate C_{2h} symmetry and consists

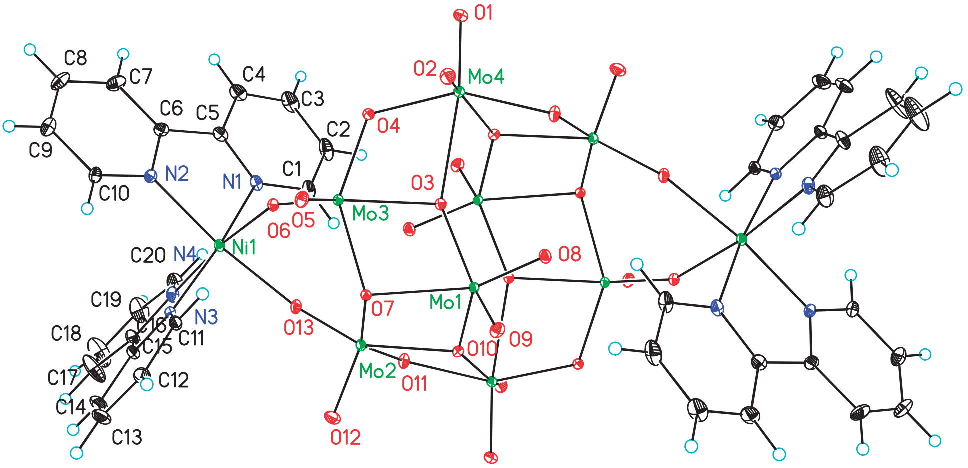

Figure 3. The crystal packing of **1**, displayed with extensive hydrogen-bond contacts.

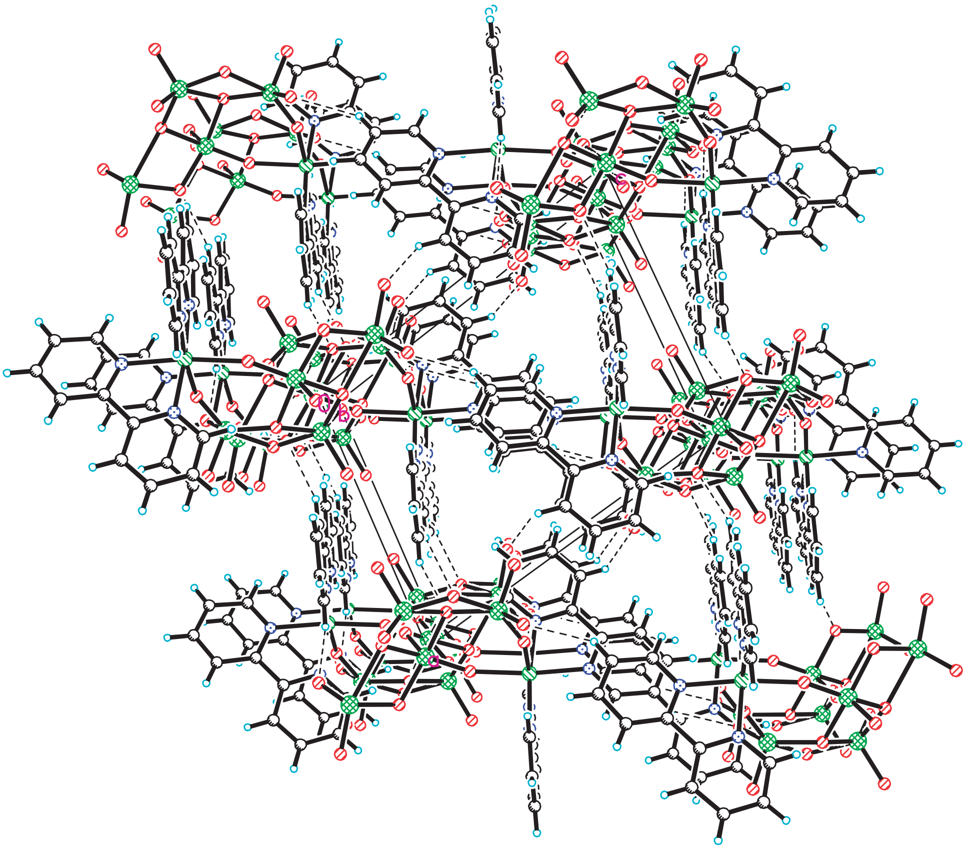

Figure 4. The crystal packing of **2**, displayed with extensive hydrogen-bond contacts.

Table 4. Hydrogen bond lengths (Å) in **1** and **2**.

Compound **1**		Compound **2**	
Bond	Distance	Bond	Distance
N(7)···O(1)	2.818(8)	C(3)···O(5)	3.382(6)
N(4)···O(6)	2.931(9)	C(3)···O(7)	3.353(5)
N(1)···O(4)	2.802(9)	C(7)···O(4)	3.143(5)
C(2)···O(11)	3.450(11)	C(10)···O(2)	3.221(5)
C(9)···O(13)	3.169(11)	C(14)···O(1)	3.187(5)
C(15)···O(2)	3.104(12)	C(19)···O(11)	3.183(6)
C(21)···O(8)	3.274(10)		
C(22)···O(2)	3.472(10)		

of a Mo_6O_6 ring capped on opposite faces by tripodal MoO_4 tetrahedra. The characteristic feature of this structure is that the Mo_6O_6 ring contains two tetrahedrally and four octahedrally coordinated Mo(V1) atoms; thus, its framework is distorted from the D_{3d} symmetry of the a-isomer [13] and elongated along a C_2 axis through two tetrahedrally coordinated Mo's in the Mo_6O_6 ring. In the ring, the linkage between two MoO_6 octahedra is an edge-shared type, while that between an MoO_6 octahedron and an MoO_4 tetrahedron is a corner-shared type. There are two types of Mo–O bonds in **2**, terminal Mo–O, and bridging μ_2-O–Mo and μ_3-O–Mo bonds. The Mo–$O_{terminal}$, Mo–O(μ_2), and Mo–O(μ_3) bond distances are in the normal ranges 1.677(2)–1.728(2), 1.866(2)–1.968(2), and 1.887(2)–2.334(2) Å, respectively [13].

Multipoint hydrogen-bonding links also exist between hydrogens from organic amines and surface oxygens of the cluster; this may make a contribution to stabilize the packing diagrams of **1** and **2**, shown in figures 3 and 4, and table 4.

Assignment of the oxidation state for Mo in these compounds is consistent with the electric charge confirmed by bond valence sum calculations [14], by which the range and average valence sum for the molybdenum atoms are 5.85–5.92 for **1**; 5.89–5.95 for **2**.

4. Conclusion

The polyoxometalate topology depends on the acidity, stoichiometry, etc., and also on the transition metal salt. This proved meaningful during the synthesis of new polyoxometalates in combination with metal–organic units. Further investigations of the optical, electronic, magnetic, and catalytic properties of these newly synthesized compounds are our future research target.

Supplementary material

Further details on the crystal structure investigations of **1** and **2** may be obtained from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Telephone: +44-(0)1223-762-910, Fax: +44-(0)1223-336-033;

Email: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/deposit], on quoting the depository number CCDC-788013 for **1** and 788014 for **2**.

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