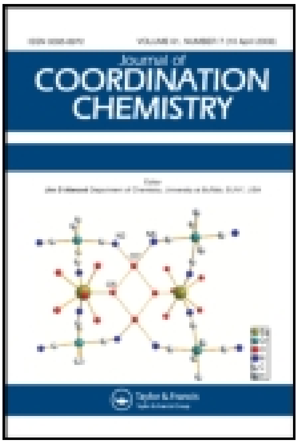

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Exploratory syntheses and structural characterizations of three organic-inorganic hybrid polyoxomolybdate frameworks linked by M(II)-L_n units (M=Ni, Co, Zn; L=2,2′-biimidazole)

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Exploratory syntheses and structural characterizations of three organic–inorganic hybrid polyoxomolybdate frameworks linked by M(II)-L_n units (M = Ni, Co, Zn; L = 2,2′-biimidazole)

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Three new polyoxomolybdate compounds, $\{[Ni(H_2biim)_2(H_2O)](Mo_3O_{10})\}_n$ (**1**), $[Co(H_2biim)_2(Hbiim)]_2(H_2Mo_8O_{26})](H_2O)_4$ (**2**), and $\{[Zn(H_2biim)_2(H_2O)][Mo_8O_{28}(MoO_2(H_2biim)_2)_2]$ (H_4biim) (**3**) (H_2biim, 2,2′-biimidazole), were designed and synthesized under hydrothermal conditions. X-ray diffraction analysis reveals that **1** is a snake-shaped chain consisting of asymmetric blocks of $\{Mo_3O_{10}\}$, in which the ratio of the octahedra $\{MoO_6\}$ and square pyramids $\{MoO_5\}$ is 1 : 2. Compounds **2** and **3** exhibit different structures, although similar synthetic environments (including pH, temperature, and reaction time) were employed. In **2**, the cluster of $H_2Mo_8O_{26}^{2-}$ is decorated by two fragments of $Co(H_2biim)_2(Hbiim)^+$ via the organic bridge of $Hbiim^-$. Compound **3** consists of one γ-$Mo_8O_{28}^{4-}$, capped by two fragments of $\{MoO_2(H_2biim)_2)_2\}^{2+}$ via terminal oxygens.

Keywords: Polyoxomolybdate; 2,2′-Biimidazole; Nickel(II); Cobalt(II); Zinc(II)

1. Introduction

Design and synthesis of polyoxometalate clusters has attracted interest not only because of their structural and topological novelty, but also due to their unusual optical, electronic, magnetic, and catalytic properties, as well as their potential medical applications [1–6].

Hydrothermal synthesis, which causes the reaction mechanism to shift from the kinetic to the thermodynamic domain as compared to traditional aqueous reactions, provides a powerful tool for synthesis of such materials [7]. Construction of hybrid materials is often realized by utilization of rigid N-donor aromatic organic ligands under hydrothermal reaction conditions [8]. Numbers of polyoxometalates bridged by organonitrogen ligands coordinated to transition metal fragments have been reported. A crucial strategy for molecular design of solid materials is how to employ

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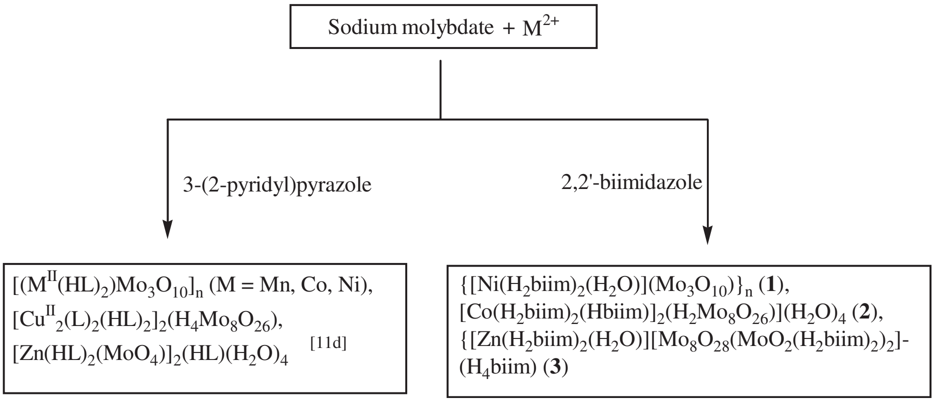
hydrothermal synthesis to introduce transition-metal-coordinated complexes, which usually serve as organic-inorganic bridging ligands, into the covalent backbone of solid materials. Normally, such transition-metal complexes are a covalent linker to molybdate, either as monomeric $[MoO_4]^{2-}$ or as oligomeric $[Mo_xO_y]^{n-}$, or 1-D or 2-D networks and are considered as charge-balancing anions for the cationic coordination polymers, to extend into higher dimensional frameworks [9]. A range of heterooxometalates existing as molybdenum oxides with second mononuclear, binuclear, and trinuclear metal centers have been reported [10]. Because of the ability of transition-metal elements to adapt various coordination geometries in different oxidation states, the influences of second metal ions as well as organic ligands on the structural types could be studied by modifying transition-metal ions, organic groups, and synthetic conditions. Combination of molybdenum oxides and metal-organic coordination fragments with their structural features might generate compounds with special properties.

We have launched a systematic program aimed at linking mono- or polyoxometalate building groups by ligands coordinated to transition-metal fragments to generate some distinctive architectures [11]. Here, we report the syntheses and structural characterizations of three new compounds, $\{[Ni(H_2biim)_2(H_2O)](Mo_3O_{10})\}_n$ (**1**), $[Co(H_2biim)_2(Hbiim)]_2(H_2Mo_8O_{26})](H_2O)_4$ (**2**), and $\{[Zn(H_2biim)_2(H_2O)][Mo_8O_{28}(MoO_2(H_2biim)_2)_2]$ (H_4biim) (**3**) (H_2biim, 2,2′-biimidazole).

2. Results and discussion

2.1. *Synthesis*

As shown in scheme 1, with 3-(2-pyridyl)pyrazole being introduced into the polyoxometalate growth environment, three isostructural wave-like chains consisting of asymmetric building blocks of $[Mo_3O_{10}]$ were successfully isolated, in which the basic units of $\{Mo_3O_{10}\}$ are linked by corner-sharing convex of $\{MoO_6\}$ octahedra [11d]. With 2,2′-biimidazole replacing 3-(2-pyridyl)pyrazole, three new molybdenum oxide



Scheme 1. Related reactions affected by different organic amine ligands under hydrothermal conditions.

structures are obtained. Compound **1** is a snake-shaped chain, built from [Mo_3O_{10}]. The cluster of $H_2Mo_8O_{26}^{2-}$ in **2** is decorated by two Co(H_2biim)$_2$(Hbiim)$^+$ fragments via bridging Hbiim$^-$. Compound **3** consists of γ-$Mo_8O_{28}^{4-}$, capped by two fragments of $\{MoO_2(H_2biim)_2)_2\}^{2+}$ via terminal oxygen. The topology of organic-inorganic molybdenum oxide phases could be attributed to synergistic interaction between organic and inorganic fragments [8]. Organic components have unique roles of a ligand coordinated to molybdenum oxide and a second metal center, a charge-compensating, and space-filling component [8].

2.1.1. Structure of {[Ni(H_2biim)$_2$(H_2O)](Mo_3O_{10})}$_n$ (1). The molecular structure of **1** is shown in figure 1. Selected bond lengths and angles are given in table 1. Single crystal X-ray diffraction analysis reveals that the asymmetric building blocks of $\{Mo_3O_{10}\}$ in **1** share the $\{MoO_6\}$ corner to form the snake-shaped chain, shown in figure 2. The ratio of $\{MoO_6\}$ and $\{MoO_5\}$ in $\{Mo_3O_{10}\}$ is 1 : 2. Charge compensation is achieved by $\{Ni(H_2biim)_2(H_2O)\}^{2+}$. There are two types of Mo–O bonds in $\{Mo_3O_{10}\}_n$, terminal and bridging (μ_2–O–Mo and μ_3–O–Mo). Related bond distances vary from 1.690 Å for one terminal Mo–O bond to 2.496 Å for one of the bonds to μ_3–O. The [MoO_6] octahedron is considerably distorted, with a spread of Mo–O bond distances from 1.71 to 2.50 Å. Similar octahedral distortions were observed in other Mo(VI) polyoxoanions, suggesting that such distortions do not result from a steric effect within the chains. Explanation for the strong distortion in [MoO_6] is related to the nature of the Mo–O interaction, which changes from strongly covalent for the shortest bond to a predominantly ionic interaction for the longest bonds in the Mo–O octahedron. Such distortion of [MoO_6], resulting from different Mo–O distances, is a requirement to

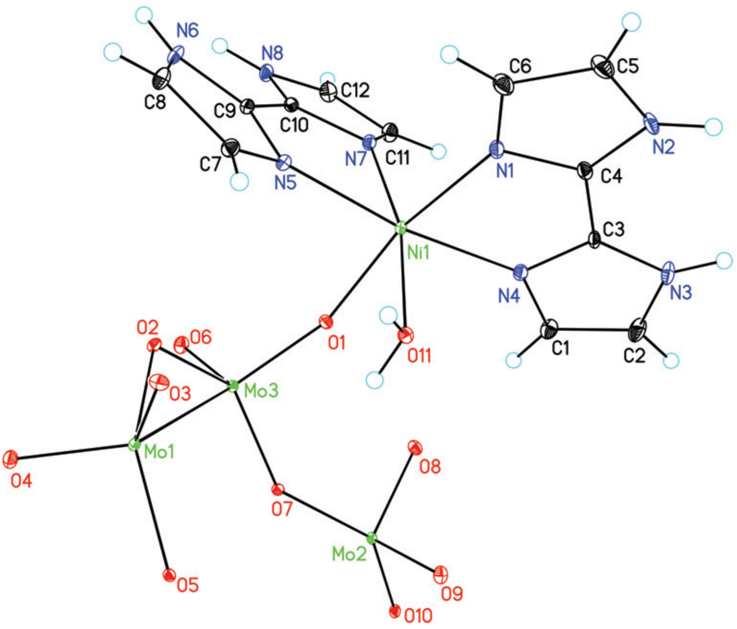


Figure 1. ORTEP view of **1** (30% thermal ellipsoids) showing the atom-labeling scheme.

Table 1. Selected bond lengths (Å) and angles (°) for **1**–**3**.

Compound **1**			
Mo(1)–O(3)	1.712(3)	Mo(3)–O(1)	1.719(2)
Mo(1)–O(4)	1.718(3)	Mo(3)–O(2)	1.899(2)
Mo(1)–O(5)	1.903(2)	Mo(3)–O(7)	1.957(2)
Mo(1)–O(2)	1.926(2)	Ni(1)–N(7)	2.064(3)
Mo(2)–O(9)	1.709(3)	Ni(1)–N(1)	2.070(3)
Mo(2)–O(8)	1.717(3)	Ni(1)–N(5)	2.077(3)
Mo(2)–O(10)	1.844(2)	Ni(1)–N(4)	2.083(3)
Mo(2)–O(7)	1.991(2)	Ni(1)–O(11)	2.097(3)
Mo(3)–O(6)	1.687(3)	Ni(1)–O(1)	2.118(2)
O(3)–Mo(1)–O(4)	106.73(13)	O(2)–Mo(3)–O(7)	143.34(10)
O(3)–Mo(1)–O(5)	100.81(11)	N(7)–Ni(1)–N(1)	102.60(13)
O(4)–Mo(1)–O(5)	98.74(11)	N(7)–Ni(1)–N(5)	80.15(13)
O(3)–Mo(1)–O(2)	100.24(11)	N(1)–Ni(1)–N(5)	93.75(13)
O(4)–Mo(1)–O(2)	101.50(12)	N(7)–Ni(1)–N(4)	96.13(13)
O(5)–Mo(1)–O(2)	145.05(10)	N(1)–Ni(1)–N(4)	80.02(13)
O(9)–Mo(2)–O(8)	104.53(13)	N(5)–Ni(1)–N(4)	171.94(13)
O(9)–Mo(2)–O(10)	100.09(12)	N(7)–Ni(1)–O(11)	167.39(11)
O(8)–Mo(2)–O(10)	104.23(12)	N(1)–Ni(1)–O(11)	88.60(12)
O(9)–Mo(2)–O(7)	100.40(11)	N(5)–Ni(1)–O(11)	93.50(12)
O(8)–Mo(2)–O(7)	98.80(11)	N(4)–Ni(1)–O(11)	91.46(11)
O(10)–Mo(2)–O(7)	144.04(10)	N(7)–Ni(1)–O(1)	85.04(11)
O(6)–Mo(3)–O(1)	105.03(13)	N(1)–Ni(1)–O(1)	169.63(12)
O(6)–Mo(3)–O(2)	100.13(12)	N(5)–Ni(1)–O(1)	94.48(11)
O(1)–Mo(3)–O(2)	103.33(11)	N(4)–Ni(1)–O(1)	92.31(12)
O(6)–Mo(3)–O(7)	97.67(12)	O(11)–Ni(1)–O(1)	84.61(10)
O(1)–Mo(3)–O(7)	102.59(11)		
Compound **2**			
Mo(3)–O(8)	1.692(3)	Mo(2)–O(3)	1.715(4)
Mo(3)–O(7)	1.755(3)	Mo(2)–O(4)	1.967(3)
Mo(3)–O(5)	1.899(3)	Mo(2)–O(6)	2.230(3)
Mo(3)–O(9)	2.184(3)	Mo(2)–O(5)	2.322(3)
Mo(3)–O(6)	2.470(3)	Co(1)–N(5)	1.912(4)
Mo(1)–N(6)	2.226(4)	Co(1)–N(8)	1.921(4)
Mo(4)–O(13)	1.701(4)	Co(1)–N(9)	1.936(4)
Mo(4)–O(11)	1.721(4)	Co(1)–N(1)	1.934(4)
Mo(4)–O(9)	1.899(3)	Co(1)–N(3)	1.938(4)
Mo(4)–O(12)	1.955(3)	Co(1)–N(11)	1.935(5)
Mo(2)–O(2)	1.709(3)		
O(1)–Mo(1)–O(10)	104.97(17)	O(8)–Mo(3)–O(9)	95.51(15)
O(1)–Mo(1)–O(4)	99.34(16)	O(7)–Mo(3)–O(9)	159.91(14)
O(10)–Mo(1)–O(4)	104.79(16)	O(5)–Mo(3)–O(9)	75.37(13)
O(1)–Mo(1)–O(5)	94.32(14)	O(8)–Mo(3)–O(6)	178.74(14)
O(10)–Mo(1)–O(5)	159.38(15)	O(7)–Mo(3)–O(6)	76.81(13)
O(4)–Mo(1)–O(5)	78.67(13)	O(5)–Mo(3)–O(6)	75.65(12)
O(1)–Mo(1)–O(9)	161.37(15)	O(9)–Mo(3)–O(6)	83.24(11)
O(10)–Mo(1)–O(9)	88.87(15)	O(13)–Mo(4)–O(11)	103.95(18)
O(4)–Mo(1)–O(9)	88.83(14)	O(13)–Mo(4)–O(9)	98.61(16)
O(5)–Mo(1)–O(9)	70.75(12)	O(11)–Mo(4)–O(9)	105.04(17)
O(1)–Mo(1)–N(6)	85.41(15)	O(13)–Mo(4)–O(12)	97.12(16)
O(10)–Mo(1)–N(6)	90.83(16)	O(11)–Mo(4)–O(12)	101.06(16)
O(4)–Mo(1)–N(6)	161.72(15)	O(9)–Mo(4)–O(12)	145.10(14)
O(5)–Mo(1)–N(6)	83.38(14)	N(5)–Co(1)–N(8)	82.03(18)
O(9)–Mo(1)–N(6)	81.92(13)	N(5)–Co(1)–N(9)	93.84(17)
O(2)–Mo(2)–O(3)	104.62(18)	N(8)–Co(1)–N(9)	91.82(19)
O(2)–Mo(2)–O(4)	100.31(16)	N(5)–Co(1)–N(1)	91.29(18)
O(3)–Mo(2)–O(4)	97.76(17)	N(8)–Co(1)–N(1)	89.1(2)
O(2)–Mo(2)–O(6)	159.28(16)	N(9)–Co(1)–N(1)	174.87(18)

(*Continued*)

Table 1. Continued.

O(3)–Mo(2)–O(6)	94.53(16)	N(5)–Co(1)–N(3)	172.06(17)
O(4)–Mo(2)–O(6)	84.62(13)	N(8)–Co(1)–N(3)	94.38(18)
O(2)–Mo(2)–O(5)	88.71(15)	N(9)–Co(1)–N(3)	93.35(17)
O(3)–Mo(2)–O(5)	165.41(16)	N(1)–Co(1)–N(3)	81.54(17)
O(4)–Mo(2)–O(5)	73.62(12)	N(5)–Co(1)–N(11)	94.22(18)
O(6)–Mo(2)–O(5)	73.25(11)	N(8)–Co(1)–N(11)	172.28(19)
O(8)–Mo(3)–O(7)	104.44(16)	N(9)–Co(1)–N(11)	81.66(19)
O(8)–Mo(3)–O(5)	104.08(16)	N(1)–Co(1)–N(11)	97.81(19)
O(7)–Mo(3)–O(5)	101.51(14)	N(3)–Co(1)–N(11)	90.14(18)
Compound **3**			
Mo(1)–O(6)	1.689(3)	Mo(4)–O(16)	1.715(3)
Mo(1)–O(14)	1.747(3)	Mo(4)–O(12)	1.883(3)
Mo(1)–O(7)	1.890(3)	Mo(4)–O(13)	2.217(3)
Mo(1)–O(8)	2.158(3)	Mo(4)–O(14)	2.342(3)
Mo(1)–O(13)	2.481(3)	Mo(5)–O(1)	1.703(4)
Mo(2)–O(9)	1.705(3)	Mo(5)–O(2)	1.706(4)
Mo(2)–O(5)	1.707(3)	Mo(5)–O(3)	1.862(3)
Mo(2)–O(3)	1.938(3)	Mo(5)–N(1)	2.183(4)
Mo(2)–O(8)	2.001(3)	Mo(5)–O(4)	2.210(3)
Mo(3)–O(11)	1.696(3)	Mo(5)–N(2)	2.320(5)
Mo(3)–O(4)	1.761(3)	Zn(1)–O(17)	2.004(5)
Mo(3)–O(10)	1.809(3)	Zn(1)–N(14)	2.076(4)
Mo(3)–O(12)	2.032(3)	Zn(1)–N(9)	2.074(4)
Mo(3)–O(13)	2.172(3)	Zn(1)–N(8)	2.136(5)
Mo(4)–O(15)	1.706(3)	Zn(1)–N(11)	2.166(5)
O(6)–Mo(1)–O(14)	105.85(16)	O(12)–Mo(3)–O(7)	79.74(12)
O(6)–Mo(1)–O(7)	103.95(15)	O(13)–Mo(3)–O(7)	73.49(11)
O(14)–Mo(1)–O(7)	101.34(15)	O(15)–Mo(4)–O(16)	105.00(17)
O(6)–Mo(1)–O(8)	98.39(15)	O(15)–Mo(4)–O(12)	105.85(16)
O(14)–Mo(1)–O(8)	155.58(14)	O(16)–Mo(4)–O(12)	99.98(15)
O(7)–Mo(1)–O(8)	75.12(13)	O(15)–Mo(4)–O(13)	155.13(14)
O(6)–Mo(1)–O(13)	178.72(14)	O(16)–Mo(4)–O(13)	99.47(14)
O(14)–Mo(1)–O(13)	75.39(13)	O(12)–Mo(4)–O(13)	73.72(12)
O(7)–Mo(1)–O(13)	76.02(11)	O(15)–Mo(4)–O(14)	84.32(14)
		O(16)–Mo(4)–O(14)	
O(8)–Mo(1)–O(13)	80.35(11)	O(12)–Mo(4)–O(14)	169.96(14)
O(9)–Mo(2)–O(5)	104.75(17)	O(13)–Mo(4)–O(14)	80.64(13)
O(9)–Mo(2)–O(3)	103.11(16)	O(1)–Mo(5)–O(2)	70.99(11)
O(5)–Mo(2)–O(3)	95.71(16)	O(1)–Mo(5)–O(3)	104.2(2)
O(9)–Mo(2)–O(8)	94.21(15)	O(2)–Mo(5)–O(3)	107.24(17)
O(5)–Mo(2)–O(8)	96.55(15)	O(1)–Mo(5)–N(1)	101.38(17)
O(3)–Mo(2)–O(8)	155.45(14)	O(2)–Mo(5)–N(1)	87.74(19)
O(9)–Mo(2)–O(10)	91.38(15)	O(3)–Mo(5)–N(1)	94.68(18)
O(5)–Mo(2)–O(10)	163.86(15)	O(1)–Mo(5)–O(4)	154.33(16)
O(3)–Mo(2)–O(10)	80.79(13)	O(2)–Mo(5)–O(4)	90.63(17)
O(8)–Mo(2)–O(10)	81.53(12)	O(3)–Mo(5)–O(4)	162.39(17)
O(9)–Mo(2)–O(7)	158.80(14)	N(1)–Mo(5)–O(4)	82.72(14)
O(5)–Mo(2)–O(7)	92.46(14)	O(1)–Mo(5)–N(2)	76.24(15)
O(3)–Mo(2)–O(7)	87.07(13)	O(2)–Mo(5)–N(2)	157.39(18)
O(8)–Mo(2)–O(7)	71.23(12)	O(3)–Mo(5)–N(2)	86.15(18)
O(10)–Mo(2)–O(7)	71.69(12)	N(1)–Mo(5)–N(2)	89.87(15)
O(11)–Mo(3)–O(4)	105.39(17)	O(4)–Mo(5)–N(2)	71.22(17)
O(11)–Mo(3)–O(10)	102.64(16)	O(17)–Zn(1)–N(9)	76.68(14)
O(4)–Mo(3)–O(10)	100.36(15)	O(17)–Zn(1)–N(14)	100.1(2)
O(11)–Mo(3)–O(12)	99.78(15)	N(9)–Zn(1)–N(14)	101.39(19)
O(4)–Mo(3)–O(12)	93.15(15)	O(17)–Zn(1)–N(8)	158.45(19)
O(10)–Mo(3)–O(12)	149.60(14)	N(9)–Zn(1)–N(8)	104.0(2)
O(11)–Mo(3)–O(13)	96.97(15)	N(14)–Zn(1)–N(8)	79.67(18)

(*Continued*)

Table 1. Continued.

O(4)–Mo(3)–O(13)	155.08(14)	O(17)–Zn(1)–N(11)	94.13(18)
O(10)–Mo(3)–O(13)	85.05(13)	N(9)–Zn(1)–N(11)	97.6(2)
O(12)–Mo(3)–O(13)	72.01(12)	N(14)–Zn(1)–N(11)	98.58(17)
O(11)–Mo(3)–O(7)	170.19(14)	N(8)–Zn(1)–N(11)	79.56(18)
O(4)–Mo(3)–O(7)	84.41(13)		158.3(2)
O(10)–Mo(3)–O(7)	74.68(13)		

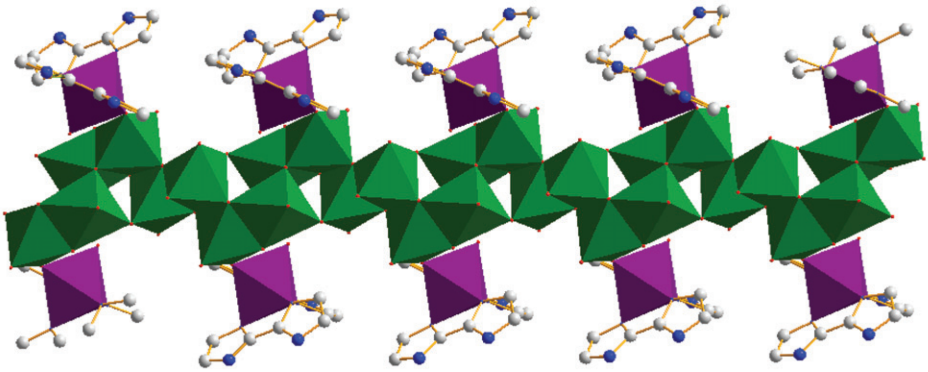


Figure 2. A polyhedral view of $\{[Ni(H_2biim)_2(H_2O)](Mo_3O_{10})\}_n$ (**1**). The polyhedra represent MoO_6 and MoO_5 (green) and NiN_4O_2 (dark red); the balls are N (blue) and C (gray).

stabilize the oxo-molybdenum framework [11]. The Mo(1)···Mo(3) distance (3.1341(4) Å) implies no direct metal–metal interactions between Mo's [12].

Ni^{2+} in $[Ni(H_2biim)_2(H_2O)]^{2+}$ is in a distorted octahedral coordination formed by four nitrogens from two chelating H_2biim ligands and two oxygens from one terminal oxygen and one water. The Ni–N and Ni–O bond lengths are 2.064(3)–2.083(3) and 2.097(3)–2.118(2) Å, respectively. The nearest Ni···Ni distance along the same side of the chain is 8.188 Å.

2.1.2. Structure of $[Co(H_2biim)_2(Hbiim)]_2(H_2Mo_8O_{26})](H_2O)_4$ (2). The molecular structure of **2** is shown in figure 3. Selected bond lengths and angles are given in table 1. The asymmetric unit in **2** contains half of $[Co(H_2biim)_2(Hbiim)]_2(H_2Mo_8O_{26})]$ and four uncoordinated waters. $\{Mo_8O_{26}N_2\}$ consists of eight edge-sharing $\{MoO_6\}$/$\{MoO_4N_2\}$ octahedra and displays the γ-octamolybdate arrangement with an inversion center. There are two types of Mo–O bonds in $\{Mo_8O_{26}N_2\}$, terminal and bridging (μ_2–O–Mo, μ_3–O–Mo and μ_4–O–Mo). The related bond distances vary from 1.692 Å for one terminal Mo–O bond to 2.470 Å for one of the bonds to μ_4–O. The Mo–N bond distance is 2.226(4) Å, in the normal range between nitrogen (from pyridine/pyrazole/biimidazole) and molybdenum [11d].

Co^{2+} in $[Co(H_2biim)_2(Hbiim)]^{2+}$ is in a distorted octahedron formed by six nitrogens from three chelating H_2biim. The Co–N bond lengths are 1.912(4)–1.935(5) Å.

2.1.3. Structure of $\{[Zn(H_2biim)_2(H_2O)][Mo_8O_{28}(MoO_2(H_2biim)_2)_2](H_4biim)$ (3). The molecular structure of **3** is shown in figure 4. Selected bond lengths and angles are given

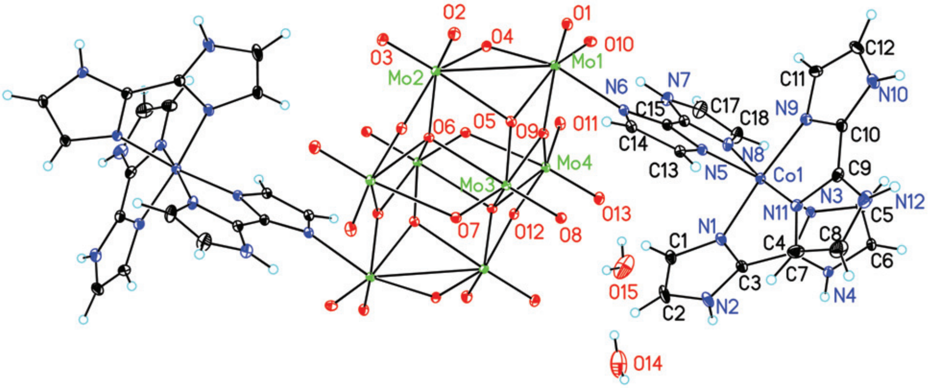


Figure 3. ORTEP view of **2** (30% thermal ellipsoids) showing the atom-labeling scheme.

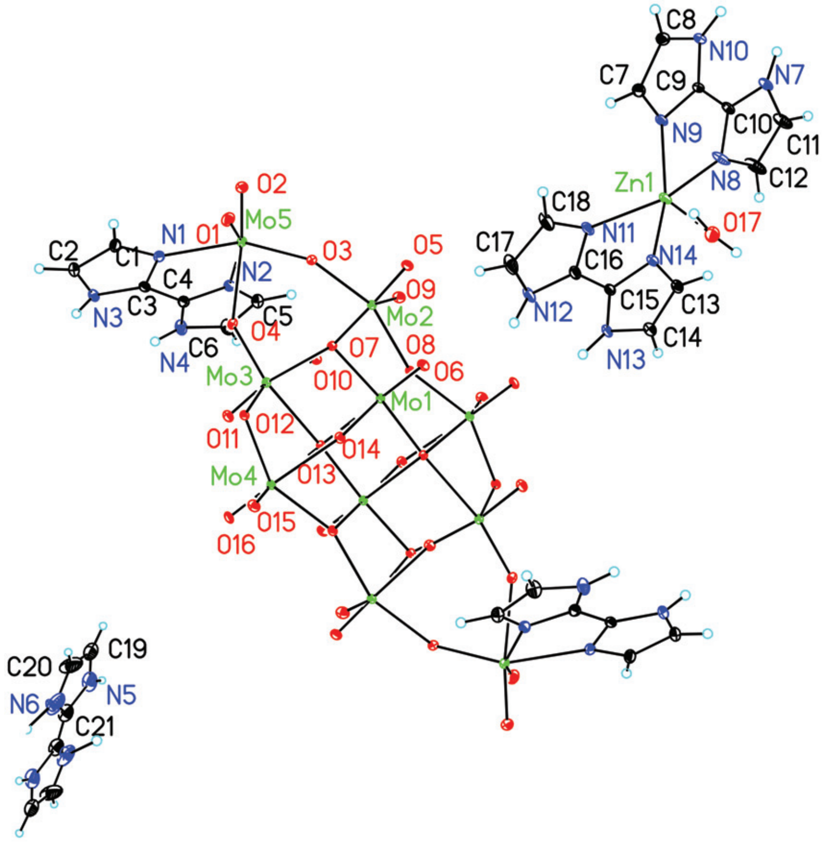


Figure 4. ORTEP view of **3** (30% thermal ellipsoids) showing the atom-labeling scheme.

in table 1. Single crystal X-ray diffraction analysis reveals that **3** consists of $[Mo_8O_{28}]^{4-}$, which is decorated by two fragments of $\{MoO_2(H_2biim)_2\}^{2+}$ via terminal oxygens. $[Mo_8O_{28}]^{4-}$ consists of eight edge-sharing $\{MoO_6\}$ octahedra and in a γ-octamolybdate arrangement. There are two types of Mo–O bonds in $[Mo_8O_{28}]^{4-}$, terminal and bridging

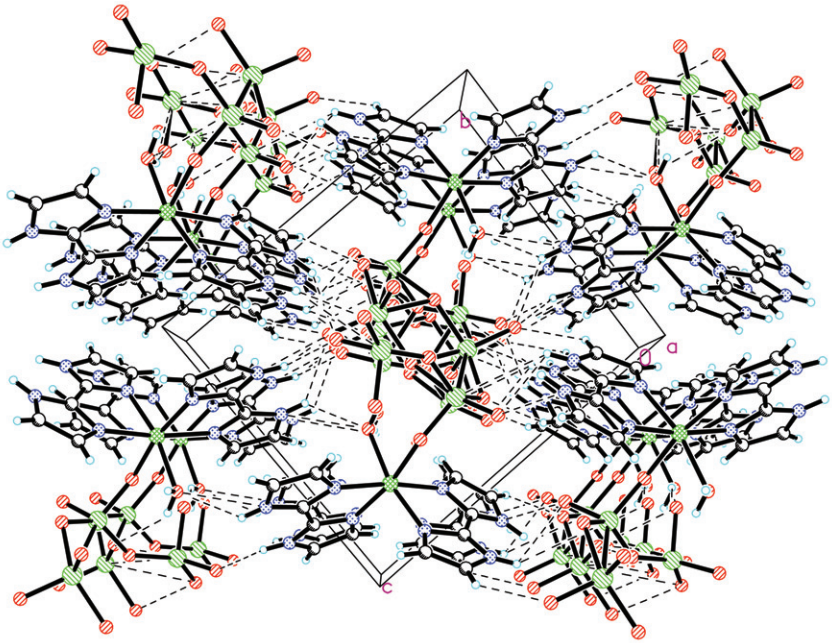


Figure 5. The crystal packing of **1** viewed along the *a* axis, interweaved by hydrogen contacts.

(μ_2–O–Mo, μ_3–O–Mo and μ_4–O–Mo) with distances varying from 1.689 Å (terminal Mo–O) to 2.481 Å for a μ_4–O. The Mo–N bond distances in $\{MoO_2(H_2biim)_2\}^{2+}$ are 2.183(4)–2.320(5) Å.

Zn^{2+} is five-coordinate is in a distorted square-pyramid formed by four nitrogens from two chelating H_2biim ligands in equatorial positions and one water in the apical position. The Zn–N bond lengths are 2.076(4)–2.166(5) Å and Zn–O is 2.004(5) Å. Moreover, one uncoordinated 2,2′-biimidazole exists in the unit.

Multipoint hydrogen-bonding links also exist between hydrogens from organic amines and surface oxygens of the cluster, stabilizing the packing diagrams of **1**–**3** (figures 5–7 and table 2).

Assignment of the oxidation state for Mo in these compounds is consistent with electric charge confirmed by bond valence sum calculations [13], by which the ranges for molybdenums are 5.82–6.06 for **1**; 5.99–6.07 for **2**; 5.79–5.90 for **3**.

2.2. *TGA analysis*

TGA measurements of **1**–**3** have been carried out on a Perkin-Elmer Diamond TG/DTA instrument with a flow of dry air and a heating rate of 5°C min^{-1} from room temperature to 1000°C. As shown in figures S1–S3 (Supplementary material), TGA curves indicate that **1**–**3** are stable to 212°C, 260°C, and 251°C, respectively. Above these temperatures, the organic ligand and crystallization waters are lost. The residual weights are *ca* 60.4% (Calcd for MoO_3 and NiO: 62.3%) for **1**, 58.1% (Calcd for MoO_3 and CoO: 59.2%) for **2** and 76.4% (Calcd for MoO_3 and ZnO: 62.8%) for **3**.

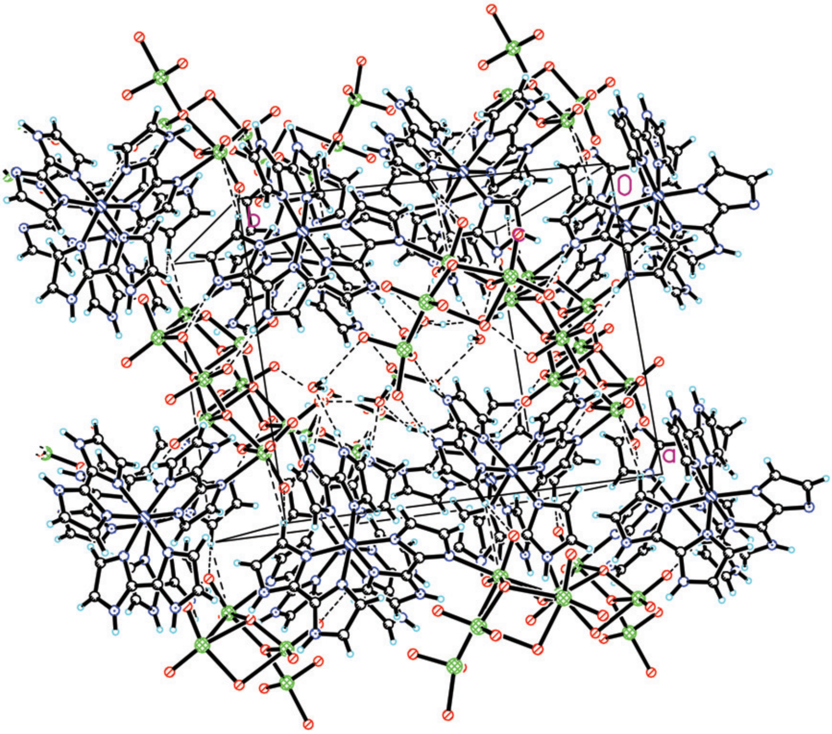


Figure 6. The crystal packing of **2** viewed along the *a*-axis, interweaved by hydrogen contacts.

3. Experimental

3.1. *Materials and methods*

2,2′-Biimidazole was purchased from Jinan Henghua Sci. & Tec.Co. Elemental analysis for C, H, and N was conducted on a Perkin-Elmer 240C elemental analyzer; elemental analysis for Mo and M (Ni, Co, Zn) was measured on an inductively coupled plasma OES spectrometer; IR spectra were recorded from 400 ∼4000 cm^{-1} on a Perkin-Elmer 2400LSII spectrometer.

3.2. *Synthesis*

3.2.1. Synthesis of 1. The synthesis is performed in 25 mL Teflon-lined stainless steel vessels. $Na_2MoO_4 \cdot H_2O$ (0.1 mmol, 0.024 g), $NiCl_2 \cdot 6H_2O$ (0.1 mmol, 0.024 g), 2,2′-biimidazole (0.1 mmol, 0.013 g), and H_2O (10 mL) were mixed in a molar ratio 1 : 1 : 1 : 556, and the pH of the mixture was adjusted to 3–4 with 1 mol L^{-1} HCl, heated to 170°C and kept at this temperature for 3 days. Green crystals were obtained after cooling to room temperature in 18% yield. Anal. Calcd for $C_{12}H_{14}Mo_3N_8NiO_{11}$: C, 18.16; H, 2.14; N,

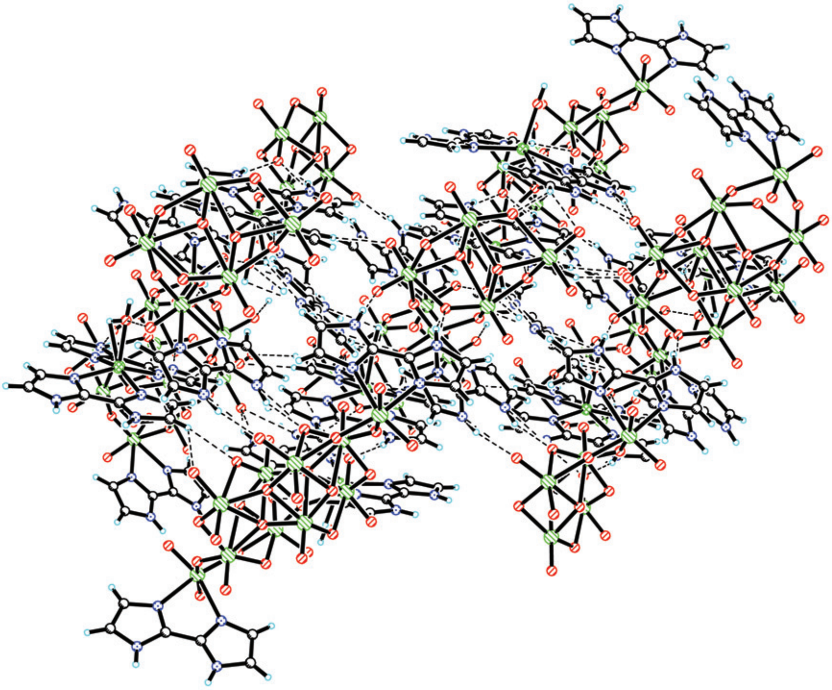


Figure 7. The crystal packing of **3** viewed along the *a* axis, interweaved by hydrogen contacts.

14.12; Mo, 36.30; and Ni, 7.40%. Found: C, 18.06; H, 2.03; N, 18.07; Mo, 36.12; and Ni, 7.23%. IR (cm^{-1}): 3271, 1524, 1428, 1094, 943, 912, 753, 692, and 609.

3.2.2. Synthesis of 2. The synthetic method is similar to that of **1** except that cobalt(II) chloride hexahydrate (0.1 mmol, 0.028 g) replaced nickel(II) chloride hexahydrate. Red crystals were obtained after cooling to room temperature in 24% yield. Anal. Calcd for $C_{36}H_{43}Co_2Mo_8N_{24}O_{30}$: C, 19.84; H, 1.98; N, 15.43; Mo, 35.25; and Co, 5.41%. Found: C, 19.62; H, 1.88; N, 15.22; Mo, 35.08; and Co, 5.21%. IR (cm^{-1}): 3221, 1649, 1527, 1424, 1349, 1108, 903, and 755.

3.2.3. Synthesis of 3. The synthetic method is similar to **1** except that zinc sulfate heptahydrate replaced nickel(II) chloride hexahydrate. Colorless crystals were obtained after cooling to room temperature in 22% yield. Anal. Calcd for $C_{42}H_{48}Mo_{10}N_{28}O_{34}Zn_2$: C, 19.56; H, 1.79; N, 15.21; Mo, 37.20; and Zn, 5.07%. Found: C, 19.49; H,1.68; N, 15.04; Mo, 37.01; and Zn, 4.85%. IR (cm^{-1}): 3351, 1599, 1504, 1429, 1363, 1062, 962, 876, and 807.

3.3. *X-ray crystallography*

Intensity data collection was carried out on a Siemens SMART diffractometer equipped with a CCD detector using Mo-Kα monochromated radiation ($\lambda = 0.71073$ Å) at

Table 2. Hydrogen bond lengths (Å) for **1**–**3**.

Compound **1**	
N(2)–H(2A)$\cdots$O(4)$^{\#1}$	2.917
N(2)–H(2A)$\cdots$O(9)$^{\#2}$	3.027
N(3)–H(3A)$\cdots$O(11)$^{\#3}$	2.826
N(3)–H(3A)$\cdots$O(4)$^{\#4}$	3.233
N(6)–H(6A)$\cdots$O(9)$^{\#5}$	3.091
N(8)–H(8A)$\cdots$O(10)$^{\#6}$	3.031
N(8)–H(8A)$\cdots$O(6)$^{\#7}$	
O(11)–H(2W)$\cdots$O(8)$^{\#8}$	2.729
O(11)–H(1W)$\cdots$O(5)$^{\#9}$	2.636
Compound **2**	
O(15)–H(4W)$\cdots$O(4)$^{\#1}$	2.86(5)
N(2)–H(2A)$\cdots$O(11)$^{\#2}$	2.851(6)
N(4)–H(4A)$\cdots$O(12)$^{\#3}$	2.753(5)
N(7)–H(7A)$\cdots$O(14)$^{\#4}$	3.197(9)
N(10)–H(10A)$\cdots$O(15)$^{\#5}$	2.915(10)
O(14)–H(2W)$\cdots$O(15)	2.810(15)
O(15)–H(3W)$\cdots$O(13)	2.861(7)
N(7)–H(7A)$\cdots$O(10)	2.798(6)
N(12)–H(12A)$\cdots$O(14)$^{\#6}$	2.733(9)
Compound **3**	
N(3)–H(3)$\cdots$O(10)$^{\#1}$	2.746(6)
N(4)–H(4)$\cdots$O(9)$^{\#2}$	2.793(6)
N(5)–H(5A)$\cdots$O(17)$^{\#3}$	2.677(11)
N(6)–H(6A)$\cdots$O(2)$^{\#4}$	2.808(9)
N(7)–H(7A)$\cdots$O(7)$^{\#5}$	2.738(5)
N(10)–H(10)$\cdots$O(12)$^{\#6}$	2.772(5)
N(12)–H(12A)$\cdots$O16)$^{\#7}$	2.932(6)
N(13)–H(13A)$\cdots$O(16)$^{\#8}$	2.750(5)
O(17)–H(2W)$\cdots$N(5)$^{\#9}$	2.677(11)
O(17)–H(1W)$\cdots$O(2)$^{\#10}$	2.893(6)

Symmetry codes for **1**: 1: $x, y, z-1$; #2: $-x+2, -y+1, -z$; #3:$-x+2, -y+1, -z$; #4: $x, y, z-1$; #5: $x, y+1, z$; #6: $x, y+1, z$; #7: $-x+1, -y+2, -z+1$; #8: $x+1, y, z$; #9: $-x+2, -y+1, -z+1$; for **2**: #1: $-x+1, y-1/2, -z+3/2$; #2: $-x+1, y-1/2, -z+3/2$; #3: $-x+1, y-1/2, -z+3/2$; #4: $-x+1, y+1/2, -z+3/2$; #5: $x-1, y, z$; #6: $x-1, y, z$; for **3**: #1: $-x+1/2, y-1/2, -z+1/2$; #2: $-x+1/2, y-1/2, -z+1/2$; #3: $x+1, y, z$; #4: $-x+1, y, -z+1/2$; #4: $-x, y+1, -z+1/2$; #5: $-x, y+1, -z+1/2$; #6: $-x+1/2, -y+1/2, -z+1$; #7: $-x+1/2, -y+1/2, -z+1$; #8: $-x+1/2, -y+1/2, -z+1$; #9: $x-1, y, z$; #10: $x, -y+1, z+1/2$.

293(2) K. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using SADABS. The structures were solved by direct methods and refined by full-matrix least-squares using SHELX-TL package [14]. Crystallographic data for **1**–**3** are given in table 3. Selected bond lengths and angles are listed in table 1. The essential atomic coordinates and equivalent isotropic displacement parameters are listed in tables S1–S3.

4. Conclusion

The polyoxometalate topology depends on acidity, stoichiometry, etc., and also on the transition metal salt. This proved meaningful during the synthesis of new

Table 3. Crystallographic data and details of diffraction experiments for **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{12}H_{14}Mo_3N_8NiO_{11}$	$C_{36}H_{43}Co_2Mo_8N_{24}O_{30}$	$C_{42}H_{48}Mo_{10}N_{28}O_{34}Zn_2$
Formula weight	792.84	2177.32	2579.22
Temperature (K)	298(2)	298(2)	298(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$	$C2/c$
Unit cell dimensions (Å, °)			
a	8.1883(6)	12.802(4)	36.781(4)
b	11.1924(8)	15.348(4)	11.3282(13)
c	12.4876(10)	16.580(5)	22.899(3)
α	89.5360(10)	90.00	90
β	84.0880(10)	94.505(4)	128.51
γ	69.4660(10)	90.00	90
Volume (Å^3), Z	1065.55(14), 2	3247.7(16), 2	7466.7(15), 4
Calculated density (g cm^{-3})	2.471	2.227	2.294
Absorption coefficient (mm^{-1})	2.671	2.088	2.351
Reflections collected	5693	16,144	18,737
Independent reflection	3733 [R(int) = 0.0599]	5573 [R(int) = 0.0509]	6510 [R(int) = 0.0600]
Refined parameters	324	463	529
Goodness-of-fit on $F^{2\,c}$	1.001	0.997	1.005
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0289^a$, $wR_2 = 0.0777^b$	$R_1 = 0.0359^a$, $wR_2 = 0.0965^b$	$R_1 = 0.03361^a$, $wR_2 = 0.0868^b$
R indices (all data)	$R_1 = 0.0311^a$, $wR_2 = 0.0794^b$	$R_1 = 0.0458^a$, $wR_2 = 0.1050^b$	$R_1 = 0.0440^a$, $wR_2 = 0.0930^b$
Largest difference peak and hole (e Å^{-3})	0.769 and −1.006	0.876 and −0.680	0.583 and −0.806

[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 $P = (F^2_o + 2F^2_c)/3$ and $x = 100.7959$, $y = 0.0400$ (**1**); $x = 79.0042$, $y = 0.0618$ (**2**); $x = 72.9399$, $y = 0.0850$ (**3**). [c] Goodness-of-fit on $F^2 = [\Sigma w(F^2_{obsd.} - F^2_{calcd.})^2/(n - p)]^{1/2}$, where n = number of reflections, p = parameter used.

polyoxomealates 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

Supplementary material (S1–S3) as well as further details on the crystal structure investigations for **1**–**3** 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; E-mail: deposit@ccdc.cam.ac.uk, www: http://www.ccdc.cam.ac.uk/deposit) quoting the depository number CCDC-753458 for **1**, 753460 for **2**, 753461 for **3**.

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