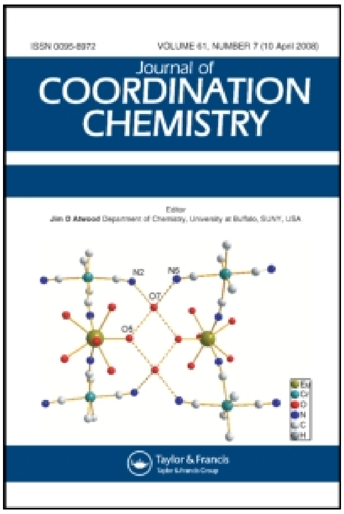

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An open-framework cobalt molybdate possessing $\{Mo_2O_7\}$ building block: hydrothermal synthesis and structural characterization of $[CoMo_2O_7(4,4'\text{-bipy})_{1.5}]$

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An open-framework cobalt molybdate possessing $\{Mo_2O_7\}$ building block: hydrothermal synthesis and structural characterization of $[CoMo_2O_7(4,4'\text{-bipy})_{1.5}]$

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The hydrothermal reaction of $Co(COO)_2 \cdot 4H_2O$, MoO_3, H_3PO_4 and 4,4′-bipyridine yields bipyridine-ligated cobalt dimolybdate $[CoMo_2O_7(4,4'\text{-bipy})_{1.5}]$ (**1**) (4,4′-bipy = 4,4′-bipyridine) in the triclinic system with space group of $P\bar{1}$ and cell parameters of $a = 7.1951(8)$ Å, $b = 11.1708(17)$ Å, $c = 11.4514(11)$ Å, $\alpha = 98.545(7)°$, $\beta = 90.315(2)°$, $\gamma = 105.777(5)°$, $V = 874.88(19)$ Å^3, and $Z = 2$. Its structure consists of Co/Mo/O bimetal oxide layers with $\{Mo_2O_7\}$ building blocks, linked by the coordination of 4,4′-bipy ligand with Co and Mo atoms, into a 3D porous hybrid framework.

Keywords: Hydrothermal synthesis; Crystal structure; Open-framework; Cobalt molybdate

1. Introduction

Metal oxide-based solids, especially microporous materials, are currently of interest due to their intriguing architectures and potential applications in a wide number of fields [1–5]. A strategy for modification of inorganic microstructures exploits organic spacers to generate diverse topologies in the resultant organic-inorganic hybrid materials. These materials reveal the structural dependence on the organic component including the relative dispositions of the ligand donor groups and the distance, thus linear rigid bipyridine-like ligands seem to a good choice for construction of microporous hybrid materials [6–8].

Molybdenum oxide is an important family of metal oxides, which tends to form polynuclear anionic metal-oxo clusters or oligomers such as $\{Mo_2O_7\}$, $\{Mo_3O_{10}\}$, $\{Mo_5O_{15}\}$, $\{Mo_6O_{19}\}$, $\{Mo_8O_{26}\}$, etc., under hydrothermal conditions. Exploiting molybdenum oxide oligomers as building blocks, Zubieta *et al.* reported a series of

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M/Mo/O/ligand hybrid materials (M = transition metal) [9–11]. In this system, both various organic ligands and geometry of a second transition-metal center provide significant structural flexibility to metal oxide-based solids [12–13]. Here we report the synthesis and structure of a three-dimensional cobalt dimolybdate $[CoMo_2O_7(4,4'\text{-bipy})_{1.5}]$ (**1**), which is based on the $\{Mo_2O_7\}$ building blocks and $[Co(4,4'\text{-bipy})]^{2+}$. The $\{Mo_2O_7\}$ unit in **1** is different from the common $\{MoO_4\}$ tetrahedral [14–17] due to one Mo atom being five coordinate with the fifth position occupied by an N of 4,4′-bipy.

2. Experimental section

2.1. *Synthesis*

All chemicals were of reagent grade and used as received from commercial sources without further purification. IR spectrum was recorded on an ABB Bomem MB102 spectrometer with KBr pellet. Thermal analysis was performed in N_2 with a heating rate of 20°C min^{-1}, using a METTLER TGA/SDTA851e thermal analyzer. The elemental analyses (C, H, and N) were determined on an Elementar Vario EL III analyzer.

2.2. *$[CoMo_2O_7(4,4'\text{-bipy})_{1.5}]$ (1)*

A mixture of $Co(COO)_2 \cdot 4H_2O$ (0.25 g, 1.14 mmol), MoO_3 (0.28 g, 1.95 mmol), 4,4′-bipyridine (0.3 g, 1.92 mmol), H_3PO_4 (0.12 mL, 2.07 mmol) and H_2O (10.0 g, 0.56 mol) in the mole ratio 3 : 5 : 5 : 5.3 : 5300 was stirred for 20 min in air (pH = 5), then transferred to a Teflon-lined autoclave (30 mL) and kept at 150°C for 4 days. After slow cooling to room temperature, red crystals were filtered off, washed with distilled water, and dried at room temperature in a yield of 70% based on Mo. Anal. Calcd for $C_{15}H_{12}N_3O_7CoMo_2$: C, 30.17; H, 2.02; N, 7.04%. Found: C, 30.10; H, 2.18; N, 7.14%. IR (KBr pellet, cm^{-1}): 3435(m), 3073(w), 1609(m), 1538(w), 1480(w), 1408(m), 1318(w), 1207(w), 1065(w), 1020(w), 903(s), 851(s), 800(m), 754(s), 670(w), 625(m), 567(w), 489(w), 450(w).

2.3. *X-ray crystallography*

Structural measurements for **1** were performed on a Siemens SMART-CCD diffractometer at a temperature of 293(2) K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization effects and absorption using SADABS. The structures were solved by direct methods. All non-hydrogen atoms were refined anistropically. After all of the non-hydrogen atoms were located, the models were refined against F^2, initially using isotropic and later anisotropic thermal displacement parameters until the final values of Δ/σ_{max} were less than 0.001 in all cases. Hydrogen atoms were introduced in calculated positions and refined isotropically. All calculations were performed using the SHELXTL97 crystallographic software package [18, 19]. Crystallographic data are given in table 1, and selected bond lengths and angles are listed in table 2.

Table 1. Crystal data of the title compound.

Experimental formula	$C_{15}H_{12}CoMo_2N_3O_7$
Formula weight	597.09
Crystal system	Triclinic
Space group (Å, °)	$P\bar{1}$
a	7.1951(8)
b	11.1708(17)
c	11.4514(11)
α	98.545(7)
β	90.315(2)
γ	105.777(5)
V (Å^3)	874.88(19)
Z	2
D (g cm^{-3})	2.267
R (F_o)	0.0496
wR (F_o^2)	0.1267

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

Mo(1)–O(1)	1.721(5)	Co(1)–O(7)#3	2.088(5)
Mo(1)–O(3)	1.739(5)	Co(1)–O(2)	2.100(5)
Mo(1)–O(2)	1.755(5)	Co(1)–N(1)	2.127(6)
Mo(1)–O(4)	1.848(5)	Co(1)–N(1)#4	2.127(6)
Mo(2)–O(5)	1.729(5)	Co(2)–O(6)#5	2.044(5)
Mo(2)–O(6)	1.742(5)	Co(2)–O(6)#3	2.044(5)
Mo(2)–O(7)	1.764(5)	Co(2)–O(3)#6	2.088(5)
Mo(2)–O(4)	1.962(5)	Co(2)–O(3)	2.088(5)
Mo(2)–N(2)#1	2.306(6)	Co(2)–N(3)	2.194(6)
Co(1)–O(7)#2	2.088(5)	Co(2)–N(3)#6	2.194(6)
O(1)–Mo(1)–O(3)	108.5(3)	O(6)–Mo(2)–N(2)#1	83.3(2)
O(1)–Mo(1)–O(2)	107.8(3)	O(7)–Mo(2)–N(2)#1	81.6(2)
O(3)–Mo(1)–O(2)	109.9(3)	O(4)–Mo(2)–N(2)#1	178.5(2)
O(1)–Mo(1)–O(4)	108.8(2)	O(7)#2–Co(1)–O(2)	87.0(2)
O(3)–Mo(1)–O(4)	110.3(3)	O(7)#3–Co(1)–O(2)	93.0(2)
O(2)–Mo(1)–O(4)	111.3(2)	O(7)#2–Co(1)–N(1)	94.0(2)
O(5)–Mo(2)–O(6)	117.9(3)	O(7)#3–Co(1)–N(1)	86.0(2)
O(5)–Mo(2)–O(7)	116.7(3)	O(2)–Co(1)–N(1)	90.9(2)
O(6)–Mo(2)–O(7)	120.0(2)	O(2)#4–Co(1)–N(1)	89.1(2)
O(5)–Mo(2)–O(4)	97.1(2)	O(6)#5–Co(2)–O(3)	88.8(2)
O(6)–Mo(2)–O(4)	98.2(2)	O(6)#3–Co(2)–O(3)	91.2(2)
O(7)–Mo(2)–O(4)	98.0(2)	O(6)#5–Co(2)–N(3)	91.9(2)
O(5)–Mo(2)–N(2)#1	81.8(2)	O(6)#3–Co(2)–N(3)	88.1(2)

Symmetry transformations used to generate equivalent atoms: #1: $x+2$, $y+1$, z; #2: $-x+2$, $-y$, $-z+1$; #3: $x-1$, y, z; #4: $-x+1$, $-y$, $-z+1$; #5: $-x+2$, $-y$, $-z$; #6: $-x+1$, $-y$, $-z$.

3. Structural description and discussion

3.1. *Synthesis*

In the $Co(COO)_2 \cdot 4H_2O$–MoO_3–H_3PO_4-4,4′-bipy reactant system, H_3PO_4 is used to keep the pH value ca 5; replacing H_3PO_4 by HCl or HF also gave the title compound, the known $H_3PMo_{12}O_{40}$ was obtained at pH = 3; while an unknown compound was formed when pH = 8.0.

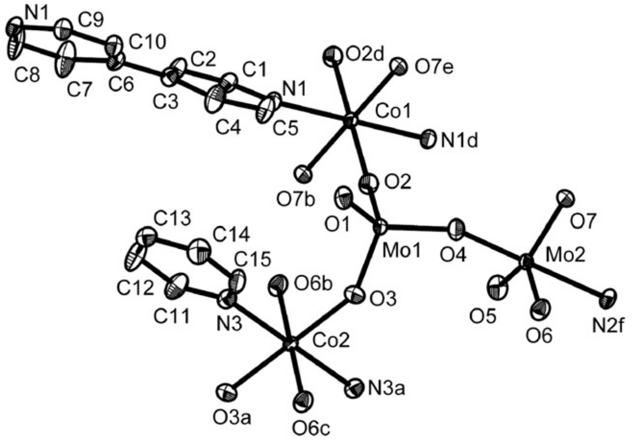

Figure 1. Thermal ellipsoid plot (50% probability) and atomic labeling scheme for the asymmetrical unit of **1**. a: $1-x$, $-y$, $-z$; b: $-1+x$, y, z; c: $2-x$, $-y$, $-z$; d: $1-x$, $-y$, $-z$; e: $2-x$, $-y$, $1-z$; f: $2+x$, $1+y$, z.

3.2. *Structural description*

Single-crystal X-ray diffraction analysis reveals that **1** has a 3D framework which consists of Co/Mo/O layers linked by coordination of 4,4′-bipy with Co and Mo atoms.

In the asymmetric unit of **1**, there are two independent molybdenum and two cobalt atoms, (figure 1) Mo1 and Mo2, respectively, reside in tetrahedral and triangular-bipyramidal environments, which are linked together corner-sharing. The tetrahedral geometry of Mo1 is defined by one terminal O, three μ_2-O atoms from adjacent $Mo(2)O_4N$, $Co(1)O_4N_2$ and $Co(2)O_4N_2$ (Mo–O 1.721(5)–1.848(5) Å), while the triangular-bipyramidal geometry of Mo2 atom is defined by a terminal O, two μ_2-O atoms from $Co(1)O_4N_2$ and $Co(2)O_4N_2$ octahedra in the equatorial plane (Mo–O 1.729(5)–1.764(5) Å), and a oxygen donor from $Mo(1)O_4$ and a nitrogen donor of 4,4′-bipy in axial positions (Mo–O 1.962(5) Å; Mo–N 2.306(6) Å). Two crystallographic dependent Co sites both have half occupation of sites, octahedrally coordinated by two μ_2-oxo donors of two $Mo(1)O_4$ (Co1–O 2.088(5)–2.100(5) Å; Co2–O 2.044–2.088 Å), two μ_2-oxo donors of two $Mo(2)O_4N$, and two N donors from 4,4′-bipy (Co1–N 2.127(6) Å; Co2–N 2.194(6) Å). Bond valence sum calculation [20] confirmed that Mo1 and Mo2 are both hexavalent.

The molybdenum oxide subunit is present as $\{Mo_2O_7\}$ in the Co/Mo/O layer as shown in figure 2. Each dimolybdate moiety is linked to four adjacent Co sites, and each Co site bridges four neighboring dimolybdate subunits to form a wrinkled $[CoMo_2O_7]$ layer. The $\{CoMo_2O_7\}$ layer in **1** is quite different from the $\{NiMo_2O_7\}$ layer found in the $[Ni(tpytrz)Mo_2O_7]$ [21] by Zubieta *et al.*, although they have similar building blocks and connections. In **1**, $\{Mo_2O_7\}$ units are arranged along the same direction, which results in a $[4^2,6^2]$ topology. However, $\{Mo_2O_7\}$ units in the $[NiMo_2O_7]$ layer are arranged along two vertical directions, resulting in a $[5^4]$ topology. The $\{Mo_2O_7\}$ unit in **1** is different from the common $\{MoO_4\}$ tetrahedron [14–17] due to one Mo atom being five coordinated through coordination with an N atom of 4,4′ bipy.

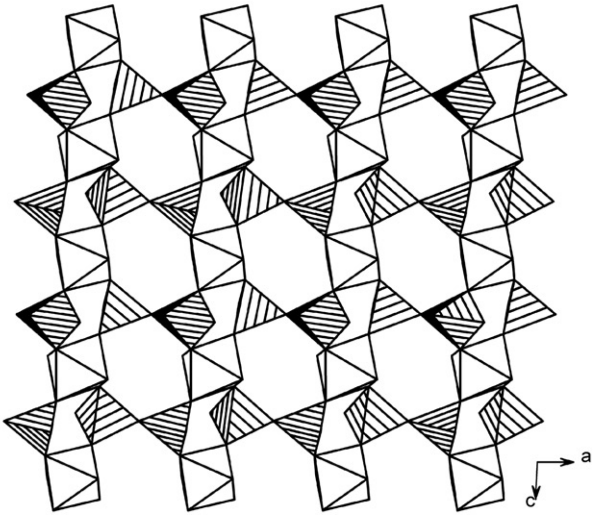

Figure 2. Polyhedral representation for bimetal Co/Mo/O inorganic layer in **1**. White octahedra, CoO_6; Hatched polyhedra, MoO_4N and MoO_4.

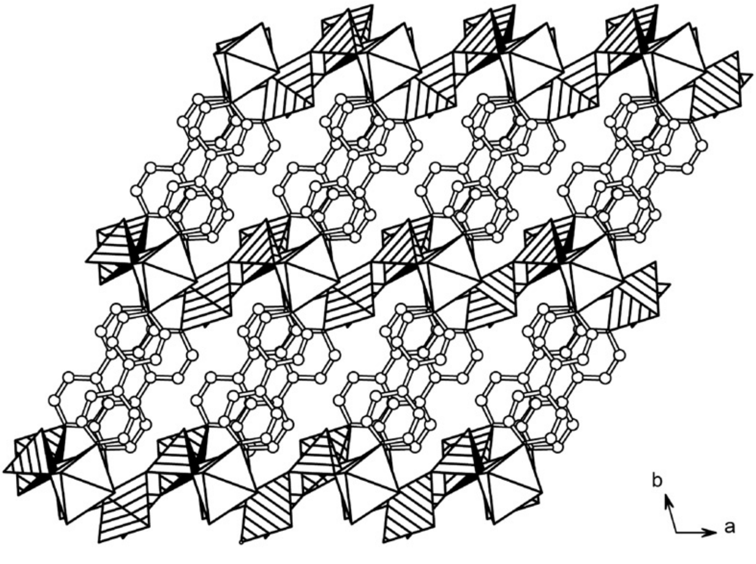

Figure 3. 3D inorganic–organic open-framework for **1** viewed along the *c*-axis. White octahedra, CoO_6; Hatched polyhedra, MoO_4N and MoO_4.

These Co/Mo/O layers are further linked through 4,4′-bipy groups into a three-dimensional covalently bonded metal oxide-organic ligand framework as shown in figure 3. The overall structure of $[CoMo_2O_7(4,4'\text{-bipy})_{1.5}]$ may be described in terms of alternating inorganic metal oxide layers and organic layers. In this hybrid framework, two different coordination modes for 4,4′-bipy are found (figure 4). In mode I, the 4,4′-bipy is planar and its two N donors directly coordinated to the Co2

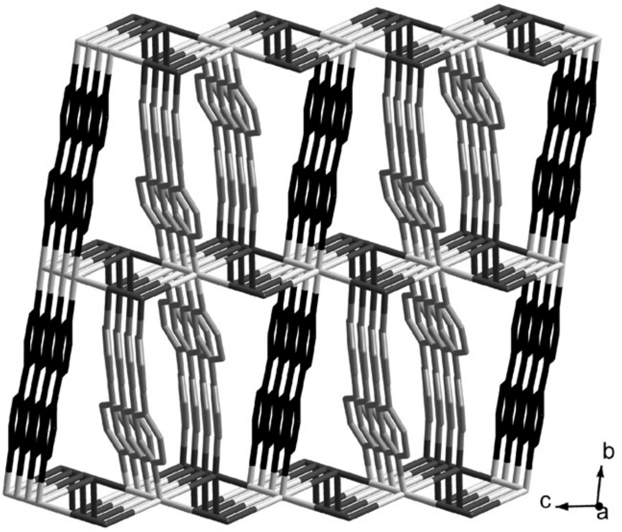

Figure 4. Stick representation for the open-framework of **1** with two coordination modes of 4,4′-bipy ligand. White, Co. Dark gray, Mo. Black, the 4,4′-bipy ligand coordinated to Co centers; light gray, the 4,4′-bipy ligand coordinated to Co and Mo centers.

sites in the Co/Mo/O layers to form a 3D hybrid framework with square channels (11.45 × 11.52 Å). While in mode II, two aryl rings of 4,4-bipy are twisted with the angle of 5.4°, and its two N donors coordinate Co1 and Mo2. Because of mode II, the square channels are subdivided into three narrow windows. A 4,4′-bipy coordinating to two different kinds of metal centers is rare in the M/Mo/O/ligand systems (M = transition metal).

3.3. *IR spectrum*

The infrared spectra of **1** exhibited a strong band in the 903 cm^{-1} range attributed to ν(Mo=O). Medium-intensity features in the 780–850 cm^{-1} region are tentatively attributed to ν(Mo–O–Mo) and ν(Co–O–Mo). A series of medium intensity bands in the 1000–1600 cm^{-1} region are associated with the organodimine ligands.

3.4. *TG analysis*

The good thermal stability of **1** is shown in figure 5 by TGA experiment. There is no noticeable weight loss up to 370°C. The compound decomposes in the temperature range 370–940°C in two steps. The first weight loss (39.63%) in the 370–450°C temperature range corresponds to the release of all 4,4′-bipy ligand (calculated 39.47%). The second weight loss after 700°C corresponds to the phase transformation of inorganic components, and the residue is confirmed as $CoO \cdot MoO_3$ (found 36.76%, Calcd 36.65%).

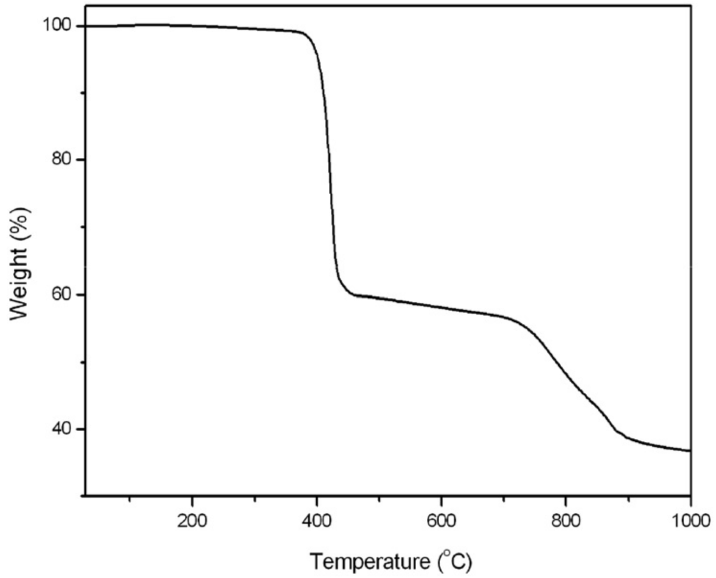

Figure 5. Thermal gravimetric curve for **1**.

4. Conclusion

We report synthesis and crystal structure of a new cobalt molybdate [$CoMo_2O_7(4,4'\text{-}bipy)_{1.5}$] with open-framework. Its structure consists of Co/Mo/O layers with [Mo_2O_7] units, linked by coordination of 4,4′-bipy ligand with Co and Mo atoms, into a 3D porous hybrid framework. The structural type presented by this compound shows that connection of building blocks and secondary metal, the ligand-to-metal ratio, and the length of spacer group between the amine nitrogen donors have profound effects on the microstructures.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Reference No. 619147. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223/336 033; Email: deposit@ccdc. cam.ac.uk).

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