Inorg. Chem. **2003**, *42*, 6956–6958

Inorganic Chemistry
Communication

A Novel Three-Dimensional Network Constructed from Tetramolybdate Clusters Linked via Two Types of Copper Complex Fragments: Synthesis, Characterization, and Magnetic Behavior of $[\{Cu^{II}(2,2'\text{-bpy})\}\{Cu^{II}(IN)_2\}\{Mo_4O_{12}(OH)_2\}]$

Jian Lü, Enhong Shen, Mei Yuan, Yangguang Li, Enbo Wang,* Changwen Hu, Lin Xu, and Jun Peng

Institute of Polyoxometalate Chemistry, Department of Chemistry, Northeast Normal University, Changchun, 130024 P. R. China

Received July 1, 2003

A novel three-dimensional copper molybdate with mixed ligands, $[\{Cu^{II}(2,2'\text{-bpy})\}\{Cu^{II}(IN)_2\}\{Mo_4O_{12}(OH)_2\}]$ (IN^- = isonicotinate ion, 2,2′-bpy = 2,2′-bipyridine), **1**, has been hydrothermally synthesized and structurally characterized, and this compound is built from an unprecedented tetranuclear molybdenum oxide cluster covalently bonded to two types of copper complex fragments, $\{Cu^{II}(2,2'\text{-bpy})\}^{2+}$ and $\{Cu^{II}(IN)_2\}$, via terminal oxygen atoms of $\{MoO_6\}$ octahedra. Crystal data for compound **1**: monoclinic, space group *C*2/*c*, $a = 16.4755$ Å, $b = 10.3714$ Å, $c = 17.4382$ Å, $\alpha = 90.0000°$, $\beta = 94.8098°$, $\gamma = 90.0000°$; $V = 2969.24$ Å^3; $Z = 2$. Variable temperature magnetic susceptibility indicates that both ferromagnetic and antiferromagnetic interactions exist in **1**.

The widespread contemporary interest in inorganic−organic hybrid compounds has been focused on their vast compositional range and structural diversity.[1] Meanwhile, polyoxometalates (POMs)[2] are of great interest in the fields of catalysis and material science[3] as well as in biology, magnetism, nonlinear optics, and medicine.[4] Therefore, new inorganic−organic hybrid materials based on POMs are expected to be endowed with enhanced or combined functionalization because of their unique features of both organic and inorganic substructures.[1,5] In recent years, the design of inorganic−organic hybrid POMs made architectures possible that contribute to the increasing understanding of the methods that control the synergistic interaction between organic and inorganic chemical compositions.[6] One promising approach for the design and synthesis of such kinds of solid materials is to introduce secondary metal−organic complexes into polyoxometalate substructures via covalent bonds.[7,8] It is reviewed by Zubieta and co-workers that polyoxomolybdate anions can be modified efficiently by metal−organonitrogen complexes to generate hybrid materials with particularly attractive prospects.[6] During the studies of such kinds of solid materials, an astonishing variety of novel phases with discrete or polymeric structures based on molybdenum oxide clusters have been isolated hydrothermally.[7−15] To date, the polyanions in these solids are limited to $\{Mo_6O_{19}\}$[9,10] (or $\{Mo_6O_nN_{19-n}\}$[11,12]) and $\{Mo_8O_{26}\}$[9,13] clusters. Hybrid solid-

---

* To whom correspondence should be addressed. E-mail: wangenbo@public.cc.jl.cn.

(1) Kressge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuni, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(2) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer: Berlin, 1983.

(3) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34.

(4) Hill, C. L. *Chem. Rev.* **1998**, *98*, 327.

(5) (a) Coronado, E.; Gómez-García, C. J. *Chem. Rev.* **1998**, *98*, 273. (b) Huang, X.-Y.; Li, J.; Fu, H.-X. *J. Am. Chem. Soc.* **2000**, *122*, 8789.

(6) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.

(7) (a) Xu, Y.; Lu, J. J.; Goh, N. K. *J. Mater. Chem.* **1999**, *9*, 1599. (b) Modec, B.; Brenčič, J. V.; Golič, L.; Giester, G. J. *Inorg. Chim. Acta* **2000**, *307*, 32. (c) Tao, J.; Zhang, X. M.; Tong, M. L.; Chen, X. M. *J. Chem. Soc., Dalton Trans.* **2001**, 770. (d) Liu, C. M.; Zhang, D. Q.; Xiong, M.; Zhu, D. B. *Chem. Commun.* **2002**, 1416.

(8) (a) Yuan, M.; Li, Y. G.; Wang, E. B.; Lu, Y.; Hu, C. W.; Hu, N. H.; Jia, H. Q. *J. Chem. Soc., Dalton Trans.* **2002**, 2916. (b) Li, Y. G.; Hao, N.; Wang, E. B.; Yuan, M.; Hu, C. W.; Hu, N. H.; Jia, H. Q. *Inorg. Chem.* **2003**, *42*, 2729.

(9) (a) Hagrman, D.; Hagrman, P.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *300−302*, 212. (b) Hagrman, D.; Zapf, P. J.; Zubieta, J. *Chem. Commun.* **1998**, 1283.

(10) Wang, X. L.; Guo, Y. Q.; Li, Y. G.; Wang, E. B.; Hu, C. W.; Hu, N. H. *Inorg. Chem.* **2003**, *42*, 4135.

(11) (a) Kwen, H.; Young, V. G., Jr.; Maatta, E. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 145. (b) Moore, A. R.; Kwen, H. Beatty, A. M.; Maatta, E. A. *Chem. Commun.* **2002**, 1793.

(12) (a) Spandl, J.; Daniel, C.; Brüdgam, I.; Hartl, H. *Angew. Chem., Int. Ed.* **2003**, 42, 1163. (b) Xu, L.; Lu, M.; Xu, B. B.; Wei, Y. G.; Peng, Z. H.; Powell, D. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 4129.

(13) (a) Xu, J. Q.; Wang, R. Z.; Wang, G. Y.; Xing, Y. H.; Li, D. M.; Bu, M. H.; Ye, L.; Fan, Y. G.; Xing, Y.; Lin, Y. H.; Jia, H. Q. *Chem. Commun.* **1999**, 983. (b) Wang, X. J.; Kang, B. S.; Su, C. Y.; Yu, K. B.; Zhang, H. X.; Chen, Z. N. *Polyhedron* **1999**, *18*, 3371. (c) Zapf, P. J.; Warren, C. J.; Haushalter, R. C.; Zubieta, J. *Chem. Commun.* **1997**, 1543.

(14) (a) La Duca, R. L., Jr.; Desciak, M.; Laskoski, M.; Rarig, R. S., Jr.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **2000**, 2255. (b) Hagrman, P. J.; Zubieta, J. *Inorg. Chem.* **2000**, *39*, 5218. (c) Guillou, N.; Ferey, G.; Whittingham, M. S. *J. Mater. Chem.* **1998**, *8*, 2277.

(15) (a) Yang, W. B.; Lu, C. Z.; Zhuang, H. H. *J. Chem. Soc., Dalton Trans.* **2002**, 2879. (b) Hagrman, D.; Sangregorio, C.; O'Connor, C. J.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **1998**, 3707. (c) Yuan, M.; Li, Y. G.; Wang, E. B.; Tian, C. G.; Wang, L.; Hu, C. W.; Hu, N. H.; Jia, H. Q. *Inorg. Chem.* **2003**, *42*, 3670.

10.1021/ic034752g CCC: $25.00

state materials based on tetramolybdate are rare.[14] On the other hand, these inorganic−organic hybrid molybdates mostly exhibit one- or two-dimensional (1-D or 2-D) structures; three-dimensional (3-D) networks constructed from polyoxomolybdate clusters covalently bonded from transition metal complexes have been rarely reported.[16] Therefore, it remains a great challenge to prepare new POM-based solid materials with high-dimensional structures. Moreover, a potential advance in the preparation of inorganic−organic hybrid materials is to introduce more than one type of organic molecule with a distinctive linking manner and coordination preference into the inorganic substructures in constructing inorganic−organic hybrid materials with remarkable structural features and attractive properties.

A noticeable tridentate ligand, which has recently shown interesting properties in constructing extended structures, is the isonicotinate anion (IN^-).[17,18] IN^- contains both a pyridyl group and a carboxylate group in the opposite position of an aromatic ring. It can connect metal ions with its one nitrogen donor and one or two oxygen donors. Several intriguing high-dimensional structures have been obtained by introducing the isonicotinato ligand and other bridging ligands into a single structure.[18,19]

In this work, by the introduction of this distinctive organonitrogen ligand via hydrothermal technology, we got a novel compound $[\{Cu^{II}(2,2'\text{-bpy})\}\{Cu^{II}(IN)_2\}\{Mo_4O_{12}(OH)_2\}]$, **1**,[20] which is built from an unprecedented tetranuclear molybdenum oxide cluster covalently bonded to two types of copper complexes. To the best of our knowledge, this is the first example of a 3-D inorganic−organic hybrid polyoxomolybdate containing two types of transition metal complex fragments.

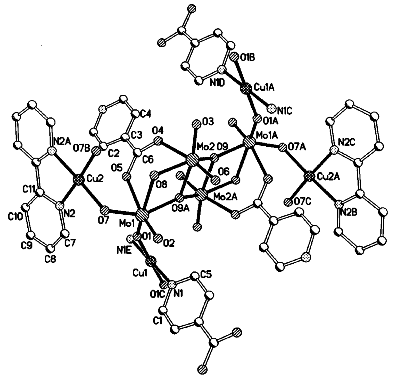

Figure 1. Structure of the fundamental building block of compound **1**. Only parts of atoms are labeled, and all the hydrogen atoms are omitted for clarity.

The X-ray diffraction analysis reveals that the structure of **1** is based on the individual $\{Mo_4O_{18}\}$ clusters linked through $\{Cu(IN)_2\}$ fragments generating a 2-D network, which is extended into a 3-D framework by means of the covalent bridging of $\{Cu(2,2'\text{-bpy})\}^{2+}$ complexes. The fundamental building block of **1** is shown in Figure 1. The $\{Mo_4O_{18}\}$ cluster can be described as a nonlinear unit, which consists of four corner- and edge-sharing distorted $\{MoO_6\}$ octahedra with Mo−O distances in the range 1.686(5)−2.329(5) Å and the bond angles in the range 72.59(16)−170.0(2)°. The valence sum calculations[21] give the values 6.04 for Mo(1) (2×), 6.06 for Mo(2) (2×), and 1.15 for O(8) (2×). The calculated results reveal that, in the structure of **1**, all the Mo centers are in +6 oxidation state and two O atoms are protonated in the need of the charge balance. There are two crystallographically unique Cu atoms in the asymmetric unit, and both are coordinated in square-planar geometry: The Cu(1) atom links to two nitrogen donors from two isonicotinato ligands and two oxygen atoms from two $\{MoO_6\}$ octahedra belonging to two $\{Mo_4O_{18}\}$ clusters with a Cu−N distance of 1.988(6) Å and Cu−O distance of 1.941(4) Å, respectively; Cu(2) is coordinated to two nitrogen donors of a 2,2′-pyridine ligand with a Cu−N distance of 2.006(6) Å and two oxygen atoms from two $\{MoO_6\}$ octahedra being part of two $\{Mo_4O_{18}\}$ clusters with a Cu−O distance of 1.948(5) Å. Cu(1) and Cu(2) are further connected by sharing a $\{MoO_6\}$ octahedron in the building block.

Interestingly, each nonlinear tetranuclear molybdenum cluster is associated with two copper atoms via bridging oxygen atoms, and extended in the copper sites where each Cu atom bonds to the two nitrogen donors from two isonicotinato ligands located in the opposite position. Two oxygen donors from the carboxyl group of each isonicotinato ligand in turn combine covalently to two Mo centers of a neighboring $\{Mo_4O_{18}\}$ cluster (see Figure 2a). Alternatively, every $\{Mo_4O_{18}\}$ cluster links to four $\{Cu(IN)_2\}$ fragments and each $\{Cu(IN)_2\}$ moiety combines with four $\{Mo_4O_{18}\}$ clusters generating a regular 2-D network. Furthermore, adjacent $\{Cu(IN)_2Mo_4O_{12}(OH)\}_n^{2n-}$ layers are connected by $\{Cu(2,2'\text{-bpy})\}^{2+}$ fragments as a third kind of bridge through terminal O atoms of $\{Mo_4O_{18}\}$ clusters (Figure 2b). It is interesting that the adjacent 2-D layers extend perpendicularly to each other, as shown in Scheme S1, exhibiting an ABAB mode.

Tetranuclear molybdenum oxide clusters have been reported in several organic−inorganic hybrid compounds;[14] however, the discrete tetranuclear cluster has not been observed in the polyoxomolybdate chemistry hitherto.[14b]

---

[16] Wu, C. D.; Lu, C. Z.; Zhuang, H. H.; Huang, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 3836.

[17] (a) Evans, O. R.; Xiong, R. G.; Wang, Z.; Wong, G. K.; Lin, W. *Angew. Chem., Int. Ed.*. **1999**, *38*, 536. (b) Tong, M.-L.; Li, L.-J.; Mochizuki, K.; Chang, H.-C.; Chen, X.-M.; Li, Y.; Kitagawa, S. *Chem. Commun.* **2003**, 428.

[18] Lu, J. Y.; Babb, A. M. *Inorg. Chem.* **2001**, *40*, 3261.

[19] (a) MacGillivray, L. R.; Groeneman, R. H.; Atwood, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 2676. (b) Fu, Z. Y.; Wu, X. T.; Dai, J. C.; Wu, L. M.; Cui, C. P.; Hu, S. M. *Chem. Commun.* **2001**, 1856. (c) Gheorghe, R.; Andruh, M.; Müller, A.; Schmidtmann, M. *Inorg. Chem.* **2002**, *41*, 5314.

[20] Compound **1** was hydrothermally synthesized from the reaction of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $CuCl_2\cdot H_2O$, isonicotinic acid, 2,2′-pyridine, and H_2O in a molar ratio of 1:5:3:2:555 under autogenous pressure at 160 °C for 4 days. After cooling to room temperature, the sapphire-colored tetra-prism crystals of **1** were isolated as a major phase (70% yield on Mo) from the pale-yellow slurry, then washed with distilled water, and dried at ambient temperature. The crystals were manually selected for structural determination and further characterization. Anal. Calcd for **1**: C, 23.23; H, 1.60; N, 4.93; Cu, 11.18; Mo, 37.74 (%). Found: C, 22.07; H, 1.65; N, 4.91; Cu, 11.06; Mo, 37.82 (%). A summary of the crystallographic data and structural determination for compound **1** is provided in Table S1. Selected bond lengths and angles are listed in Table S2. CCDC-211193 contains the supplementary crystallographic data for this paper.

[21] Brwon, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

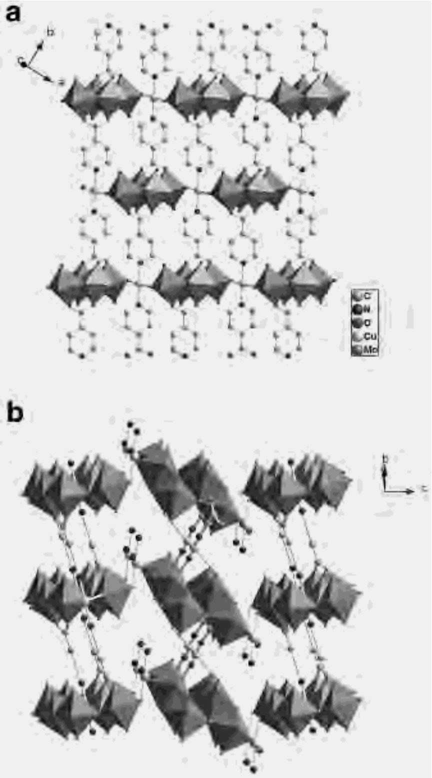

Figure 2. (a) Polyhedral representation of individual 2-D network of compound **1**. The polyhedra represent {MoO_6} octahedra. (b) Polyhedral representation of the 3-D framework of compound **1**. For the sake of clarity, all the hydrogen atoms and the carbon atoms from the 2,2′-bpy ligands are omitted, and the pyridyl groups of the isonicotinato ligands are shown as bold lines.

Therefore, the preparation of a new tetramolybdate cluster is of great significance for the continuing research on this point. The {Mo_4O_{18}} cluster in **1** is quite distinct from the reported precursors: (i) the tetranuclear molybdenum cluster in [{Ni(3,3′-bpy)$_2$}$_2$$Mo_4O_{14}$] consists of two {$MoO_6$} octahedra and two {$MoO_5$} distorted trigonal bipyramids in an edge-sharing arrangement;[14a] (ii) the {Mo_4O_{14}}$^{4-}$ cluster in [Cu(terpy)Mo_2O_7] is constructed from four edge- and corner-sharing {MoO_5} distorted square pyramids;[14b] (iii) in the compound ($C_2H_{10}N_2$)[Mo_4O_{12}], the {Mo_4O_{16}} unit is composed of two Mo^{VI} and two Mo^{V} edge-sharing molybdenum octahedra.[14c] This is mostly because carboxyl groups of the isonicotinato ligands coordinate directly to the Mo centers affording additional oxygen donors leading to the formation of the unprecedented tetranuclear molybdate clusters. It can be proved that the tetramolybdate cluster is the same, if the carboxyl oxygen atoms were removed, as the {Mo_4O_{14}} cluster in [Cu(terpy)Mo_2O_7].[14b] It is also believed that the organic molecules, especially the carboxyl-containing components, play a critical role in the construction of this unusual compound.

The EPR spectrum of **1** at room temperature shows a Cu^{2+} signal with $g_\perp = 2.065$, $g_\parallel = 2.164$ (see Figure S5),[22] in good accordance with the valence sum calculations.

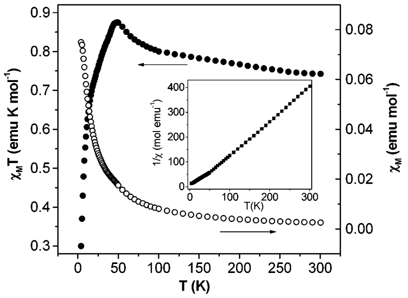

Figure 3. Thermal variation of $\chi_m T$ and $1/\chi_m$ for compound **1**.

The experimental and simulated XRPD pattern of compound **1** is shown in Figure S3. Their peak positions are in good agreement with each other, indicating the phase purity of the products.

The thermal variations of χ_m, $\chi_m T$, and $1/\chi$ of compound **1** are displayed in Figure 3. The plot of $\chi_m T$ versus T exhibits a value of 0.74 emu K mol^{-1} at 300 K, and continuously increases on cooling to a value of 0.87 emu K mol^{-1} at 46 K. This behavior of the $\chi_m T$ curve shows that there exist ferromagnetic interactions in **1**. However, the curve drops abruptly below 46 K, indicating that an antiferromagnetic interaction exists in **1** at lower temperatures. The inverse susceptibility plot as a function of temperature is linear, closely following the Curie–Weiss law with $C = 0.75$ emu K mol^{-1}, corresponding to about one $S = {}^1/_2$ spin per formula unit with $g = 2.136$ for Cu(II) centers. The effective magnetic moment at 300 K, 1.85 μ_B, is in the range of experimentally observed values for Cu(II) ions. The Weiss temperature $\theta = 1.913$ K, indicating that there exist predominantly ferromagnetic interactions in **1**. According to the crystal structure of **1**, it can be assumed that the magnetic behavior of **1** may be due to the superexchange interactions between Cu(1) and Cu(2) centers through a {MoO_6} octahedron. It could be further presumed that the unpaired electrons in the Cu(II) ions might have the same spin direction above 46 K (T_N), resulting in the ferromagnetic interactions, while the antiferromagnetic interactions below T_N might be due to the cancellation of spin.

In summary, we have prepared and structurally characterized a novel inorganic–organic hybrid copper molybdate with mixed ligands. The successful preparation of **1** indicates that the introduction of mixed organic ligands is an optional route for the construction of novel high-dimensional inorganic–organic hybrid polyoxometalates with unique structures and remarkable properties. Future research may focus on attempting to explore the effects of transition metal–organic fragments on the reaction systems.

Acknowledgment. The authors thank the National Natural Science Foundation of China (20171010) for financial support.

Supporting Information Available: X-ray crystallographic files in CIF format for **1**. Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034752G

---

[22] Beyer, L.; Kimse, R.; Stach, J.; Szargan, R.; Hoyer, E. *Z. Anorg. Allg. Chem.* **1981**, *476*, 7.