Two new organo-inorganic octamolybdate anion-based materials: hydrothermal synthesis and structure of complexes $[\{Cu(4,4'\text{-bipy})\}_4(Mo_8O_{26})]$ and $(NH_4)_{10}Mn(H_2O)_6[(NH_2C_6H_4COO)_2(Mo_8O_{26})]_2 \cdot 15H_2O$

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Two new hybrid organo-inorganic compounds $[\{Cu(4,4'\text{-bipy})\}_4(Mo_8O_{26})]$ (bipy is bipyridyl) (**1**) and $(NH_4)_{10}Mn(H_2O)_6[(NH_2C_6H_4COO)_2(Mo_8O_{26})]_2 \cdot 15H_2O$ (**2**) were prepared under mild hydrothermal conditions and structurally characterized by single-crystal X-ray diffraction. A new type of one-dimensional network consisting of four linear chains Cu—4,4′-bipy and isolated α-octamolybdate anions was found in the complex **1** structure. Complex **2** is the first example of molybdenum oxide with a template structure involving 4-aminobenzoic acid.

Key words: octamolybdate, hydrothermal synthesis, crystal structure.

Hybrid organo-inorganic compounds based on metal oxides are of great interest because of their hierarchical structure, possible application in catalysis and sorption, and as optically, electrically, and magnetically active materials.[1] Therefore, the development of new materials and the rational construction of such solid oxides is an urgent task. The incorporation of organic subunits in the structure of inorganic oxide phases provides an efficient method for the structural modification and synthesis of novel organo-inorganic hybrid compounds.[2] A number of organo-inorganic hybrid metal oxide compounds based on transition metal coordination compounds, for example $[M(4,4'\text{-bipy})(VO_2)_2(HPO_4)_4]$ (M is Co, Ni; bipy is bipyridyl),[3] $[Ni(2,2'\text{-bipy})_3]_{1.5}[Ni(2,2'\text{-bipy})_2(H_2O)(PW_{12}O_{40})] \cdot 0.5H_2O$,[4] and $[Cu(bpe)(MoO_4)]$ (bpe is 1,2-*trans*-bis(4-pyridyl)ethylene),[5] have been synthesized over the past few years. Organic components of these solid oxides are not only structure-forming cations but also ligands directly bound to an inorganic framework. Studies of molybdenum oxides structured as templates with organic diamines have been reviewed.[6]

Among various molybdenum oxide structures, different structural isomers of the octamolybdate family such as α-, β-, and γ-octamolybdates,[7] δ-isomer in the complexes $[(\eta\text{-}C_5Me_5Rh)_2(\mu\text{-}SMe)_3]_4[(Mo_8O_{26})] \cdot 2CHCN$ [8] and $[\{Cu(4,4'\text{-bipy})\}_4Mo_8O_{26}]$,[9] ε-isomer in the complex $[\{Ni(H_2O)_2(4,4'\text{-bipy})_2\}_2Mo_8O_{26}]$,[9] and ξ-isomer in the complexes $[\{M(phen)_2\}(\xi\text{-}Mo_8O_{26})]$ (M is Ni or Co; phen is 1,10-phenantrolin)[10] are of most interest. Such isomeric octamolybdates are universal structural blocks for the formation of organo-inorganic hybrid materials with specified properties.[11] Recent studies[6] showed that the hydrothermal synthesis under relatively low temperature (110—260 °C) and pressure is the efficient method for the introduction of organic ligands to inorganic oxides. A number of substances based on octamolybdates thus obtained and contained N-donor ligands have been reported. In this work, we describe the synthesis and structures of two low-dimemtional hybrid solids: the chain compound $[\{Cu(4,4'\text{-bipy})\}_4(Mo_8O_{26})]$ (**1**) and the discrete compound $(NH_4)_{10}Mn(H_2O)_6[(NH_2C_6H_4COO)_2(Mo_8O_{26})]_2 \cdot 15H_2O$ (**2**).

Discussion

Synthesis. Since the low-temperature hydrothermal synthesis depends on "self-assembly" and therefore frequently produces multiphase products or suffers from problems such as poor yields and reproducibility, compound **1** was obtained in low yield (17%). Our attempts to improve the yield by variation the conditions of hydrothermal synthesis (stoichiometry, reaction temperature, pH *etc.*) produced a blue uniform slurry or a black powder only. Meanwhile, when the isopolymolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was introduced in the reaction system, the crystals of **1** were obtained in higher yield (68%). This can be due to the fact that isopolymolybdate can slowly release molybdenic species, favoring the formation of large monocrystals. It is also impor-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1767—1772, August, 2005.

1066-5285/05/5408-1819

tant that when complex **1** is formed, Cu^{2+} ion is reduced. The 4,4′-bipy molecule in the composition of complex **1** can operate as an efficient reducing agent for Cu^{2+} to Cu^{+}, whereas the reduced ion Cu^{+} is coordinated to another 4,4′-bipy molecule, forming the complex cation $[Cu(4,4'\text{-bipy})]^{+}$. It is known[12] that metals in the high oxidation states are reduced by organic amines under the conditions of hydrothermal synthesis. Compounds **1** and **2** are insoluble in water and most organic solvents. IR spectra of compounds **1** and **2** exhibit characteristic bands for Mo=O and Mo—O—Mo groups (939—538 cm^{-1}). The ESR spectrum of **2** was recorded at room temperature, giving a *g* value of 2.0012 and a peak-to-peak linewidth of 467 G. This g value is characteristic of octahedrally coordinated Mn^{2+} ion.[13]

Crystal structure. Crystal **1** consists of separate α-octamolybdate anions $[Mo_8O_{26}]^{4-}$ and four infinite one-dimensional straight chains $[Cu(4,4'\text{-bipy})]_n^{n+}$ (Fig. 1). α-Isomer of octamolybdate has been found previously as a structural fragment in the complexes $[\{Cu(bpe)\}_4(\alpha\text{-}Mo_8O_{26})]\cdot 2H_2O$,[14] $[Cu(dpp)]_2[Cu_2(\alpha\text{-}Mo_8O_{26})(dpp)_2]\cdot 2H_2O$ (dpp is 4,4′-trimethylenepyridine)[15] and $[\{Cu(py)_3\}_2\{Cu(py)_2\}_2(\alpha\text{-}Mo_8O_{26})]$ (py is pyridyne).[12a] The structure is constructed from six edge- and corner-sharing $\{MoO_6\}$ octahedra and two $\{MoO_4\}$ tetrahedra. The overall cluster geometry may be depicted as six edge-sharing $\{MoO_6\}$ octahedra comprising the equatorial ring and capped on both poles by corner-sharing $\{MoO_4\}$ tetrahedra. Thus, each $\{MoO_6\}$ octahedra is engaged in an edge-sharing interaction with an adjacent octahedron, along with corner-sharing interactions with two capping tetrahedra. The capping tetrahedra participate in three corner-sharing interactions with the octahedral sites to leave a single terminal oxo group. The three bridging oxo groups are μ_2-bridges between the edge-sharing sets of octahedra.

It is more interesting that in the structure of crystal **1** there are four one-dimensional linear chains around the

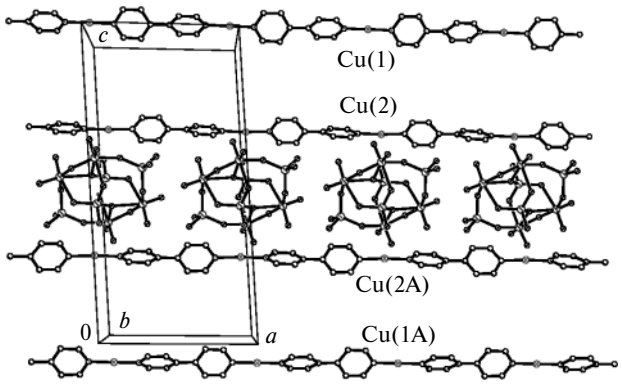

Fig. 1. Molecular structure of complex **1** displaying the incorporation of the $[Mo_8O_{26}]^{40-}$ anions between the Cu—4,4′-bipy chains. All H atoms are omitted.

α-octamolybdate anions $[Mo_8O_{26}]^{4-}$. The crystallographically independent Cu(1) and Cu(2) atoms have a similar coordination environment CuN_2, each atom being linked with 4,4′-bipy ligands to form one-dimensional chains along the *a* axis. The dihedral angle between two pyridine rings of the 4,4′-bipy ligand in the Cu(1)—4,4′-bipy chain is 33.5°, and the separation between the adjacent Cu(1)···Cu(1) atoms is 10.813 Å. The dihedral angle between two pyridine rings of the 4,4′-bipy ligand in the Cu(2)—4,4′-bipy chain is 34.7°, and the distance Cu(2)···Cu(2) is also 10.813 Å. The distance Cu(1)···Cu(2) between two chains Cu—4,4′-bipy is 8.489 Å. The overall structure can be represented as four Cu-4,4′-bipy chains encapsulating the discrete α-octamolybdate anions.

It is worthwhile to point out a hydogen bond between the chains Cu—4,4′-bipy and inorganic α-octamolybdate clusters: the distances C—H···O are 3.08(2)—3.34(2) Å and the corresponding angles C—H···O are 136.1—173.7° (Table 1). As can be seen in Fig. 2, the molecular structure of **1** is a three-dimensional supramolecular network.

It is known that 4-aminobenzoic acid has been extensively studied in coordination chemistry as a bifunctional organic ligand because of a variety of its coordination modes.[16] In view of this point, we have recently attempted to incorporate the 4-aminobenzoic acid into the molybdenum oxide backbone and successfully isolated a new organo-inorganic hybrid product **2**. To the best of our knowledge, this is the first example of 4-aminobenzoic acid templated molybdenum oxide.

The crystal of **2** consists of the organo-inorganic hybrid anions $[(NH_2C_6H_4COO)_2(Mo_8O_{26})]^{6-}$, $[Mn(H_2O)_6]^{2+}$ and NH_4^{+} cations, and lattice water molecules (Fig. 3). The cluster $[(NH_2C_6H_4COO)_2(Mo_8O_{26})]^{6-}$ has an almost centrosymmetrical structure and is built up by combining two units $\{NH_2C_6H_4CO_2MoO_5\}$ and six octahedra $\{MoO_6\}$ sharing edges. The cluster can also be described as two almost centrosymmetric $\{NH_2C_6H_4CO_2Mo_4O_{13}\}$ units that are cross-linked by bridging oxygen atoms. Atoms Mo(1) and Mo(4) in the two units are coordinated by two carboxyl oxygen atoms (O(2) and O(4)) of two 4-amino-

Table 1. Hydrogen bond lengths (*d*) and angles in compound **1**

Bond D—H...A	*d*(D...A)/Å	Angle D—H—A/deg
C(5)—H(5A)...O(4)$^{\#1}$	3.238(17)	136.5
C(7)—H(7A)...O(10)$^{\#2}$	3.334(17)	137.5
C(8)—H(8A)...O(12)$^{\#2}$	3.343(16)	138.0
C(17)—H(17A)...O(8)$^{\#3}$	3.311(17)	173.7
C(18)—H(18A)...O(5)$^{\#4}$	3.084(17)	136.1

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $x-1,-y+5/2,z-1/2$; $^{\#2}$ $x,-y+3/2,z-1/2$; $^{\#3}$ $-x-1,y-1/2,-z+1/2$; $^{\#4}$ $-x,y-1/2,-z+1/2$.

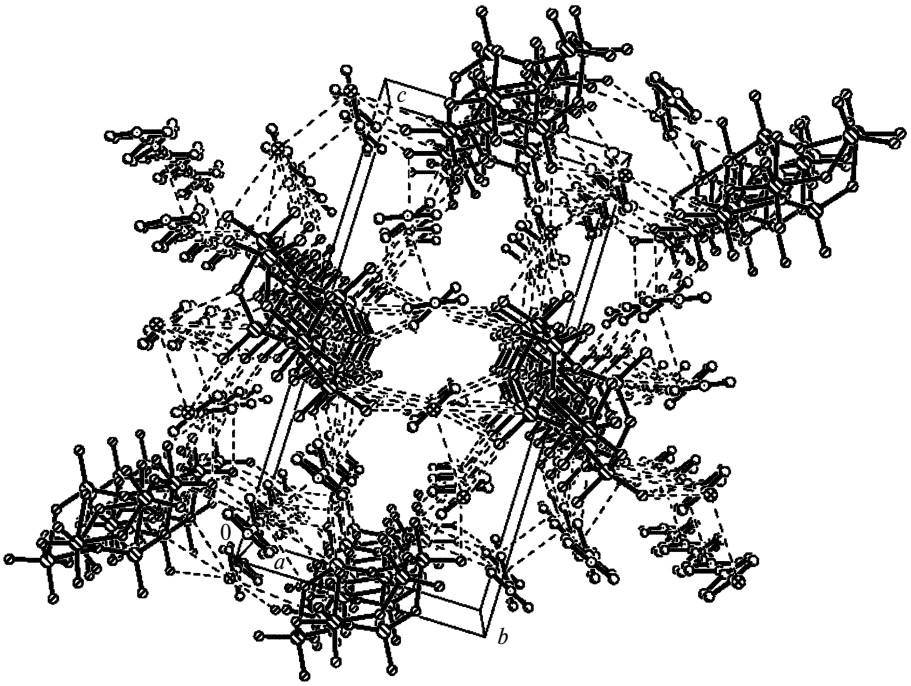

Fig. 2. Packing of structure of **1** showing the three-dimensional supramolecular network. All H atoms are omitted.

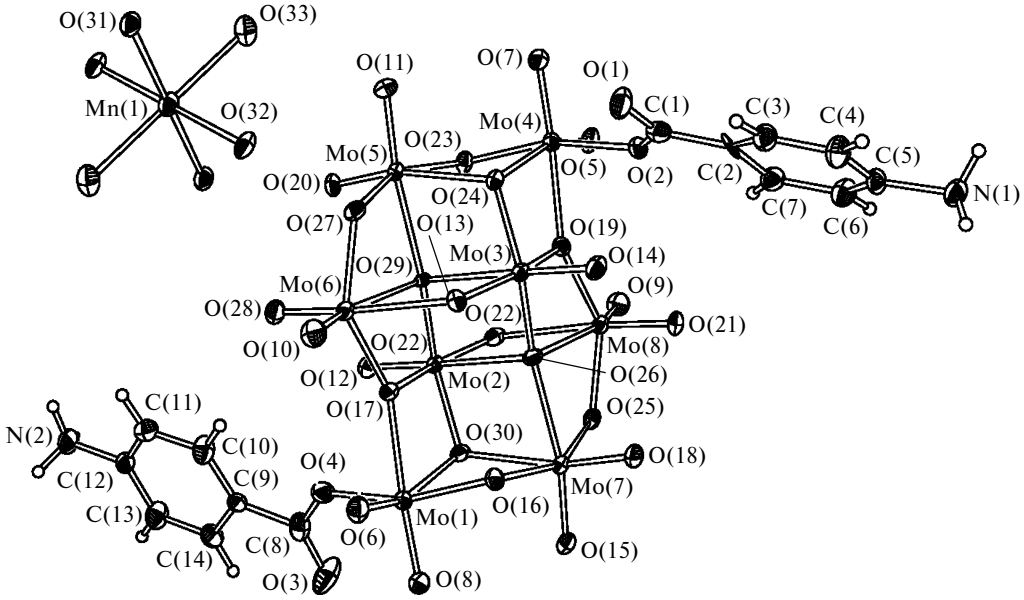

Fig. 3. Asymmetric unit of crystal **2**, showing the atom labeling scheme and 30% thermal ellipsoids.

benzoate ligands, with the corresponding Mo—O distances of 2.014(8) and 2.025(7) Å, respectively. These distances are slightly shorter than those in other similar octamolybdate anions, $[(HCOO)_2(Mo_8O_{26})]^{6-}$,[17] $[(NH_3CH_2COO)_2(Mo_8O_{26})]^{4-}$,[18] $[(CH_3COO)_2(Mo_8O_{26})]^{6-}$,[19] and $[(C_5H_5NCOO)_2(Mo_8O_{26})]^{6-}$.[20] The Mo—O distances in each distorted octahedral are in the range from 1.686(7) Å (Mo(2)—O(12)) to 2.367(7) Å (Mo(8)—O(22)). According to the coordination mode, the oxygen atoms in the anion can be divided into four different groups: 14 terminal O atoms with Mo—O distances of 1.686(7)—1.721(8) Å, six μ_2-O atoms (except for O(2) and O(4)) with Mo—O distances of 1.757(7)—2.367(7) Å, four μ_3-O atoms with Mo—O distances of 1.882(7)—2.267(7) Å, and two μ_4-O atoms with Mo—O distances of 1.949(7)—2.412(7) Å. Manganese

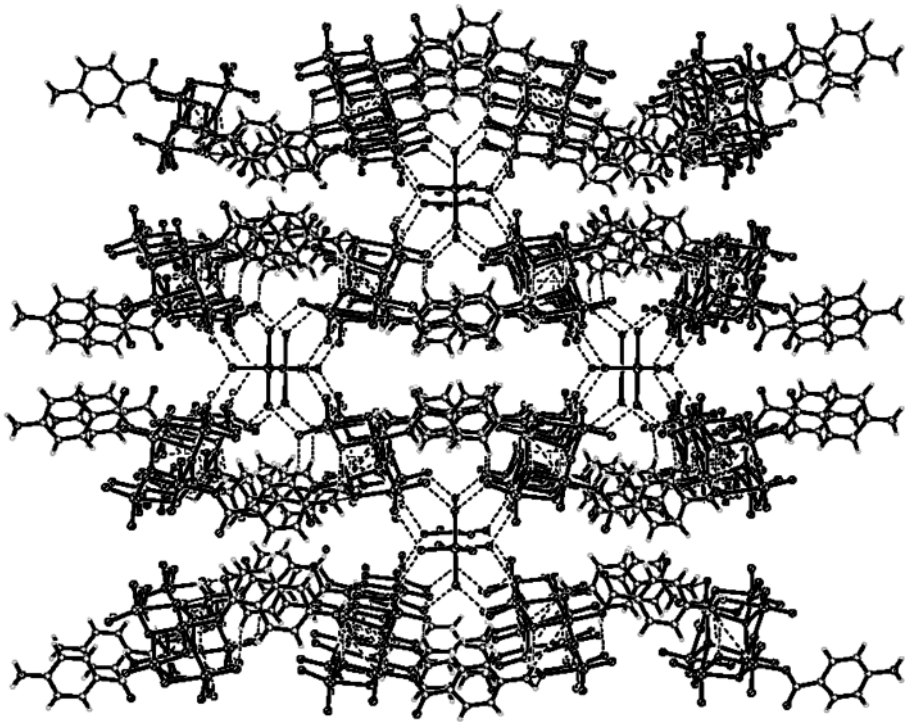

Fig. 4. Three-dimensional network formed by the MoO···OMn hydrogen bonding along the *a* axis.

atom in the cation $[Mn(H_2O)_6]^{2+}$ is coordinated to six water molecules in a strictly regular octahedral geometry, with the Mn—O distances in the 2.202(8)—2.169(7) Å range.

An interesting feature of compound **2** is the complex hydrogen bond involving the octamolybdate anions, $[Mn(H_2O)_6]^{2+}$ and NH_4^+ cations, and lattice water molecules. The coordinated water molecules in the cation $[Mn(H_2O)_6]^{2+}$ are linked with the anions $[(NH_2C_6H_4COO)_2(Mo_8O_{26})]^{6-}$ by hydrogen bond to form a three-dimensional structure (Fig. 4). Furthermore, the NH_4^+ cations and lattice water molecules further strengthen the three-dimensional network *via* this kind of weak interactions. The MoO···OMn, MoO···O_w and MoO···NH_4^+ distances are 2.667—3.033, 2.794—3.190, and 2.870—3.127 Å, respectively. No hydrogen bonds between the neighboring clusters $[(NH_2C_6H_4COO)_2(Mo_8O_{26})]^{6-}$ were found.

Summing up, we synthesized two new organo-inorganic substances based on octamolybdate anions: $[\{Cu(4,4'\text{-bipy})\}_4(Mo_8O_{26})]$ (**1**) and $(NH_4)_{10}Mn(H_2O)_6[(NH_2C_6H_4COO)_2(Mo_8O_{26})]_2 \cdot 15H_2O$ (**2**). The crystal of compound **1** consists of the one-dimensional structure constructed from four straight Cu—4,4′-bipy chains and the isolated α-octamolybdate anions. Compound **2** is the first example of 4-aminobenzoic acid-templated molybdenum oxide. Though the reaction temperature, pH value, and oxidation sate of the molybdenum atom are important, the organic base plays a crucial role in dictating the final structure of the solids. By taking advantage of suitable organic ligands and molybdenum sources in the designed synthesis of organo-inorganic hybrid materials, more and more interesting new materials with the desired architectures and useful properties may be obtained through hydrothermal synthesis.

Experimental

All chemicals commercially available were of reagent grade and used without further purification. Infrared spectra were recorded on an FTS-40 spectrophotometer in the region 4000—400 cm^{-1} in KBr pellets. Elemental C,H,N analyses were performed on a Vario EL III CHNOS Elemental Analyzer.

Tetra-4,4′-bipyridinecopper(I)octamolybdate $[\{Cu(4,4'\text{-bipy})\}_4(Mo_8O_{26})]$ (1). A Teflon-lined stainless steel reactor was charged with a mixture of $MoO_3 \cdot H_2O$ (0.32 g), $CuSO_4 \cdot 5H_2O$ (0.21 g), 4,4′-bipy (0.15 g), and water (10 mL) and heated for 3 days at 170 °C. After the reaction system was slowly cooled down to room temperature, brown crystals were isolated in 17 % yield (based on Mo). Found (%): C, 23.21; H, 1.64; N, 5.49. $C_{40}H_{32}Cu_4N_8O_{26}Mo_8$. Calculated (%): C, 23.29; H, 1.56; N, 5.43. IR (KBr), ν/cm^{-1}: 1610 s, 1531 m, 1485 m, 1416 s, 1221 m, 939 vs, 885 s, 845 s, 798 s, 650 s, 538 m.

Hexaaquamanganese(II)decaammoniumbis-4-aminobenzoateoctamolybdate pentadecahydrate $(NH_4)_{10}Mn(H_2O)_6[(NH_2C_6H_4COO)_2(Mo_8O_{26})]_2 \cdot 15H_2O$ (2). A Teflon-lined stainless steel reactor was charged with a mixture of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.41 g), $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.33 g), 4-aminobenzoic acid (0.23 g), and water (10 mL) and heated for

Table 2. Selected bond lengths (*d*) in molecules **1** and **2**

Bond	*d*/Å	Bond	*d*/Å
[{Cu(4,4′-bipy)}$_4$(Mo_8O_{26})] (**1**)			
Mo(1)—O(2)	1.712(9)	Mo(3)—O(6)	1.828(9)
Mo(1)—O(1)	1.757(9)	Mo(3)—O(9)	1.833(8)
Mo(1)—O(13)	1.766(8)	Mo(4)—O(11)	1.691(9)
Mo(1)—O(3)	1.829(9)	Mo(4)—O(10)	1.697(10)
Mo(2)—O(5)	1.708(9)	Mo(4)—O(12)	1.911(9)
Mo(2)—O(4)	1.711(10)	Mo(4)—O(9)	1.954(9)
Mo(2)—O(6)	1.949(9)	Mo(4)—O(13)	2.260(8)
Mo(2)—O(3)	2.303(9)	Cu(1)—N(2)	1.886(11)
Mo(3)—O(8)	1.686(10)	Cu(2)—N(4)	1.890(10)
Mo(3)—O(7)	1.696(10)		
$(NH_4)_{10}Mn(H_2O)_6[(NH_2C_6H_4COO)_2(Mo_8O_{26})]_2\cdot 15H_2O$ (**2**)			
Mn(1)—O(31)	2.129(7)	Mo(4)—O(24)	2.241(7)
Mn(1)—O(32)	2.169(7)	Mo(5)—O(20)	1.707(7)
Mn(1)—O(33)	2.202(8)	Mo(5)—O(11)	1.721(8)
Mo(1)—O(6)	1.706(8)	Mo(5)—O(23)	1.932(7)
Mo(1)—O(8)	1.716(8)	Mo(5)—O(27)	1.967(7)
Mo(1)—O(16)	1.944(7)	Mo(5)—O(29)	2.230(6)
Mo(1)—O(4)	2.014(8)	Mo(5)—O(24)	2.257(6)
Mo(1)—O(17)	2.142(7)	Mo(6)—O(10)	1.707(8)
Mo(1)—O(30)	2.264(7)	Mo(6)—O(28)	1.715(8)
Mo(2)—O(12)	1.686(7)	Mo(6)—O(17)	1.904(7)
Mo(2)—O(22)	1.765(7)	Mo(6)—O(27)	1.940(7)
Mo(2)—O(30)	1.894(7)	Mo(6)—O(29)	2.248(6)
Mo(2)—O(29)	1.969(6)	Mo(6)—O(13)	2.358(7)
Mo(2)—O(17)	2.132(7)	Mo(7)—O(15)	1.717(8)
Mo(2)—O(26)	2.412(7)	Mo(7)—O(18)	1.723(7)
Mo(3)—O(14)	1.689(7)	Mo(7)—O(16)	1.918(7)
Mo(3)—O(13)	1.757(7)	Mo(7)—O(25)	1.972(7)
Mo(3)—O(24)	1.882(7)	Mo(7)—O(26)	2.216(7)
Mo(3)—O(26)	1.949(7)	Mo(7)—O(30)	2.267(7)
Mo(3)—O(19)	2.160(7)	Mo(8)—O(21)	1.705(7)
Mo(3)—O(29)	2.407(6)	Mo(8)—O(9)	1.707(8)
Mo(4)—O(5)	1.694(8)	Mo(8)—O(19)	1.911(7)
Mo(4)—O(7)	1.706(8)	Mo(8)—O(25)	1.950(7)
Mo(4)—O(23)	1.935(7)	Mo(8)—O(26)	2.232(7)
Mo(4)—O(2)	2.025(7)	Mo(8)—O(22)	2.367(7)
Mo(4)—O(19)	2.131(7)		

4 days at 170 °C, then slowly cooled to room temperature to give yellow crystals in 57% yield (based on Mo). Found (%): C, 9.51; H, 2.81; N, 5.51. $C_{28}H_{94}MnMo_{16}N_{14}O_{81}$. Calculated (%): C, 9.57; H, 2.70; N, 5.58. IR (KBr), ν/cm^{-1}: 3404 b, 3317 b, 1670 s, 1608 s, 1591 s, 1518 s, 1427 s, 924 s, 897 s, 860 s, 810 s, 725 s.

X-ray diffraction analysis. Crystallographic data were collected for the crystals **1** and **2** 0.11×0.15×0.32 mm and

Table 3. Crystal data and structure refinement parameters for crystals **1** and **2**

Parameter	**1**	**2**
Molecular formula	$C_{40}H_{32}Cu_4Mo_8N_8O_{26}$	$C_{28}H_{94}MnMo_{16}N_{14}O_{81}$
Molecular weight	2062.42	3513.15
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	10.8126(3)	11.050(4)
b/Å	11.2959(4)	20.490(7)
c/Å	22.0229(8)	21.230(7)
β/deg	94.1100(10)	97.7200(10)
V/Å^3	2682.92(16)	4763(3)
Z	2	2
T/K	293(2)	293(2)
d_{calc}/g cm^{-3}	2.553	2.449
F(000)	1976	3410
μ/mm^{-1}	3.444	2.280
λ/Å	0.71073	0.71073
GOOF^2	1.327	1.260
Largest difference peak and hole/e ·Å^{-3}, ρ_{max}/ρ_{min}	1.067/1.002	0.706–0.791
Final *R* indices ($I > 2\sigma(I)$)*		
R_1	0.0766	0.0715
wR_2	0.1357	0.1643
R indices (for all data)		
R_1	0.1135	0.1057
wR_2	0.1524	0.1722

* $R_1 = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$, $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{0.5}$.

0.10×0.11×0.21 mm in size, respectively, at 293 K on a Siemens SMART CCD diffractometer with a graphite monochromator (Mo-Kα-radiation, λ = 0.71073 Å) at room temperature. The structures were solved by direct metods followed by differential Fourier syntheses and refined by the full-matrix least-squares method based on F^2 using the SHELXTL-97 program package. All the C-attached H atoms were generated theoretically, while the other H atoms were not located. Selected bond lengths and angles are given in Table 2. Crystallographic data for complexes **1** and **2** are listed in Table 3.

Crystallographic data for the structures reported have been deposited with the Cambridge Crystallographic Data Center as supplementary publication (No. CCDC-267318 for **1** and No. CCDC-267319 for **2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

This work was financially supported by the 973 program of the MOST (Grant 001CB108906), the National Natural Science Foundation of China (Grants 20425313, 90206040, 20333070, and 20303021), the NSF of Fujian Province and the State Key Laboratory of Structural Chemistry (Grant 030065).

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Received May 18, 2005