

## RAPID COMMUNICATION

# Hydrothermal Synthesis and Crystal Structure of $\{[\text{Cu}(2,2'\text{-bpy})_2]_2\text{Mo}_8\text{O}_{26}\}$ : a $\beta$ -octamolybdate Cluster Covalently Bonded to Two $\{\text{Cu}(2,2'\text{-bpy})_2\}^{2+}$ Coordination Complexes via Bridging oxo Groups

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An organic–inorganic hybrid solid,  $(\text{Cu}(2,2'\text{-bpy})_2)_2\text{Mo}_8\text{O}_{26}$ , has been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction. Dark green crystals crystallize in the orthorhombic system, space group *Pna*21,  $a = 24.164(5)$ ,  $b = 18.281(4)$ ,  $c = 11.877(2)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 5247(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $\lambda(\text{MoK}\alpha) = 0.71073$  Å ( $R(F) = 0.0331$  for 5353 reflections). Data were collected on a Siemens P4 four-circle diffractometer at 293 K in the range  $1.69^\circ < \theta < 25.04^\circ$  using the  $\omega$ -scan technique. The structure was solved by the direct method and refined by full-matrix least squares on  $F^2$  using SHELXL-93. The structure of this compound consists of discrete  $(\text{Cu}(2,2'\text{-bpy})_2)_2\text{Mo}_8\text{O}_{26}$  clusters, constructed from  $\beta$ -octamolybdate subunits ( $(\text{Mo}_8\text{O}_{26})^{4-}$ ) covalently bonded to two  $(\text{Cu}(2,2'\text{-bpy})_2)^{2+}$  coordination complexes via bridging oxo groups that connect two adjacent molybdenum sites. © 2001

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**Key Words:** organic–inorganic hybrid solids; octamolybdate; transition metal coordination complexes; hydrothermal synthesis; crystal structure.

## INTRODUCTION

Organic–inorganic solid-state hybrid materials consisting of organic and inorganic components, especially metal oxides, are attracting significant attention, for these materials can exhibit synergetic properties such as electrical, magnetic and optical properties (1). A number of such materials constructed from metal–oxo clusters (polyoxometalates,

POMs) linked to transition metal coordination complexes have been hydrothermally synthesized (2–4), such as  $[\text{M}(4,4'\text{-bpy})(\text{VO}_2)_2(\text{HPO}_4)_4]$  ( $M = \text{Co}, \text{Ni}$ ; bpy = bipyridine) (2),  $[\text{Ni}(2,2'\text{-bpy})_3]_{1.5}[\text{PW}_{12}\text{O}_{40}\text{Ni}(2,2'\text{-bpy})_2(\text{H}_2\text{O})] \cdot 0.5\text{H}_2\text{O}$  (3), and  $[\text{Cu}(\text{bpe})(\text{MoO}_4)]$  (bpe = 1,2-trans-bis(4-pyridyl)ethene) (4). In particular, Zubieta *et al.* have reported a series of novel organic–inorganic composite materials consisting of molybdenum-oxo clusters attached to various transition metal complexes. These solids exhibit a remarkable structural diversity, including one-, two-, three-dimensional or discrete cluster structures (4–10). Typical examples include  $[\text{Mo}_3\text{O}_{12}\{\text{Fe}(2,2'\text{-bpy})_2\}_2] \cdot 0.25\text{H}_2\text{O}$  (6), a 1-D chain,  $[\{\text{Ni}(3,3'\text{-bpy})_2\}_2\text{Mo}_4\text{O}_{14}]$  (7), a 2-D layered network,  $[\{\text{Ni}(2,2'\text{-bpy})_2\}_2\text{Mo}_4\text{O}_{14}]$  (8), which displays a simple ring structure, and  $[\{\text{Fe}(\text{tpyor})\}_3\text{Fe}(\text{Mo}_6\text{O}_{19})_2] \cdot x\text{H}_2\text{O}$  (tpyor = tetrapyrrolylporphyrin) (9), which has a 3-D framework. Moreover, Zubieta and his co-workers have investigated the interplay of ligand geometries and secondary metal coordination preferences in the design of such materials. The successful synthesis of these materials demonstrates that some control is achievable in defining their structures (5).

In addition, it is noteworthy that so far five isomers of the octamolybdate clusters, including the  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\epsilon$  forms, have been depicted, the structures of which differ in number, type, and fusion mode of the molybdenum polyhedra (5). The first three isomers had been isolated in some salts (11–15). The  $\delta$  form has been reported as the  $(\alpha\text{-}\delta)$  or  $(\beta\text{-}\delta)$  “intermediate” structure (16). The  $\epsilon$  form is unique to the heterometal–diamine molybdenum oxide materials (5). Moreover, a number of organic–inorganic hybrid solids constructed from the five isomers covalently bonded to

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various transition metal coordination complex moieties have been synthesized by the hydrothermal method (17–25). For example,  $(\text{Ni}(4,4'\text{-bpy})_2)_2(\text{H}_2\text{O})_2\text{Mo}_8\text{O}_{26}$  (19) displays a 2-D network structure consisting of  $\epsilon\text{-(Mo}_8\text{O}_{26})^{4-}$  linked to 1-D  $(\text{Ni}(4,4'\text{-bpy})_2)^{2+}$  chains. However, all of these octamolybdate isomers are linked with transition metal complexes through terminal oxo groups.

In this paper we report the hydrothermal synthesis and structural characterization of an organic–inorganic hybrid solid,  $(\text{Cu}(2,2'\text{-bpy})_2)_2\text{Mo}_8\text{O}_{26}$ . In the structure of this solid, a  $\beta$ -octamolybdate cluster covalently bonds to two  $(\text{Cu}(2,2'\text{-bpy})_2)^{2+}$  coordination complexes via bridging oxo groups. Despite the fact that in the chemistry of organometallic POMs the organometallic sites may be coordinated with the POM skeleton through terminal and/or bridging oxygen atoms (26), such an unusual linking fashion is, to the best of our knowledge, unique in the coordination chemistry of octamolybdates with transition metal complexes and even in that of the whole molybdenum–oxo clusters.

## EXPERIMENTAL

### General Procedures

All chemicals were commercially available reagent grade and used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN elemental analyzer. Mo and Cu were determined using a Leeman inductively coupled plasma (ICP) spectrometer. The IR spectrum was recorded in the range  $4000\text{--}400\text{ cm}^{-1}$  on an Alpha Centauri FT/IR spectrophotometer using a KBr pellet.

### Hydrothermal Synthesis

The title compound was hydrothermally synthesized under autogenous pressure. A mixture of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.0341 g), *p*-phthalic acid (0.0338 g), 2,2'-bipyridine (0.0313 g),  $\text{MoO}_3$  (0.0866 g), NaOH (0.0145 g), and  $\text{H}_2\text{O}$  (10 mL) in a molar ratio 1:1:1:3:1.8:2780 was sealed in a 20-ml Teflon-lined stainless steel autoclave and heated at  $180^\circ\text{C}$  for 5 d. After cooling to room temperature, dark green block crystals were isolated by filtration and washed with distilled water (9.2% yield based on Mo). The elemental analyses found C, 24.92; H, 1.70; N, 5.85; Cu, 6.41; Mo, 39.87%. Calc. for  $\text{C}_{40}\text{H}_{32}\text{Cu}_2\text{Mo}_8\text{N}_8\text{O}_{26}$ : C, 24.80; H, 1.65; N, 5.79; Cu, 6.57; Mo, 39.66%.

### X-Ray Crystallography

The structure of the title compound was determined by single crystal X-ray diffraction. A single dark green crystal with approximate dimensions of  $0.52 \times 0.40 \times 0.32\text{ mm}$  was mounted inside a glass fiber capillary. Data were collected

**TABLE 1**  
Crystallographic Data and Structure Refinement for  
 $(\text{Cu}(2,2'\text{-bpy})_2)_2\text{Mo}_8\text{O}_{26}$

Chem formula	$\text{C}_{40}\text{H}_{32}\text{N}_8\text{O}_{26}\text{Cu}_2\text{Mo}_8$
Formula weight	1935.34
Crystal system	orthorhombic
Space group	<i>Pna</i> 21
<i>a</i> , Å	24.164(5)
<i>b</i> , Å	18.281(4)
<i>c</i> , Å	11.877(2)
$\alpha$ , °	90
$\beta$ , °	90
$\gamma$ , °	90
<i>V</i> , Å <sup>3</sup>	5247(2)
<i>Z</i>	4
<i>T</i> , K	293(2)
$\lambda$ , Å	0.71073
<i>D</i> <sub>calc</sub> , g cm <sup>-3</sup>	2.450
<i>F</i> (000)	3720
$\mu$ , mm <sup>-1</sup>	2.733
Reflections collected	6193
Independent reflections	5353 ( <i>R</i> <sub>int</sub> = 0.0186)
<i>R</i> 1 <sup>a</sup> , <i>wR</i> 2 <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.0331, 0.0727
<i>R</i> 1 <sup>a</sup> , <i>wR</i> 2 <sup>b</sup> (all data)	0.0422, 0.0749
Goodness of fit	1.016

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR2 = [\sum w(|F_o| - |F_c|)^2 / \sum [w|F_o|^2]]^{1/2}.$$

on a Siemens P4 four-circle diffractometer at 293 K using graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda(\text{MoK}\alpha) = 0.71073\text{ \AA}$ ) and the  $\omega$ -scan technique in the range of  $1.69^\circ < \theta < 25.04^\circ$ . A semiempirical absorption correction (PSI SCAN) was applied for selected reflections. The structure was solved by the direct method and refined by full-matrix least-squares on  $F^2$  using the SHELXL-93 software. All of the nonhydrogen atoms were refined anisotropically. All the hydrogen atoms were located from difference Fourier maps. A total of 6193 (5353 unique, *R*<sub>int</sub> = 0.0186) reflections were measured. Structure solution and refinement based on 5353 independent reflections with *I* > 2σ(*I*) on 1 restraint and 757 parameters gave *R*1 (*wR*2) = 0.0331 (0.0727). Crystallographic details for the structure of the title compound are summarized in Table 1. Atomic coordinates, bond lengths and angles, and anisotropic displacement parameters are deposited in supplementary information.

## RESULTS AND DISCUSSION

The original intention of introducing *p*-phthalic acid into the reaction system was to obtain a novel organic–inorganic hybrid solid containing mixed organic ligands. However, the results of the elemental analyses and X-ray crystallography reveal that the title compound is obtained and it contains no *p*-phthalic acid but contains 2,2'-bipyridine ligands. It is also noteworthy that the title compound was not

obtained when the reaction was performed under the same conditions except that the reaction mixture contained no *p*-phthalic acid. Study of the role of *p*-phthalic acid in this synthesis is under way. In addition, this solid does not dissolve in water, alcohols, ketones, or acetonitrile. After many days' exposure to the air it has not decomposed, indicating fairly good stability.

Figure 1 indicates the structure of  $(\text{Cu}(2,2'\text{-bpy})_2)_2\text{Mo}_8\text{O}_{26}$ , showing atom-labeling schemes and the 50% probability displacement ellipsoids. As shown in Fig. 1, the crystal structure of the title compound consists of discrete  $(\text{Cu}(2,2'\text{-bpy})_2)_2\text{Mo}_8\text{O}_{26}$  clusters, constructed from  $\beta$ -octamolybdate subunits,  $(\text{Mo}_8\text{O}_{26})^{4-}$ , covalently linked to two  $(\text{Cu}(2,2'\text{-bpy})_2)^{2+}$  coordination cations. The present structure highlights an unusual mode of bonding between the molybdenum-oxo clusters and the copper coordination complexes; that is, the  $\beta$ - $(\text{Mo}_8\text{O}_{26})^{4-}$  cluster bonds to the  $(\text{Cu}(2,2'\text{-bpy})_2)^{2+}$  cations via bridging oxo groups that connect two adjacent molybdenum sites. The  $(\text{Mo}_8\text{O}_{26})^{4-}$  moiety is composed of eight edge-sharing  $(\text{MoO}_6)$  octahedra and thus displays the characteristic  $\beta$ -octamolybdate arrangement with two  $\text{Mo}_4\text{O}_{13}$  subunits stacking together (27). All molybdenum sites exhibit +6 oxidation state and are crystallographically independent, possessing octahedral coordination geometry with different distortion extents. The

Mo–O bonds can be grouped into four categories: (i) Mo–O(t) bonds, 1.675(8)–1.706(8) Å; (ii) Mo–O( $\mu_2$ ) bonds, 1.720(7)–2.310(7) Å; (iii) Mo–O( $\mu_3$ ) bonds, 1.925(6)–2.390(6) Å; and (iv) Mo–O( $\mu_5$ ) bonds, 2.158(7)–2.482(7) Å. The +6 oxidation state is also confirmed by bond valence sum calculations (28). The empirical bond valence calculation,  $S = \exp(1.907 - R)/0.37$  ( $S$  = bond valence,  $R$  = bond length), leads to  $S$  values for Mo(1), Mo(2), Mo(3), Mo(4), Mo(5), Mo(6), Mo(7), and Mo(8) of 6.044, 6.131, 6.057, 6.044, 6.053, 6.076, 5.950, and 6.076, respectively. The average value for the calculated oxidation state of Mo is 6.054, consistent with the formula of the title compound given by X-ray structure determination.

Each of the two copper coordination complex subunits,  $(\text{Cu}(2,2'\text{-bpy})_2)^{2+}$ , is covalently linked to the octamolybdate core via a single bridging oxo ligand ligated to two adjacent molybdenum centers (Fig. 1). The two bridging oxo ligands, O(2) and O(22), thus serve as  $\mu_3$ -oxo bridges. The bond distances of Mo(1)–O(2), Mo(2)–O(2), Mo(7)–O(22), and Mo(8)–O(22) are 1.938(6), 1.967(7), 1.930(6), and 1.960(7) Å, respectively. The copper (II) sites exhibit distorted square pyramidal  $\text{CuN}_4\text{O}$  geometry, that is, each copper center is coordinated to four nitrogen donors of the 2,2'-bipyridine ligands at the basal plane and one bridging oxo group of the octamolybdate cluster at the apical position. The eight

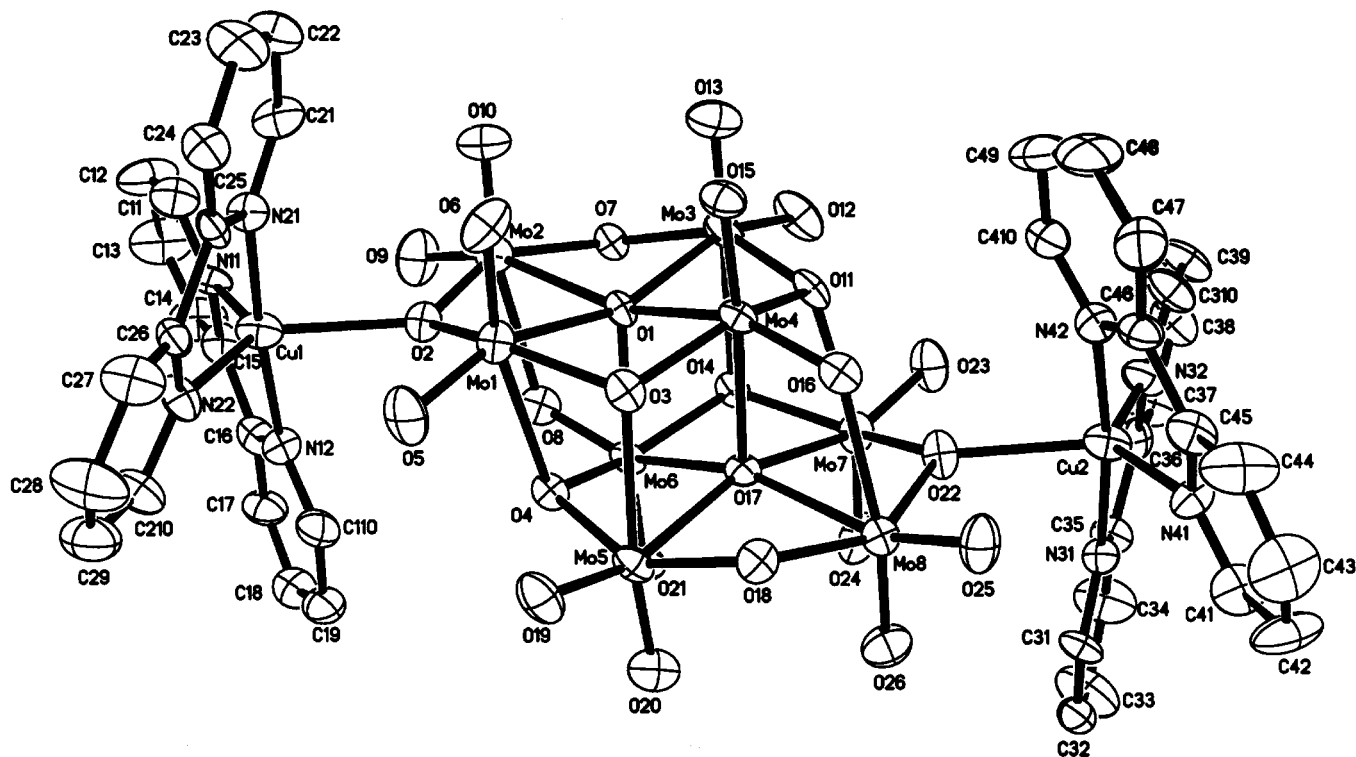


FIG. 1. The structure of  $(\text{Cu}(2,2'\text{-bpy})_2)_2\text{Mo}_8\text{O}_{26}$  showing the atom-labeling scheme and the 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Cu–N bond distances range from 1.963(8) to 2.052(10) Å and the two Cu–O bond lengths are 2.221(8) and 2.244(8) Å. In fact, such a 4 + 1 square pyramidal geometry for Cu (II) is not uncommon, and has been observed in several compounds such as Cu(pz)<sub>0.5</sub>MoO<sub>4</sub> (11), Cu(*o*-phen)MoO<sub>4</sub> (22) and (Cu(*o*-phen)<sub>2</sub>)<sub>2</sub>Mo<sub>8</sub>O<sub>26</sub> (22). Furthermore, among the four 2,2'-bipyridine ligands attached to the copper sites (1, 2, 3, and 4), 1 and 4 are nearly parallel with a dihedral of ca. 9.2°. So are 2 and 4 with a dihedral angle of 7.8°. However, with respect to the two 2,2'-bipyridine ligands attached to the same copper site (1 and 2, 3 and 4), the dihedrals between them are ca. 45°.

Further, the title compound does not form a 1-D chain, 2-D layer, or 3-D structure, but exhibits a discrete cluster structure. The present structure is reminiscent of (Cu(phen)<sub>2</sub>)<sub>2</sub>(Cu(phen))<sub>2</sub>Mo<sub>8</sub>O<sub>26</sub>·H<sub>2</sub>O reported by Xu and co-worker (24) and (Ni(2,2'-bpy)<sub>2</sub>)<sub>2</sub>Mo<sub>4</sub>O<sub>13</sub> by Zubieta and co-workers (18), both containing (β-Mo<sub>8</sub>O<sub>26</sub>)<sup>4-</sup> subunits. In the former structure cluster anions ((Cu(phen))<sub>2</sub>Mo<sub>8</sub>O<sub>26</sub>)<sup>2-</sup> and coordinated cations (Cu(phen)<sub>2</sub>)<sup>+</sup> are arranged alternatively by layers in the unit cell, while in the latter structure the β-(Mo<sub>8</sub>O<sub>26</sub>)<sup>4-</sup> clusters are linked by (Ni(2,2'-bpy)<sub>2</sub>)<sup>2+</sup> bridges into a 1-D chain. However, not only in these two compounds but also in those aforementioned organic–inorganic hybrid solids containing different octamolybdate isomers are the (Mo<sub>8</sub>O<sub>26</sub>)<sup>4-</sup> cores linked with the transition metal complex cations via terminal oxo ligands (17–25). Therefore, to the best of our knowledge, the unique linking mode in this case, i.e., the β-(Mo<sub>8</sub>O<sub>26</sub>)<sup>4-</sup> clusters bond to the (Cu(2,2'-bpy)<sub>2</sub>)<sup>2+</sup> complexes via bridging oxo groups, represents the first example in the coordination chemistry of octamolybdates with transition metal complex fragments and even in that of the whole molybdenum–oxo clusters, except in the chemistry of organometallic POMs where the organometallic sites may be coordinated with the POM skeleton through terminal and/or bridging oxygen atoms (26).

In the IR spectrum of the title compound the characteristic peaks at 945, 910, 849, 710, 666, and 551 cm<sup>-1</sup> are due to β-octamolybdate, and the feature bands in the range 1100–1600 cm<sup>-1</sup> are assigned to 2,2'-bipyridine.

In summary, we have successfully synthesized a novel organic–inorganic hybrid solid by the hydrothermal method. Its structure consists of discrete (Cu(2,2'-bpy)<sub>2</sub>)<sub>2</sub>Mo<sub>8</sub>O<sub>26</sub> clusters, constructed from (β-Mo<sub>8</sub>O<sub>26</sub>)<sup>4-</sup> subunits covalently bonded to two (Cu(2,2'-bpy)<sub>2</sub>)<sup>2+</sup> coordination cations via bridging oxo groups. Endeavors are being devoted to the synthesis of other organic–inorganic hybrid solids containing different transition metal coordination complexes as well as exhibiting various structures.

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