

An extended two-dimensional copper–molybdate compound with mixed dicarboxyl and organodiamine ligands

Xiao-Yuan Wu, Quan-Guo Zhai, Li-Juan Chen and Can-Zhong Lu*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou, Fujian 350002, People's Republic of China

Correspondence e-mail: czlu@ms.fjirsm.ac.cn

Received 21 March 2006

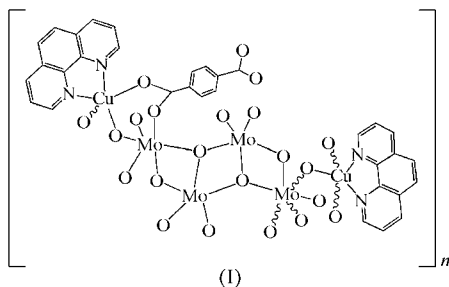
Accepted 13 April 2006

Online 24 May 2006

The title complex, poly[di- μ_3 -oxo-hepta- μ_2 -oxo-tetraoxo-bis(1,10-phenanthroline)- μ_4 -terephthalato-dicopper(II)tetramolybdate(VI)], $[\text{Cu}_2\text{Mo}_4(\text{C}_8\text{H}_4\text{O}_4)\text{O}_{13}(\text{C}_{12}\text{H}_8\text{N}_2)_2]_n$, represents a novel two-dimensional copper–molybdate compound with mixed ligands. Tetranuclear molybdenum oxide clusters are joined through corner-sharing into a ribbon-like chain, with $[\text{Cu}(\text{phen})]^{2+}$ (phen is 1,10-phenanthroline) complexes grafted onto either side. The terephthalate ligand lies about an inversion centre and links these chains to form a layer *via* Cu–O and Mo–O bonds. Face-to-face π – π stacking interactions between adjacent phen ligands stabilize the structure.

Comment

New organic–inorganic hybrid materials based on polyoxometalates have attracted much attention due to the diversity of their structures and the vast range of potential applications



in many fields, such as catalysis, electrical conductivity, magneto-chemistry and photochemistry (Yamase *et al.*, 1999; Rhule *et al.*, 1998; Hill & Prosser-McCarthy, 1995). One promising approach for the design and synthesis of this class of solid materials is to introduce secondary metal–organic complexes into polyoxometalates *via* covalent bonds (Gaunt *et al.*, 2003; Strukan *et al.*, 2000; Wilson *et al.*, 1983; Wu *et al.*, 2003; Zapf *et al.*, 1997). To date, an astonishing variety of polyoxometalate-based organic–inorganic hybrid materials

with discrete or high-dimensional structures have been isolated. However, the organic molecules introduced into these polyoxometalate-based materials are mostly restricted to organonitrogen ligands (Luan *et al.*, 2000; Reinoso *et al.*, 2003; Kang *et al.*, 1989). Extended polyoxomolybdate-based carboxyl ligands are rare (Liu *et al.*, 1987; Quintal *et al.*, 2001), which may be due to the fact that the negative charge on carboxyl ligands prevents charge balance with the polyoxomolybdate anions. In the course of our development of the chemistry of organic–inorganic hybrid materials based on polyoxomolybdates, organonitrogen and carboxyl ligands were introduced into the polyoxomolybdate system simultaneously, and the title novel compound, $[\{\text{Cu}(\text{phen})\}_2(\text{tp})\text{Mo}_4\text{O}_{13}]_n$ (phen is 1,10-phenanthroline and tp is terephthalate), (I), was isolated. This compound exhibits a two-dimensional layer formed by crosslinking one-dimensional copper–molybdate chains through tp ligands.

X-ray diffraction analysis reveals that the structure of (I) exhibits a layered network constructed from $[\{\text{Cu}(\text{phen})\}_2\text{Mo}_4\text{O}_{13}]_n^{2n+}$ ribbons bridged by tp ligands. The basic building block of (I) is shown in Fig. 1. In the asymmetric unit, there are two crystallographically independent Mo atoms and one Cu atom. Atom Mo1 has a distorted octahedral environment, with Mo–O distances ranging from 1.6865 (16) to 2.3022 (14) Å, while atom Mo2 has a square-pyramidal coordination, with Mo–O distances ranging from 1.6876 (16) to 2.1123 (15) Å. The Cu atom is pentacoordinated in a square-pyramidal environment by two N atoms from the phen ligand, one O atom from the tp ligand and two O atoms from the molybdenum oxide chain. The carboxyl group of the tp ligand offers two O atoms, one to Mo and one to Cu. An extensive bond-valence-sum calculation (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991; Thorp, 1992) indicates the valences for Mo

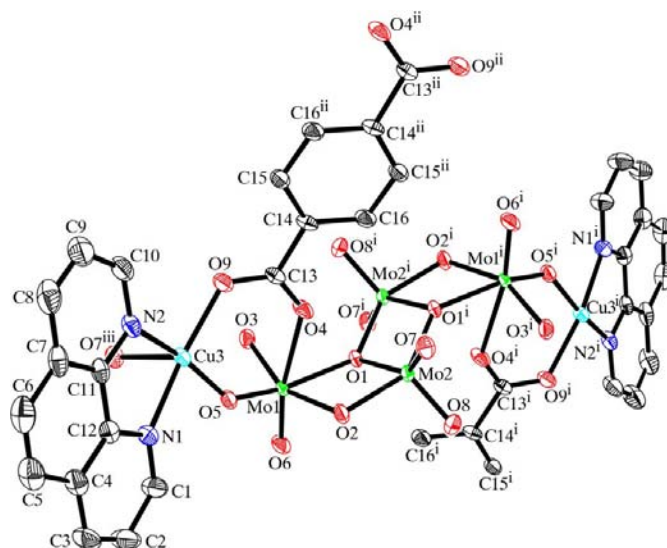


Figure 1

A view of (I), showing the coordination environment around the Cu and Mo atoms, and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) $-x - 2, -y, -z + 2$; (ii) $-x - 2, -y + 1, -z + 2$; (iii) $x + 1, y, z$.]

metal-organic compounds

and Cu to be 6 and 2, respectively (Mo1 = 6.149, Mo2 = 5.917 and Cu3 = 1.874).

The structure of (I) can be described as follows. Two $[\text{MoO}_6]$ octahedra and two $[\text{MoO}_5]$ square pyramids form a tetramolybdate unit through edge-sharing, and these tetramolybdate units form an infinite molybdenum oxide chain through corner-sharing. $[\text{Cu}(\text{phen})]^{2+}$ complexes are grafted onto either side of the molybdenum oxide chain *via* Cu—O bonds (Fig. 2). It is noteworthy that the second ligand (tp), in a bis-bidentate mode, coordinates to Cu and to the octahedral Mo atom, thus serving to extend the chains into a two-dimensional network (Fig. 3). Weak C—H \cdots O hydrogen bonds (Fig. 4), together with face-to-face π – π stacking interactions between adjacent phen ligands, stabilize the structure.

As shown in Fig. 5, there are two different π – π stacking interactions. One relates phen ring R1 (atoms N1, C1, C2, C3, C4 and C12) to phen ring R3 (atoms C7, C8, C9, C10, N2 and C11) of an adjacent phen ligand, denoted $R1\cdots R3^i$ [symmetry code: (i) $-1-x, 1-y, 1-z$]. The second is formed between phen ring R2 (atoms C4, C5, C6, C7, C11 and C12) and its symmetry-related counterpart $R2^{ii}$ [symmetry code: (ii) $-x, 1-y, 1-z$]. The two phen rings involved in each π – π stacking interaction are nearly parallel, with dihedral angles of 4.79 (12°) for $R1\cdots R3^i$ and 0.00 (11°) for $R2\cdots R2^{ii}$, plane-to-plane distances of 3.51 ($R1\cdots R3^i$) and 3.29 Å ($R2\cdots R2^{ii}$), and centroid-to-centroid distances of 3.628 (13) ($R1\cdots R3^i$) and 3.481 (8) Å ($R2\cdots R2^{ii}$). Two $R1\cdots R3^i$ and one $R2\cdots R2^{ii}$ π – π stacking interactions alternate along the *a* axis.

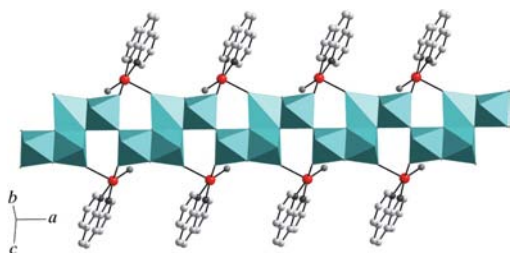


Figure 2
A view showing the one-dimensional copper-molybdate chain in (I). Polyhedra represent $[\text{MoO}_6]$ and $[\text{MoO}_5]$ units.

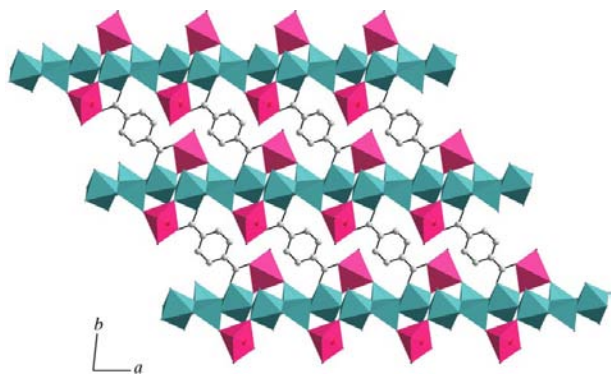


Figure 3
A polyhedral representation of the two-dimensional framework of (I). For clarity, all H atoms and the C atoms of the phen ligands have been omitted.

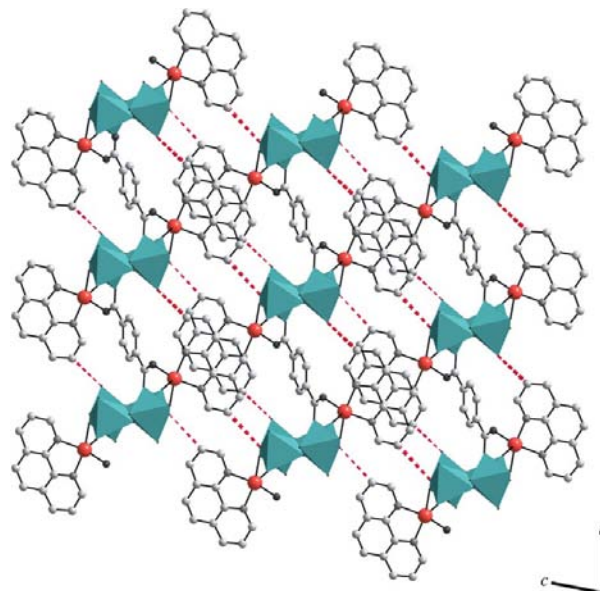


Figure 4
A view showing the hydrogen bonding involving the C atoms of the phen ligands and the O atoms of the molybdates. Hydrogen bonds are drawn as dashed lines.

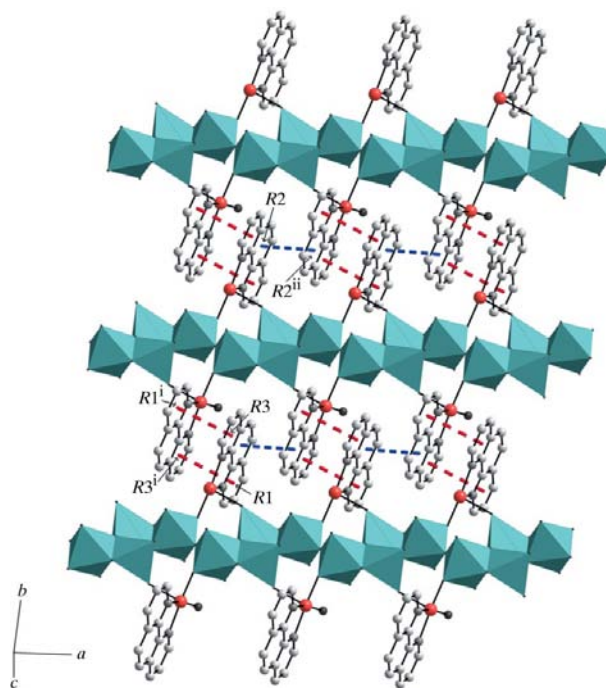


Figure 5
The π – π interactions between pairs of adjacent phen ligands. Dashed lines represent $R1\cdots R3^i$ interactions and dotted lines represent $R2\cdots R2^{ii}$ interactions. [Symmetry codes: (i) $-1-x, 1-y, 1-z$; (ii) $-x, 1-y, 1-z$.]

Experimental

A mixture of $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ (0.5 mmol), $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.5 mmol), 1,10-phenanthroline (0.5 mmol) and terephthalic acid (0.25 mmol) in water (20 ml) was adjusted to pH 4.2 and then heated at 423 K for 3 d. After slow cooling to room temperature, green crystals of (I) were

isolated in 41% yield (based on Mo). Elemental analysis for (I): calculated: H 1.62, C 30.91, N 4.51, Cu 10.22, Mo 30.86%; found: H 1.71, C 30.89, N 4.50, Cu 10.22, Mo 30.85%. IR (ν , cm^{-1} , KBr): 3549, 3479, 3414, 3237, 1638, 1618, 1565, 1425, 1382, 1372, 1152, 1111, 954, 947, 913, 903, 883, 872, 787, 723.

Crystal data

$[\text{Cu}_2\text{Mo}_4(\text{C}_8\text{H}_4\text{O}_4)\text{O}_{13}(\text{C}_{12}\text{H}_8\text{N}_2)_2]$	$V = 863.8 (3) \text{ \AA}^3$
$M_r = 1243.36$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 2.390 \text{ Mg m}^{-3}$
$a = 7.4592 (17) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.251 (2) \text{ \AA}$	$\mu = 2.71 \text{ mm}^{-1}$
$c = 11.624 (3) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\alpha = 78.603 (5)^\circ$	Prism, green
$\beta = 85.529 (7)^\circ$	$0.22 \times 0.12 \times 0.06 \text{ mm}$
$\gamma = 83.151 (8)^\circ$	

Data collection

Rigaku Saturn 70 CCD area-detector diffractometer	6795 measured reflections
CCD profile-fitting scans	3888 independent reflections
Absorption correction: multi-scan (<i>CrystalClear</i> ; Rigaku, 2002)	3469 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.588$, $T_{\max} = 0.855$	$R_{\text{int}} = 0.017$
	$\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.020$	$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2]$
$wR(F^2) = 0.054$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} = 0.001$
3888 reflections	$\Delta\rho_{\text{max}} = 0.70 \text{ e \AA}^{-3}$
268 parameters	$\Delta\rho_{\text{min}} = -0.49 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C2}-\text{H2A}\cdots\text{O2}^{\text{i}}$	0.93	2.38	3.205 (3)	147
$\text{C9}-\text{H9A}\cdots\text{O6}^{\text{ii}}$	0.93	2.36	3.056 (3)	132

Symmetry codes: (i) $-x - 1, -y, -z + 1$; (ii) $x, y + 1, z$.

All H atoms were positioned geometrically and treated as riding on their parent atoms, with C–H distances of 0.93 \AA and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

This work was supported by the '973' programme of the MOST (grant No. 001CB108906), the National Natural Science Foundation of China (grant Nos. 20425313, 90206040, 20333070, 20303021 and 20521101), the Natural Science Foundation of Fujian Province (grant No. 2005HZ01-1) and the Chinese Academy of Sciences.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3010). Services for accessing these data are described at the back of the journal.

References

- Brandenburg, K. (1998). *DIAMOND*. Version 2.0. Crystal Impact GbR, Bonn, Germany.
- Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.
- Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
- Gaunt, A. J., May, L., Collison, D. & Helliwell, M. (2003). *Acta Cryst.* **C59**, i65–i66.
- Hill, C. L. & Prosser-McCartha, C. M. (1995). *Coord. Chem. Rev.* **143**, 407–455.
- Kang, H., Liu, S., Shaikh, S. N., Nicholson, T. & Zubieta, J. (1989). *Inorg. Chem.* **28**, 920–933.
- Liu, S., Shaikh, S. N. & Zubieta, J. (1987). *Inorg. Chem.* **26**, 4303–4305.
- Luan, G.-Y., Wang, E.-B., You, W.-S., Xu, L. & He, Q.-L. (2000). *Acta Cryst.* **C56**, e284–e285.
- Quintal, S. M. O., Nogueira, H. I. S., Carapuca, H. M., Felix, V. & Drew, M. G. B. (2001). *J. Chem. Soc. Dalton Trans.* pp. 3196–3201.
- Reinoso, S., Vitoria, P., Lezama, L., Luque, A. & Gutiérrez-Zorrilla, J. M. (2003). *Inorg. Chem.* **42**, 3709–3711.
- Rhule, J. T., Hill, C. L. & Judd, D. A. (1998). *Chem. Rev.* **98**, 327–357.
- Rigaku (2005). *CrystalClear*. Version 1.3.6. Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Strukan, N., Cindrić, M., Kajfez, T., Kamenar, B. & Giester, G. (2000). *Acta Cryst.* **C56**, e443–e444.
- Thorp, H. H. (1992). *Inorg. Chem.* **31**, 1585–1588.
- Wilson, A. J., Robinson, W. T. & Wilkins, C. J. (1983). *Acta Cryst.* **C39**, 54–56.
- Wu, C. D., Lu, C. Z., Lin, X., Wu, D. M., Lu, S. F., Zhuang, H. H. & Huang, J. S. (2003). *J. Chem. Soc. Chem. Commun.* pp. 1284–1285.
- Yamase, T., Inoue, M., Naruke, H. & Fukaya, K. (1999). *Chem. Lett.* pp. 563–564.
- Zapf, P. J., Warren, C. J., Haushalter, R. C. & Zubieta, J. (1997). *J. Chem. Soc. Chem. Commun.* pp. 1543–1544.