Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Chains of (4,4′-bipyridyl)copper(I) bridged by dimolybdate units

Wan-Sheng You, En-Bo Wang,* Lin Xu, Chang-Wen Hu and Guo-You Luan

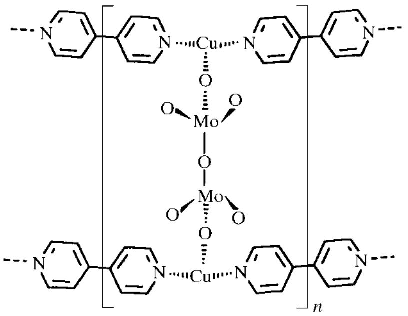
Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024, People's Republic of China
Correspondence e-mail: huchw@nenu.edu.cn

Received 27 October 1999
Accepted 22 November 1999

The crystal structure of the title compound, poly[bis-[copper(I)-μ-(4,4′-bipyridyl)-N:N']-μ-dimolybdato-O:O'], $[Cu_2(C_{10}H_8N_2)_2\{Mo_2O_7\}]_n$, consists of $\{Mo_2O_7\}^{2-}$ units (with the central O atom lying on twofold symmetry axes) and $[Cu(4,4'\text{-bipy})]_n^{n+}$ chains (bipy = bipyridyl); the chains are generated by a c-glide-plane operation. The $\{Mo_2O_7\}^{2-}$ units are covalently bridged to two $[Cu(4,4'\text{-bipy})]_n^{n+}$ chains, forming a complex with a bridged double-chain structure. The Cu—O and Cu—N distances are 2.191 (3) and 1.933 (3) Å, respectively.

Comment

While bidendate bipyridyl complexes with copper(I) are known, those with 4,4′-bipy are uncommon (Hathaway, 1987). In recent years, however, some groups have reported a few 4,4′-bipy complexes with an open framework structure, such as $[Cu(4,4'\text{-bipy})Cl]_n$ (Yaghi & Li, 1995*a*), which was synthesized in non-aqueous solvents, $[Cu(4,4'\text{-bipy})_{1.5}NO_3(H_2O)_{1.25}]$ (Yaghi & Li, 1995*b*), and $[Cu(4,4'\text{-bipy})Mo_8O_{26}]$ and $[\{Cu(4,4'\text{-bipy})\}_4Mo_{15}O_{47}]$(Hagrman *et al.*, 1997), which were synthesized under hydrothermal conditions. We report here the structure of a new compound, (I), which is the first example of a polyoxoanion-bridged copper(I) complex.



(I)

The structure of (I) consists of a covalently bridged framework built up from $\{Mo_2O_7\}^{2-}$ units and $[Cu(4,4'\text{-bipy})]_n^{n+}$ chains (Fig. 1). The dimolybdate units are structurally related to the discrete dimolybdate anions which were isolated as the tetrabutylammonium salt by Day *et al.* (1977). The unit possesses crystallographic $C2$ symmetry and is built up from two distorted MoO_4 tetrahedra by sharing a vertex. The Mo···Mo distance is 3.713 (1) Å. The $\{Mo_2O_7\}^{2-}$ unit has three kinds of Mo—O bonds: 1.709 (4) and 1.721 (3) Å for Mo—O$_{\rm terminal}$, 1.869 (1) Å for Mo—O$_{\rm bridge}$ and 1.732 (3) Å for Mo—O$_{\rm Cu}$. The Mo—O—Mo angle is 166.9 (3)°, which is greater than that of the discrete $\{Mo_2O_7\}^{2-}$ anion (153.6°).

Copper(I) ions and 4,4′-bipy ligands are linked by means of a coordination bond, forming $[Cu(4,4'\text{-bipy})]_n^{n+}$ chains. Two $[Cu(4,4'\text{-bipy})]_n^{n+}$ chains are covalently linked through $\{Mo_2O_7\}^{2-}$ units to form $[Cu_2(4,4'\text{-bipy})_2\{Mo_2O_7\}]_n$ with a bridged double-chain structure. The distance of the two chains is 3.376 (7) Å (based on the C1···C1*A* distance). It is interesting that $\{Mo_2O_7\}^{2-}$ units are positioned alternately on both sides of the two chains.

The title complex displays distorted trigonal planar geometry at the copper(I) centre. The N1—Cu—N2$^{\rm i}$, N1—Cu—O1 and N2$^{\rm i}$—Cu—O1 angles are 152.59 (14), 100.78 (12) and 103.37 (12)°, respectively [symmetry code: (i) x, $-1-y$, $\frac{1}{2}+z$]. Atoms N1, N2$^{\rm i}$, O1 and Cu are nearly in the same plane. The two pyridine rings of the bipyridyl molecule are not coplanar; the bipyridyl dihedral angle is 34.2 (6)°. As the calculated valence sum of Mo is 6.06 (Brown & Altermatt, 1985), the valence sum of Cu is deduced to be 1.

Experimental

The synthesis of (I) was carried out by the hydrothermal reaction of $Na_2MoO_4{\cdot}2H_2O$, $CuSO_4{\cdot}5H_2O$, 4,4′-bipy, As_2O_3 and H_2O (molar ratio 1:1:1:0.5:500) in a 30 ml Teflon-lined stainless steel autoclave for 5 d at 443 K. The resulting rectangular parallelepiped orange crystals were separated from the green paste by washing in water after cooling down to room temperature.

Crystal data

$[Cu_2(C_{10}H_8N_2)_2\{Mo_2O_7\}]$
$M_r = 743.33$
Orthorhombic, $Pbcn$
$a = 11.839$ (2) Å
$b = 9.108$ (2) Å
$c = 21.319$ (4) Å
$V = 2298.8$ (8) Å^3
$Z = 4$
$D_x = 2.148$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 33 reflections
$\theta = 4.89$–11.53°
$\mu = 2.942$ mm^{-1}
$T = 293$ (2) K
Block, orange
0.50 × 0.42 × 0.38 mm

Data collection

Siemens $P4$ diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical (North *et al.*, 1968)
$T_{\rm min} = 0.229$, $T_{\rm max} = 0.325$
2750 measured reflections
2016 independent reflections
1549 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\rm max} = 25°$
$h = -1 \rightarrow 14$
$k = -1 \rightarrow 10$
$l = -25 \rightarrow 1$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.069$
$S = 0.899$
2016 reflections
191 parameters
All H-atoms parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0414P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.001$
$\Delta\rho_{\rm max} = 0.510$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.901$ e Å^{-3}

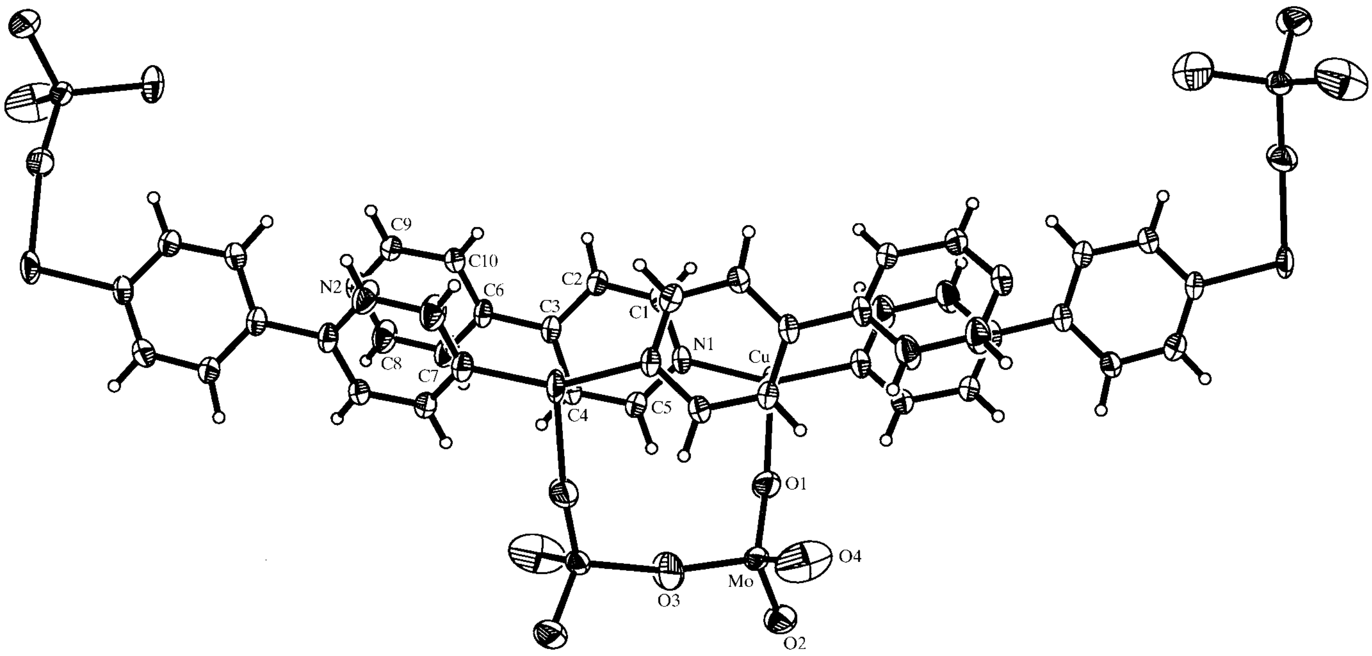


Figure 1
A view of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

Table 1
Selected geometric parameters (Å, °).

Mo—O4	1.709 (4)	Cu—O1	2.191 (3)
Mo—O2	1.721 (3)	N1—C1	1.343 (5)
Mo—O1	1.732 (3)	N1—C5	1.344 (5)
Mo—O3	1.8687 (8)	N2—C8	1.332 (5)
Cu—N1	1.933 (3)	N2—C9	1.339 (5)
Cu—N2^{i}	1.933 (3)	C3—C6	1.489 (5)
O4—Mo—O2	109.2 (2)	O2—Mo—O3	108.8 (2)
O4—Mo—O1	109.3 (2)	O1—Mo—O3	110.1 (2)
O2—Mo—O1	110.2 (2)	N1—Cu—O1	100.8 (1)
O4—Mo—O3	109.3 (2)		

Symmetry code: (i) $x, -1-y, \frac{1}{2}+z$.

All H atoms were refined and C—H distances are in the range 0.87 (5)—0.98 (5) Å.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was funded by the National Nature Science Foundation of China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1440). Services for accessing these data are described at the back of the journal.

References

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–249.

Day, V. W., Fredrich, M. F., Klemperer, W. G. & Shum, W. (1977). *J. Am. Chem. Soc.* **99**, 6146–6148.

Hagrman, D., Zubiet, C., Rose, D. J., Zubiet, J. & Haushalter, R. C. (1997). *Angew. Chem. Int. Ed. Engl.* **36**, 873–876.

Hathaway, B. J. (1987). *Comprehensive Coordination Chemistry*, edited by G. Wilkinson, R. D. Gillard & J. A. McCleverty, pp. 534–774. Oxford: Pergamon.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL*93. University of Göttingen, Germany.

Siemens (1994). *XSCANS* (Version 2.1) and *SHELXTL* (Release 5.03). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Yaghi, O. M. & Li, G. (1995*a*). *Angew. Chem. Int. Ed. Engl.* **34**, 207–209.

Yaghi, O. M. & Li, H. (1995*b*). *J. Am. Chem. Soc.* **117**, 10401–10402.

290 Wan-Sheng You *et al.* • [$Cu_2(C_{10}H_8N_2)_2\{Mo_2O_7\}$] *Acta Cryst.* (2000). C**56**, 289–290