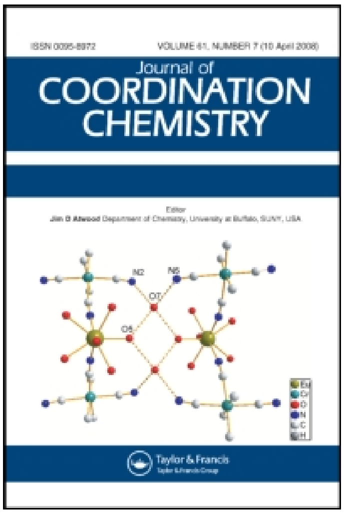

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and structure of a hybrid-metallic complex [$Cu_4(obpy)_4(Mo_2O_7)$] containing Cu^I/Cu^{II} unit

Dexin Hu[a]; Yunxia Che[a]; Pangkuan Chen[a]; Jimin Zheng[a]
[a] Department of Chemistry, Nankai University, Tianjin 300071, P. R. China

To cite this Article Hu, Dexin , Che, Yunxia , Chen, Pangkuan and Zheng, Jimin(2007) 'Synthesis and structure of a hybrid-metallic complex [$Cu_4(obpy)_4(Mo_2O_7)$] containing Cu^I/Cu^{II} unit', Journal of Coordination Chemistry, 60: 18, 1959 — 1964

To link to this Article: DOI: 10.1080/00958970701195733

URL: http://dx.doi.org/10.1080/00958970701195733

Journal of Coordination Chemistry
Vol. 60, No. 18, 15 September 2007, 1959–1964

Synthesis and structure of a hybrid-metallic complex $[Cu_4(obpy)_4(Mo_2O_7)]$ containing Cu^I/Cu^{II} unit

DEXIN HU, YUNXIA CHE, PANGKUAN CHEN and JIMIN ZHENG*

Department of Chemistry, Nankai University, Tianjin 300071, P. R. China

(*Received in final form 26 May 2006*)

An organic–inorganic hybrid mixed-valence Cu^I/Cu^{II} tetranuclear polymer $[Cu_4(obpy)_4(Mo_2O_7)]$ **1** (Hobpy = 6-hydroxy-2,2′-bipyridine) has been prepared and structurally determined. $[Cu_4(obpy)_4(Mo_2O_7)]$ **1** crystallizes in the triclinic space group *P*-1, with $a = 9.995(5)$, $b = 10.678(6)$, $c = 10.838(6)$ Å, $\alpha = 90.698(6)$, $\beta = 113.891(6)$, $\gamma = 106.018(6)$ °, $Z = 1$. Two $[Cu_2(obpy)_2]^+$ building units linked with one μ_2-bridging molybdate dimer $Mo_2O_7^{2-}$ result in a dumbbell-like tetranuclear complex, which extends to a one-dimensional chain by π–π stacking interaction between adjacent 2,2′-bipy ligands.

Keywords: Organic-inorganic hybrid; Polyoxometalates; Tetranuclear; Polymer

1. Introduction

Interest in crystal engineering of organic–inorganic hybrid solid-state materials reflects their structural diversity and vast range of properties with applications to catalysis, sorption, clathration, electrical conductivity, magnetism, and photochemistry [1–3]. Polyoxometalates (POMs) [4], as one kind of significant metal oxide cluster with nanosizes and abundant topologies, have been employed as inorganic hybrid building blocks for the construction of organic–inorganic hybrid materials with various transition metal complexes as the bridging ligands [5–7]. Design and synthesis of mixed-valance Cu^I/Cu^{II} complexes have received attention for their electronic properties and biological importance [8]. 1,10-phenanthroline, 2,2′-bipyridine, and their substituted derivatives have played an important role in the development of coordination chemistry [5, 9–12], and over the decades a number of so-called anomalies have been reported in the reactions of their metal complexes. However, the hydroxylation of phen and bipy is not very common, as only a few compounds have been obtained [13]. In this communication, we described the preparation and structural characterization of a hybrid mixed-valence Cu^I/Cu^{II} tetranuclear polymer $[Cu_4(obpy)_4(Mo_2O_7)]$ **1**. To the best of our knowledge, there are only a few examples where an inorganic bridging ligand serves as a 'handle' between two metal-organic hybrid coordination fragments to form a dumbbell-like complex [14].

---

*Corresponding author. Tel.: +86-22-23501942. Fax: +86-22-23502458. Email: jmzheng@public.tpt.tj.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970701195733

2. Experimental section

2.1. *Physical measurements*

The elemental analysis was carried out on a Perkin-Elmer 2400 analyzer and the inductively coupled plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300 DV spectrometer. IR spectrum was recorded in the range 400–4000 cm^{-1} on a FT-IR 170SX (Nicolet) Spectrometer using KBr pellets. X-ray photoelectronic spectra (XPS) were carried out on an Escalab MKII photoelectronic spectrometer with Mo Kα as X-ray source.

2.2. *Synthesis*

A mixture of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.195 g), $Cu(NO_3)_2 \cdot 3H_2O$ (0.30 g), 2,2′-bipyridine (0.06 g) and water (10 mL) in the molar ratio of 1 : 7.5 : 2.5 : 667 were reacted at 180°C for 60 h in a 25 mL Teflon-lined stainless-steel vessel. The reaction vessel cooled to room temperature at a rate of ca. 5°C h^{-1} to give small brown/black single crystals of **1** in 55% yield (based on molybdenum). Anal. Calcd for $C_{40}H_{28}Cu_4Mo_2N_8O_{11}$: C, 39.02; H, 2.16; N, 9.14%. Found: C, 38.66; H, 2.27; N, 9.02%.

2.3. *X-ray crystallography*

Single-crystal X-ray diffraction of **1** was performed on a Bruker SMART 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo-Kα radiation ($\lambda = 0.71073$ Å) by $\omega - 2\theta$ scan mode in the range of $2.00 < \theta < 25.03°$ at 293(2) K. All data were corrected for absorption by semi-empirical methods using SADABS. The program SAINT [15] was used for integration of the diffraction profiles.

The structure was solved by direct methods using SHELXS program of the SHELXL-97 package and refined with SHELXL [16]. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2. The hydrogen atoms of the ligands were placed in geometrically calculated positions. Further crystallographic data and experimental details for structure analysis of complex **1** are summarized in table 1, and the selected bond lengths and angles with estimated standard deviations in table 2.

3. Results and discussion

3.1. *Crystal structure*

Single crystal X-ray diffraction analysis reveals the title complex is constructed from one μ_2-bridging molybdate dimer $Mo_2O_7^{2-}$ and two Cu dimers $[Cu_2(obpy)_2]^+$ to form a neutral tetranuclear dumbbell-like complex figure 1.

The μ_2-bridge ligand is composed of one molybdate dimer $Mo_2O_7^{2-}$ with two Mo atoms joined together by a μ_2-O and the Mo–O–Mo angle is 180.00(2)°. It can be seen

Table 1. Crystal data and structure refinement summary for complex **1**.

Empirical formula	$C_{40}H_{28}Cu_4Mo_2N_8O_{11}$
Formula weight	1242.74
Crystal system	triclinic
Space group	P-1
Unit cell dimensions (Å, °)	
a	9.995(5)
b	10.678(6)
c	10.838(6)
α	90.698(6)
β	113.891(6)
Γ	106.018(6)
V (Å^3)	1006.3(9)
Z	1
D_c (g cm^{-3})	2.051
μ (mm^{-1})	2.754
Crystal size (mm^{-3})	0.35 × 0.20 × 0.15
F (000)	612
θ range (°)	$2.00 < \theta < 25.03$
Reflections measured	5406
Independent reflections (R_{int})	3501 (0.0128)
Goodness-of-fit on F^2	1.064
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0231$, $wR_2 = 0.0605$

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Bond lengths					
Cu1–N1	1.910(2)	Cu1–N2	2.027(2)	Cu1–O2	1.895(2)
Cu1–O3	2.340(2)	Cu1–Cu2	2.379(10)	Cu2–N3	1.900(2)
Cu2–N4	2.021(2)	Mo1–O3	1.733(2)	Mo1–O6	1.853(7)
Mo1–O5	1.720(2)	Mo1–O4	1.712(3)	C1–O1	1.289(3)
Bond angles					
O1–Mo1–O2	108.06(18)	Mo1–O3–Mo1(1)	180.00(2)		
Mo1–O2–Cu1	121.94(18)	O4–Mo1–O5	107.46(13)		
O2–Cu1–Cu2	90.96(6)	N1–Cu1–N2	80.42(10)		
N2–Cu1–O3	101.77(9)	Mo1–O3–Cu1	141.56(12)		

each Mo atom is four-coordinated, with a slightly distorted tetrahedral geometry, the Mo–O bond distances range from 1.720(2) to 1.853(7) Å. In the half-unit of **1**, Mo1 is linked with Cu1 through O3 with the Mo–O–Cu angle of 141.56(12)°, another oxygen atom from the 'handle' $Mo_2O_7^{2-}$ has a weak interaction with Cu2 (Cu2–O5 = 3.152 Å).

It is quite interesting that two crystallographically independent copper atoms have different coordination environments in the $[Cu_2(obpy)_2]^+$ unit of **1**. The coordination geometry of Cu1 is five-coordinate square pyramid by two nitrogen atoms from one obpy with bond distances of Cu1-N in the range 1.910(2)–2.027(2) Å, a deprotonated hydroxyl group from another obpy with Cu1–O2 1.895(2) Å, by an oxygen atom of the molybdate dimer in the apical position with Cu1–O3 bond distance is 2.340(2) Å, and a bond to the adjacent copper atom at the equatorial position with Cu1–Cu2 distance of 2.379(10) Å. The Cu2 atom is four-coordinate square-plane, two nitrogen atoms from a obpy ligand occupying two coordination sites with the distance Cu2–N from 1.900(2) to 2.021(2) Å, an oxygen atom of a deprotonated hydroxy group from another obpy

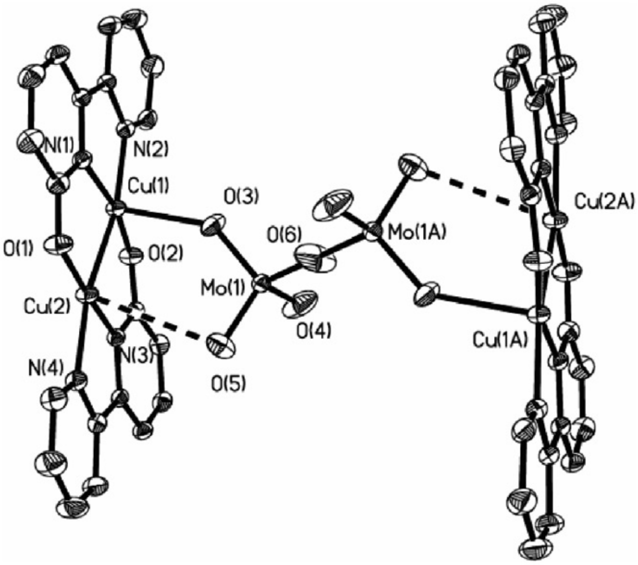

Figure 1. ORTEP view of the building block units in crystalline of **1**. Only parts of atoms are labeled, and all H atoms are omitted for clarity.

occupies the third coordination site with Cu2–O1 1.871(2) Å, and the adjacent copper atom at the equatorial position occupies the last coordination site with the bond distance mentioned above. As can be seen an oxygen atom from the μ_2-bridge ligand molybdate dimer $Mo_2O_7^{2-}$ has a weak interaction with Cu2. Table 2 summarizes the major bond distances and angles

The unusually short Cu–Cu distance (<2.5 Å) in **1** indicates that the metal has a mixed Cu(I)/Cu(II) valence, and is consistent with the majority of $[Cu_2]^{3+}$ dimers in mixed-valance dicopper complexes reported previously [17, 18]. Other structural evidence for these comes from the necessity to balance charge of the ligands in **1**. The XPS measurement also prove the presence of mixed-valence of Cu(I)/Cu(II) (figure 4).

In the structure of **1**, as shown in figure 2, the Cu_2^{3+} dimers of adjacent units are in van der Waals contact with each other to form a parallelogram with the longer side 3.745 Å in **1**. Packing interactions between organic ligands play an important role in the packing of compound **1**, with neighboring aromatic rings of obpy stacking face-to-face with a separation of 3.2−3.8 Å which indicates strong packing interactions between them. Thus, the stabilization and insolubility of **1** may result from Cu ... Cu interaction and the intermolecular packing interaction among aromatic rings figure 3.

3.2. *Spectral characterizations*

The infrared spectrum of **1** exhibits intense bands in the range 700–950 cm^{-1}, attributed to *v*(Mo=O) and *v*(Mo–O–Mo), features at 1614, 1598, 1491, 1462, 1167 cm^{-1} are characteristic of 2,2′-bipyridine, the absorption at 3469.81 cm^{-1} can be attributed to the stretching vibration of hydroxyl, further confirming the composition of **1**.

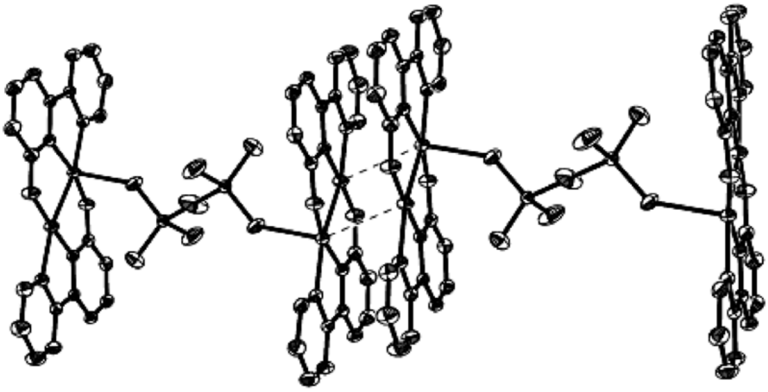

Figure 2. The intermolecular Cu···Cu interaction of adjacent molecules in **1** down the *a*-axis.

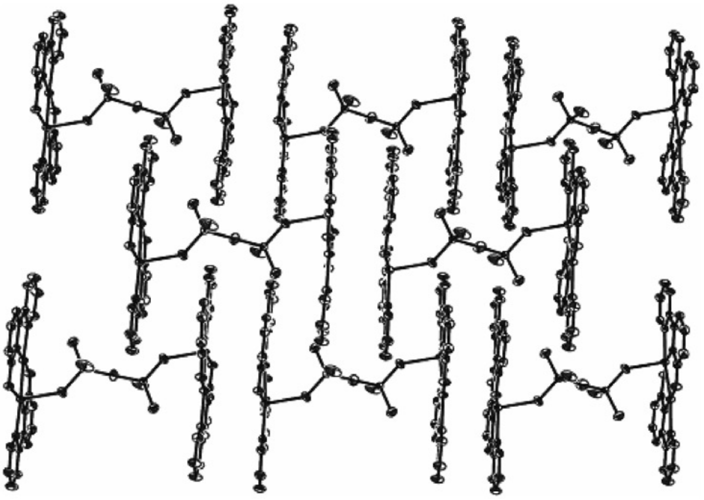

Figure 3. The packing arrangement of compounds **1** along *a*-axis.

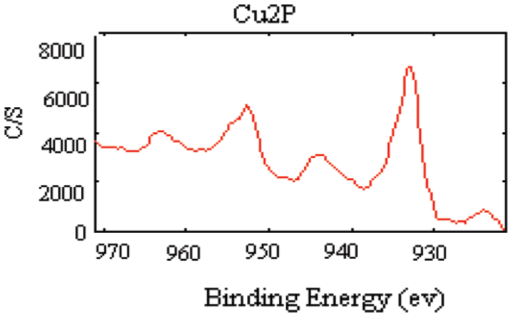

Figure 4. The XPS of **1**.

The oxidation state of Cu(I,II) cation in **1** can be verified by XPS measurement (figure 4). The XPS spectra of the brown/black complex **1** with shoulder peaks of $^2P_{3/2}$ and $^2P_{1/2}$ at 932.6 and 952.5 eV, display the presence of Cu(I); while the weak satellite peaks at 944.5 and 963.0 eV represent the Cu(II) positive ion. All these indicate that Cu(I) and Cu(II) co-exist in the title compound, consistent with those reported [13a, 17, 18].

Supplementary material

Crystallographic data for the structure analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Reference numbers: 282477. Copy of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44) 1223 336-033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 50572040), and we gratefully acknowledge Dr. Jianhua Guo for collection of XRD data.

References

[1] (a) *Supramolecular Architecture: Synthetic Control in Thin Films and Solids*, T. Bein (Ed.), ACS Symp. Ser. 499 (1992); (b) *Magnetic Molecular Materials*, D. Gatteschi, O. Kahn. J.S. Miller, F. Palacio (Eds.), NATO AST Ser. Ser. E. **198**, (1991); (c) *Inorganic Materials*, D.W. Bruce, D. O'Hare (Eds.), Wiley, Chichester (1992); (d) *Introduction to Molecular Electronics*, M.C. Petty, M.R. Bryce, D. Bloor (Eds.), Edward Arnold, London (1995).
[2] M. Fujita, Y.J. Kwon, O. Sasahi, K. Yamaguchi, K. Ogura. *J. Am. Chem. Soc.*, **117**, 7278 (1995).
[3] N. Masciocchi, D. Cairati, L. Carlucci, G. Mezza, G. Ciani, A. Sireni. *J. Chem. Soc. Dalton Trans.*, 2739 (1996).
[4] M.T. Pope. *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, New York (1983).
[5] Y. Liu, Y. Xu, E.B. Wang, J. Lü, C.W. Hu, L. Xu. *Cryst. Growth Des.*, **5**, 257 (2005).
[6] C.T. Kressge, M.E. Leonowicz, W.J. Roth, J.C. Vartuni, J.S. Beck. *Nature.*, **359**, 710 (1992).
[7] (a) E. Coronado, C.J. Gómmez-García, *Chem. Rev.* **98**, 273 (1998); (b) X.Y. Huang, J. Li, H.X. Fu, *J. Am. Chem. Soc.* **122**, 8789 (2000).
[8] M.L. Tong, L.J. Li, K. Mochizuki, H.C. Chang, X.M. Chem, Y. Li, S. Kitagawa. *Chem. Commun.*, 428 (2003).
[9] C. Kaes, A. Katz, M.W. Hosseini. *Chem. Rev.*, **100**, 3553 (2000).
[10] K. Warnmark, J.A. Thomas, O. Heyke, J.M. Lehn. *Chem. Commun.*, 701 (1996).
[11] J.Q. Xu, R.Z. Wang, G.Y. Yang, Y.H. Xing. *Chem. Commun.*, 983 (1999).
[12] C.M. Liu, D.Q. Zhang, M. Xiong, D.B. Zhu. *Chem. Commun.*, 1416 (2002).
[13] (a) X.M. Chen, G.F. Liu. *Chem. Eur. J.*, **8**, 4811 (2002); (b) X.M. zhang, M.L. Tong, M.L. Gong, H.K. Lee, L. Luo, K.F. Li, Y.X. Tong, X.M. Chen. *Chem. Eur. J.*, **8**, 3187 (2002); (c) X.M. Zhang, M.L. Tong, X.M. Chen. *Angew. Chem. Int. Ed.*, **41**, 1029 (2002); (d) S.L. Zheng, J.P. Zhang, W.Y. Wong, X.M. Chen. *J. Am. Chem. Soc.*, **125**, 6882 (2003).
[14] Q.H. Zhao, X.F. Wang, Y.Q. Liu, R.B. Fang. *Chem. Lett.*, **33**, 138 (2004).
[15] S. Garcia-Granda, A.D. Morales, E.R. Ruiz, J.F. Beltran. *Acta Crystallogr.*, **52**, 1679 (1996).
[16] G.M. Sheldrick. *SHELXLTL: Structure Determination Software Progaramas*, Bruker Analytical X-ray System, Inc., Madison, WI, USA. (1997).
[17] X. He, C.Z. Lu. *Z. Anorg. Allg. Chem.*, **630**, 756 (2004).
[18] Y.H. Feng, Z.G. Han, J.Peng, X.R. Hao. *J. Mol. Struct.*, **734**, 171 (2005).