Synthesis and Structural Characterization of an Unusual Oxygen-Linked Double Cubane-Like Cluster $\{[Mo_3PbOS_3](OAc)_2(py)_3(dtp)_2O\}_2$

Rong-Min Yu, Shao-Fang Lu,* Xiao-Ying Huang, Qiang-Jin Wu, and Jian-Quan Huang†

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

Received April 4, 1997

The unusual oxygen-linked double cubane-like cluster compound $\{[Mo_3PbOS_3](OAc)_2(py)_3(dtp)_2O\}_2$ (**A**) (dtp = $S_2P(OEt_2)^-$, OAc = CH_3COO^-, py = C_5H_5N) was obtained for the first time by the reaction of the mixed S/O-bridged cluster $[Mo_3(\mu_3\text{-}O)(\mu\text{-}S)_3(dtp)_4H_2O]$ (**B**) with $Pb(OAc)_2 \cdot 3H_2O$ in the presence of excess CH_3COOH and pyridine. It has been characterized by IR, Raman, UV−vis, and X-ray structure analysis. The molecule contains a crystallographic center of inversion and can be viewed as consisting of two $[Mo_3PbOS_3]^{6+}$ cubane-like cores linked through a pair of oxygen bridges with Mo−(μ-O) bond lengths of ca. 1.89 Å. The cell dimensions are $a = 11.705(8)$ Å, $b = 19.527(8)$ Å, $c = 20.670(9)$ Å, $\beta = 98.14(4)°$, $V = 4677(8)$ Å^3, $Z = 2$ in the space group $P2_1/n$. The final $R = 0.056$, $R_w = 0.068$ for 5424 reflections with $I \geq 3\sigma(I)$. The average Mo−Mo bond distance is 2.613(1) Å and the nonbonding Mo−Pb distances lie in the range from 3.997(1) to 4.090(1) Å. The spectra of IR, Raman, and UV−vis spectra are also shown in this paper.

Introduction

Hybrid transition-main group metal clusters have attracted considerable attention in recent years. According to the literature, the main group metal elements have the tendency to stabilize the cluster framework in the catalytic reaction processes. They are often used as promoters and selectivity enhancers.[1] In addition, they have different bonding characters from the transition metals.[2] Therefore, it is hoped that some new reactions and specific physico-chemical properties of the hybrid transition−main group metal clusters will be found.[2] Moreover, the study of the effects of heavy metals such as Pb, Hg, and Bi on the biological systems are also interesting in the bioinorganic chemistry. Recently, some heterometallic cubane-like clusters synthesized from the reactions of the cluster compounds containing a $[Mo_3S_4]^{4+}$ core with either main group metals M (In,[3] Hg,[4] Ga[5]) or their complexes (Sb,[6] Pb,[7] Bi[7]) have been reported. However, few samples have been reported on the metal-incorporation reaction of mixed S/O-bridged trinuclear clusters $[Mo_3(\mu_3\text{-}O)(\mu\text{-}S)_3]^{4+}$.[8] In this paper, the synthesis, structure, and spectral characterization of the title cluster $\{[Mo_3PbOS_3](OAc)_2(py)_3(dtp)_2O\}_2$ (**A**) are described. This is the first example of the Mo−Pb oxygen-linked double cubane-like cluster containing $[Mo_3PbOS_3]$ cores.

Experimental Section

General Procedures. All manipulations were carried out in the air. $Mo_3OS_3(dtp)_4H_2O$ was prepared by the literature method.[9] Other reagents were purchased and used as received. Elemental analyses of Mo and Pb were carried out with an inductively coupled plasma-atomic emission spectrometer (ICP-AES). The IR and Raman spectra (KBr pellet) were recorded on Nicolet Magna 750 and 910 Raman spectrophotometers, respectively. UV−vis spectrum was recorded on a Shimadzu UV-3000 spectrophotometer in CH_2Cl_2 solution.

Preparation of $\{[Mo_3PbOS_3]\ (OAc)_2(py)_3(dtp)_2O\}_2$ (A). A mixture of compound $Mo_3OS_3(dtp)_4 \cdot H_2O$ (**B**) (360 mg, 0.31 mmol), $Pb(OAc)_2 \cdot 3H_2O$ (120 mg, 0.32 mmol), 1 mL of CH_3COOH, and 0.5 mL of pyridine in 20 mL of acetone was stirred vigorously under reflux for 5 h. The resultant red-brown solution was filtered. The filtrate was set openly in the air. The next day, some black crystals of **A** were obtained (110 mg, 26.3%). The metal elements of the compound were proved to be Mo and Pb by ICP-AES analysis.

X-ray Structural Characterization. A suitable crystal was mounted with epoxy on a glass fiber. The diffraction work was performed on a CAD4 four-circle diffractometer with graphite-monochromatized Mo Kα radiation. The cell parameters were obtained and refined by 25 reflections with $10° < \theta < 14°$. The reflections were collected in the range of $2° < \theta < 25°$ using the $\omega-2\theta$ scan mode. A total of 8480 unique reflections were measured, of which 5424 reflections with $I > 3\sigma(I)$ were used for structure solution and refinements. The intensity data were corrected for Lp factors and for an empirical absorption using the ψ scan technique. The Mo and Pb atoms were located by directed methods. All the other non-hydrogen atoms were located by the successive different Fourier synthesis. The hydrogen atoms were calculated by assuming idealized geometries. Their scattering contributions were added to the structure factor calculations, but their positions were not refined. All the non-hydrogen atoms were refined with anisotropic temperature factors. The calculations were carried out with a Molen program package. A summary of the crystal data and intensity collection parameters are shown in Table 1. Selected bond distances and angles are listed in Tables 2 and 3, respectively. Additional crystallography data are available as Supporting Information.

---

* Corresponding author.

† Invited professor at Fuzhou University.

(1) (a) Whitmire, K. H. *J. Cluster Sci.* **1991**, *12*(4), 231−258. (b) Shich, M.; et al. *Inorg. Chem.* **1993**, *32*, 2785−2787.

(2) Basolo, F. *Coord. Chem. Rev.* **1993**, *25*, 13−34.

(3) Sakane, G.; Shibahara, T. *Inorg. Chem.* **1993**, *32*, 777−778.

(4) Shibahara, T.; Akashi, H.; Yamasaki, M.; Hashimoto, K. *Chem. Lett.* **1991**, 689−692.

(5) Shibahara, T.; Kobayashi, S.; Tsuji, N.; Sakane, G.; Fukuhara, M. *Inorg. Chem.* **1997**, 1702−1706.

(6) Lu, S.-F.; Huang, J.-Q.; Lin, Y.-H.; Huang, J.-L. *Acta Chim. Sinica* **1987**, *3*, 191−208.

(7) Lu, S.-F.; Huang, J.-Q.; Wu, Q.-J.; Huang, X.-Y.; Yu, R.-M.; Zheng, Y.; Wu, D.-X *Inorg. Chim. Acta* **1997**, *261*, 201−209.

(8) Huang, J.-Q.; Lu, S.-F.; Huang, X.-Y.; Wu, Q.-J.; Yu, R.- M. *J. Cluster Sci.* **1997**, *8*(1), 47−57.

(9) Lu, S.-F.; Shang, M.-Y; Huang, J.-Q.; Huang, J.-L.; Lu, J.-X. *Scientia Sinica* (*Ser. B*) **1988**, *4*(2), 47.

10.1021/ic9703890 CCC: $18.00

Table 1. Crystal Parameters and X-ray Diffraction Data for Compound **A**

formula	$Pb_2Mo_6S_{14}P_4O_{20}N_6C_{54}H_{82}$
fw	2698.10
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	11.705(8)
b, Å	19.527(8)
c, Å	20.670(9)
β, deg	98.14(4)
V, Å^3	4677(8)
Z	2
D_{calcd}, g cm^{-3}	1.92
μ(Mo Kα), cm^{-1}	4.80
T, K	293
λ, Å	0.71073
transm coeff	0.543, 0.997
no. of total data	8480
no. of observations	5424
no. of variables	478
R^a, $R_w{}^b$	0.056, 0.068
goodness of fit, s	0.86
max shift in final cycle	0.01

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. $s = (\sum w(|F_o - F_c|)^2/N_{obs.} - N_{param.})^{1/2}$.

Table 2. Selected Bond Distances (Å)[a]

atom	atom	distance	atom	atom	distance
Pb	Mo1	4.090(1)	Mo3	S2	2.336(4)
Pb	Mo2	3.997(1)	Mo3	S3	2.370(4)
Pb	Mo3	4.037(1)	Mo1	O	1.973(8)
Mo1	Mo2	2.610(2)	Mo1a*	O1	1.88(1)
Mo1	Mo3	2.647(2)	Mo2	O	2.002(9)
Mo2	Mo3	2.611(2)	Mo3	O	1.988(8)
Pb	S1	3.083(4)	Mo3	O1	1.89(1)
Pb	S2	3.004(4)	Mo1	O11	2.225(9)
Pb	S3	2.986(4)	Mo2	O12	2.123(9)
Pb	S11	2.744(6)	Mo2	O21	2.16(1)
Pb	S12	3.094(6)	Mo3	O22	2.187(9)
Pb	S21	2.889(6)	Mo1	N1	2.28(1)
Pb	S22	2.816(5)	Mo2	N2	2.25(1)
Mo1	S1	2.357(4)	Mo3	N3	2.26(1)
Mo1	S2	2.331(4)	S11	P1	1.993(9)
Mo2	S1	2.299(4)	S12	P1	1.958(9)
Mo2	S3	2.309(4)	S21	P2	1.972(8)
			S22	P2	1.982(8)

[a] The coordinates for the atom marked with the asterisk are ($-x$, $-y$, $-z$).

Table 3. Selected Bond Angles (deg)[a]

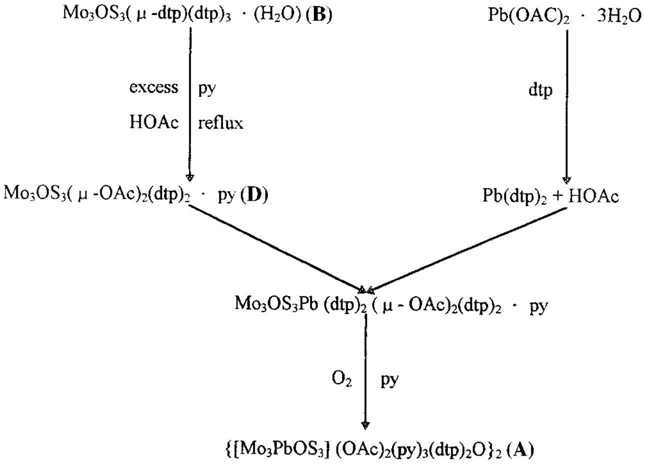
atom	atom	atom	angle	atom	atom	atom	angle
Mo2	Mo1	Mo3	59.56(5)	S2	Mo1	O1a*	101.1(3)
Mo1	Mo2	Mo3	60.91(6)	O	Mo1	O1a*	87.2(4)
S3	Pb	S11	164.4(2)	Mo1	S1	Mo2	68.2(1)
S3	Pb	S21	94.6(1)	Mo1	S2	Mo3	69.1(1)
S3	Pb	S22	98.5(1)	Mo2	S3	Mo3	67.8(1)
S1	Pb	S21	87.1(2)	Pb	S3	Mo2	97.2(1)
S11	Pb	S22	96.6(2)	Pb	S3	Mo3	97.2(1)
S21	Pb	S22	70.3(2)	Mo1	O	Mo2	82.1(3)
S1	Mo1	S2	94.7(1)	Mo1	O	Mo3	83.9(3)
S1	Mo1	O	103.7(3)	Mo2	O	Mo3	81.8(3)
S1	Mo1	O1a*	158.2(3)	Mo1a*	O1	Mo3	161.2(6)

[a] The coordinates for atoms marked with an asterisk are ($-x$, $-y$, $-z$).

Results and Discussion

Comments on Synthesis. As mentioned in the Experimental Section, the title cluster **A** was prepared by the reaction between $Mo_3OS_3(\mu\text{-dtp})(dtp)_3(H_2O)$ (**B**) and $Pb(OAC)_2{\cdot}3H_2O$ in the presence of excess CH_3COOH and pyridine. Although the formation mechanism of compound **A** is not yet clear now, its crystal structure allows us to propose a general reaction scheme (Scheme 1).

Scheme 1



The transform **B** → **D** has been proven by our previous work,[10] and the formation of $Pb(dtp)_2$ from $Pb(OAc)_2$ has been reported.[11] It is reasonable to believe that an intermediate product $Mo_3OS_3Pb(dtp)_2(\mu\text{-OAc})_2(dtp)_2py$ occurred in the reaction process. But this cluster may be unstable and can easily react with O_2 and py to form cluster **A**. Further work is now in progress.

Structure. An ORTEP drawing of the molecular structure of compound $\{[Mo_3PbOS_3](OAc)_2(py)_3(dtp)_2O\}_2$ (**A**) is shown in Figure 1.

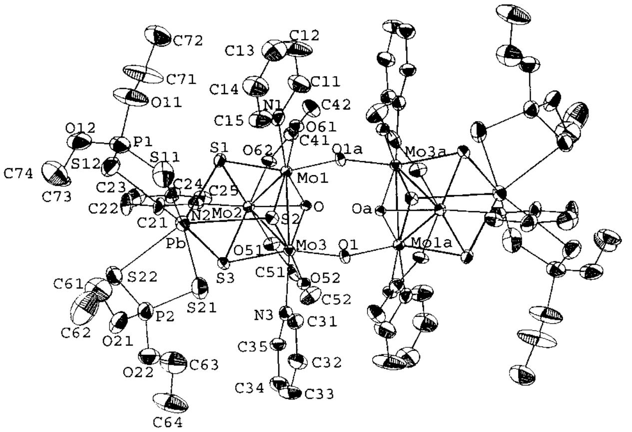


Figure 1. Perspective view of $\{[Mo_3PbOS_3](OAc)_2(py)_3(dtp)_2O\}_2$.

The molecule can be viewed as consisting of two crystallographically identical $\{[Mo_3PbOS_3](OAc)_2(py)_3(dtp)_2O\}$ cubane-like units bound together by two Mo−(μ-O) bridging bonds and contains a center of inversion which is situated in the center of the $[Mo_4O_2S_2]$ ring ([S2−Mo1−O1a−Mo3a−S2a-Mo1a−O1−Mo3]). The Mo−(μ-O) bond length for Mo3−O1 is 1.89(1) Å, that for Mo1a−O1 is 1.88(1) Å, and the angle of the bridge Mo3−O1−Mo1a is 161.2(6)°. In each $[Mo_3PbOS_3]$ core, there are two short and one slightly long Mo−Mo bonds with bond lengths 2.610(2) Å for Mo1−Mo2, 2.611(2) Å for Mo2−Mo3, and 2.647(2) Å for Mo1−Mo3. The shortening of the former two bonds is probably due to the bridging effect of the

---

(10) Lu, S.-F.; Huang, J.-Q.; Huang, Z.-X.; Zhang, B.; Huang, J.-L. *Chin. J. Chem.* **1992**, *10*(6), 500−507.

(11) Schluter, R. D.; Krauter, G.; Rees, W. S., Jr. *J. Cluster Sci.* **1997**, *8*(1), 123−154.

(OAc) ligand. The average Mo−Mo bond distance is 2.613(1) Å. Each Mo atom is surrounded by six atoms, which form a distorted octahedron coordinated geometry. Among the Mo atoms, Mo1 and Mo3 atoms are bonded to a μ_3-O atom, two μ_3-S atoms, a N atom of a terminal pyridine, an O atom of a OAc ligand and a μ-O atom shared by the two identical single cubane-like units, while for the Mo2 atom, the fifth and sixth coordinated atoms are all O atoms from two OAc ligands. The average of Mo−(μ_3-O) bonds is 1.998(9) Å, which is comparable with that of $[Mo_3OS_3](\mu\text{-}OAc)_2(dtp)_2Py$[10] and smaller than those found in the $[Mo_3OS_3](dtp)_4L$ and $[Mo_3OS_3](\mu\text{-}OAc)(dtp)_3L$ (L = py, H_2O, $C_3H_3N_2$, C_3H_3ON; 2.03−2.07 Å).[12−14] The Pb atom is in coordination with seven S atoms with a distorted pentagonal bipyramid, of which three are μ_3-S atoms and the other four are from two dtp ligands. The Pb−S_{dtp} distances fall in a relatively large range from 2.744(7) to 3.094(6) Å.

Unlike the double-cubane clusters reported previously by Shibahara and co-workers, the double-cubane-like core in the title cluster is neither the edge-linked type $[Mo_3S_4M'M'S_4Mo_3]$ (M′ = Co,[5] Pd,[15] Cu[16]) nor the corner-shared type $[Mo_3S_4M'S_4Mo_3]$ (M′ = Sn,[17] In[18]), it is a new type in which two cubane-like cores share two μ-O atoms, thus resulting in a $[Mo_4O_2S_2]$ cavity. This configuration is somewhat similar to the structure of FeMoco in the nitrogenase.[19]

Spectral Characterization. IR Spectrum (cm^{-1}): In addition to the characteristic absorption peaks of (dtp) ligand,[20] very sharp bands with high intensity at 1604.5, 1444.4, and 692.3 cm^{-1} have been observed as the most characteristic absorptions of py.[21]The band at 713.5 cm^{-1} in the IR spectrum is attributed to Mo−(μ_3-O) as compared to the already known compounds having similar cluster core.[20] Moreover, 443.6 cm^{-1} is attributed to Mo−(μ_3-S); 744.4 to Mo−(μ-O); 673.0 to Mo−(μ-O(OAc)); 651.8 to ν ^{as}(Mo−N(py)) and 538.0 to ν ^{as}(Mo−N(py)). In the Raman spectrum, the intense absorption at 219.2 cm^{-1} is assigned to be characteristic of the Mo−Mo mode.[22]

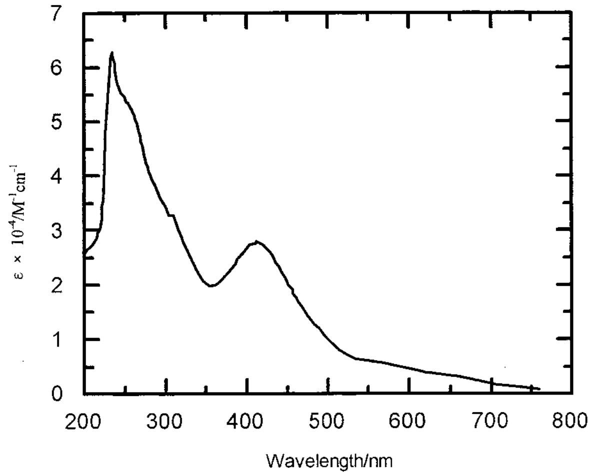


Figure 2. Electronic spectrum of $\{[Mo_3PbOS_3](OAc)_2(py)_3(dtp)_2O\}_2$.

UV−Vis Spectrum: Four absorption peaks were observed in the UV−vis spectrum as shown in Figure 2. λ_{max} nm (ϵ, M^{-1} cm^{-1}): 415 (2.81 × 10^4), 310 (3.31 × 10^4), 255 (5.47 × 10^4), 235 (6.33 × 10^4). It is different from the UV−vis spectrum of a $[Mo_3PbS_4]$ cluster reported recently by Bronson;[23] no signal was observed above 415 nm in this case.

Acknowledgment. We thank Yu Zheng for her kind assistance in the spectral experiments. Financial supported by State Key Laboratory of Structural Chemistry, NNSF of China, and NSF of Fujian Province is greatly appreciated.

Supporting Information Available: Raman and IR data for complex $\{[Mo_3PbOS_3]$ $(OAc)_2(py)_3(dtp)_2O\}_2$ an X-ray crystallographic file, in CIF format, for $\{[Mo_3PbOS_3]$ $(OAc)_2(py)_3(dtp)_2O\}_2$ are available free of charge via the Internet at http://pubs.acs.org.

IC9703890

---

(12) Huang, M.-D.; Lu, S.-F.; Huang, J.-Q.; Huang, J.-L. *Chin. J. Struct. Chem.* **1987**, *7*, 29.

(13) Lu, S.-F.; Shang, M.-Y.; Huang, J.-Q.; Huang, J.-L.; Lu, J.-X. *Scientia Sinica (Ser. B)* **1987**, *4*, 358.

(14) Wang, Z.-M.; Zhang, B.; Huang, W.; Wang, J.-Q.; Huang, J.-L *Chin. J. Struct. Chem.* **1992**, *11*, 127.

(15) Murata, T.; Gao, H.; Mizobi, Y.; Nakano, F.; Motomura, S.; Tanase, T.; Yano, S.; Hidai, M. *J. Am. Chem. Soc.* **1992**, *114*, 8287−8288.

(16) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1988**, *110*, 3313−3314.

(17) Akashi, H.; Shibahara, T. *Inorg. Chem.* **1988**, *28*, 2906−2907.

(18) Sakane, G.; Yao, Y.-G.; Shibahara, T. *Inorg. Chim. Acta* **1994**, *216*, 13−14.

(19) Kim, J.; Rees, G. D. *Science* **1992**, *257*, 1677.

(20) Zheng, Y.; Shang, M.-Y.; Zhang, L.-N.; Huang, J.-L.; Lu, J.-X. *Spectrosc. Anal.* **1983**, *2*, 72.

(21) *Sadtler Infrared Grating Spectra*; Sadtler Research Laboratories: Philadelphia, PA, 1980; No. 12.

(22) Saito, T. *Chalcogenide cluster complexes of the early transition metals: Early transition metal clusters with π-donor ligands*; Chisholm, M. H., Ed.; VCH Publishers Inc.: Deerfield Beach, FL, 1995; p 133.

(23) Brorson, M.; Jacobsen, C. J. H.; Helgesen, H. K. M.; Schmidt, I. *Inorg. Chem.* **1996**, *35*, 4808−4809.