Synthesis and Structural Characterization of a Pyridine Oxalato Molybdenum(V) Complex

Quan-Liang Chen

***Abstract*—Molybdenum complexes cause much attract due to their potential applications in the fields of material, medicine and catalysis. In this paper, a pyridine oxalato molybdenum(V) complex *trans*-$(PyH)_2[Mo_2O_4(ox)_2(Py)_2]$ (1) was synthesized with a yield of 75% in aqueous solution. Its structure was characterized by x-ray single crystal analysis. Complex 1 consists of dinuclear molybdate(V) anions and pyridine cations. The structure of molybdate(V) anion contains a dinuclear $[Mo^{V}_{2}O_4]^{2+}$ core with Mo–Mo bond [2.549(2) Å]. Moreover, complex 1 displays a *trans* arrangement for the pyridine and oxalato ligands. The pyridine ligand coordinates to molybdenum atom through nitrogen atom. The oxalato ligand coordinates to each molybdenum atom through two carboxylate oxygens in a bidentate chelating manner.**

***Index Terms*—Molybdenum; oxalate; pyridine; crystal structure**

I. INTRODUCTION

Molybdenum complexes attract much interest due to their importance in biochemistry, catalysis, medicine and material[1-3]. Until now, a number of molybdenum compounds supported by the other transition metals and organic ligands have been synthesized and characterized[3-6]. Some potential applications of the molybdenum complexes have also been investigated[7]. In the reported molybdenum complexes, the oxidation state +6 is common for the molybdenum atoms. If reducing agent used in the synthesis, molybdenum can be reduced to lower oxidation state (+3, +4 and +5)[8-11]. Mo−Mo metal bonds are frequently observed in molybdenum complexes with lower oxidation state molybdenum atoms[12-14].

Oxalate is a useful ligand for the preparations of molybdenum complexes. Different types of oxalato molybdenum complexes depend on the ratio of molybdenum and ligand, the pH value of the reaction solution and the countercation[15]. In the reported oxalato molybdenum complexes, each oxalate can take multiple coordination manners with molybdenum atoms. Oxalates bidentely coordinated to molybdenum are frequently reported. Moreover, interesting μ_4 and μ_8 modes are also found in the reported dimeric molybdenum complexes. Although some oxalato molybdenum complexes have been investigated, mixed-ligand oxalato molybdenum complexes especially on low-valent molybdenum complex are still little known. In this paper, we make an attempt to study the coordination chemistry between molybdenum and oxalate with pyridine.

A pyridine oxalato molybdenum complex was synthesized and structurally characterized in aqueous solution.

II. EXPERIMENT

A. *Materials and instrumentation*

Ammonium, sodium molybdates (99%), pyridine and oxalic acid dihydrates were purchased from Sigma. All chemicals were analytical reagents and used without further purification. Elemental analyses were performed using EA 1110 elemental analyzers. pH value was determined by PHB-8 digital pH meter.

B. *Preparation of complex*

Preparation of *trans*-$(PyH)_2[Mo_2O_4(ox)_2(Py)_2]$ (**1**). $Na_2MoO_4\cdot 2H_2O$ (0.48 g, 2.0 mmol), $H_2ox\cdot 2H_2O$ (0.76 g, 6.0 mmol) and pyridine (6.0 mmol) were dissolved in 6 mL water. Then the mixture was added by hydrazine hydrochloride (0.16 g, 1.5 mmol) to give a brown solution with constant stirring. The mixture was kept stirring for 3 h and the pH value of the mixture was adjusted to 3.5 by dilute hydrocloric acid. After that, the solution was transferred to a serum bottle and refluxed for 1.5 h. After cooling to room temperature, the filtrate was evaporated at room temperature to give yellow crystals of **1** after one week. The crystals were collected and washed with water and ethanol. Yield: (75 %) Anal. Found (%): C, 36.7; H, 2.1; N, 7.8. Calc. (%) for $C_{22}H_{15}Mo_2N_4O_{12}$: C, 36.8; H, 2.2; N, 7.8.

C. *X-Ray crystallography*

Suitable single crystal of **1** was selected and quickly mounted onto thin glass fibers to prevent the loss of water molecules. X-ray intensity data for compounds **1** was measured at 173 K on a Oxford CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). Empirical adsorption was applied to all data using SADABS and CrysAlis (multi-scan) program. The initial model was obtained through direct methods and the completion of the rest of the structure achieved by difference Fourier strategies. The structure was refined by least squares on F^2, with anisotropic displacement parameters for non-H atoms. Hydrogen atoms unambiguously defined by the stereochemistry were placed at their calculated positions and allowed to ride onto their host carbons both in coordinates as well as in thermal parameters (C–H, 0.97 Å). Those attached to oxygen atoms and needed for the H-bonding description were located in a late Fourier map and refined with similarity restrains [O–H, 0.85(1) Å; H···H, 1.39(1) Å]. All calculations to solve and refine the structures and to obtain derived results were carried out with the computer programs SHELXS 97, and SHELXL

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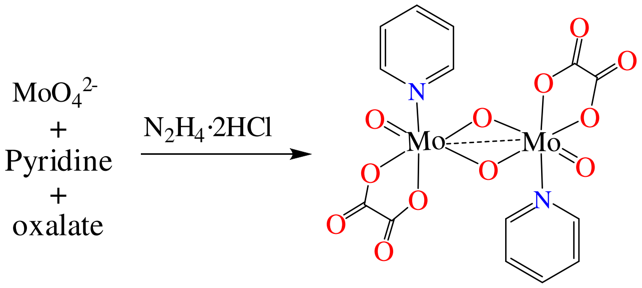
97 programs. Full use of the CCDC package was also made for searching in the CSD Database

III. RESULTS AND DISCUSSION

Preparations of the mixed-ligand molybdenum complex mainly depend on the requisite proportions of molybdate and ligand, countercations, pH value and the reaction temperature[16-19]. Synthesis of pyridine oxalato molybdenum **1** was carried out in aqueous solution as shown in Scheme 1. The molar ratio of Mo:ox:Py was 1:3:3. Hydrazine hydrochloride was used as the reducing agent to reduce molybdenum(VI) to low-valent molybdenum(V). According to our experiment, excess of ligand and hydrizine hydrochloride helps the formation of **1**. Moreover, high temperature and acidic solution are better for the synthesis of **1**. In an optimal condition of pH 3.5, complex **1** can be obtained in the yield of 75%. However, further reduction of **1** to get lower-valent pyridine oxolato molybdenum(IV) complex was unsuccessful.



Scheme 1. Synthesis of complex **1**.

The structure of **1** was tested by X-ray single crystal diffraction. Crystal data and structure refinements for **1** is shown in Table 1. Its anion structure is shown in Figure 1. Crystal structure of **1** consists of dinuclear molybdate(VI) anions, pyridine caions. The anion structures of **1** contains dinuclear $[Mo^{V}{}_2O_4]^{2+}$ cores with Mo–Mo bond. The oxalato ligand coordinates each molybdenum atom through two carboxylate oxygens in a bidentate chelating manner. The pyridine ligand coordinates to molybdenum atom through nitrogen atom. Each molybdenum atom exists in a distorted octahedral geometry defined by two O atoms of oxalate, two bridging oxo group, one terminal oxo atom and a N atom of pyridine. The *trans* arrangement was observed for **1**. The position of the pair of oxalates and pyridines are on opposite sides of the plane defined by the Mo_2O_4 unit. The same arrangement was observed for other mixed ligand molybdenum complexes such as *trans*-$(Him)_2[Mo_2O_4(ox)_2(H_2O)_2]$ and *trans*-$Na(Him)[Mo_2O_4(ox)_2(H_2O)_2]\cdot H_2O$[15].

Based on the rule of bond valence sum (BVS), oxidation states of molybdenum atoms are calculated with a linear correlation. The bond valence sums are +5.008 and +5.093 for Mo1 and Mo2 of **1**, respectively. Therefore, the oxidation states are +5 for molybdenum atoms of **1**. The detail bond distances and angles of **1** is shown in Table 2. In the dimeric moieties of **1**, the bond distances of Mo=O (terminal) is between 1.65(2) ~ 1.70(2) Å and the bond distances of Mo–O–Mo (bridge) is between 1.92(2) ~ 1.93(2) Å. In **1**, one of the two coordinated oxalato oxygen atoms is *trans* to the bridging oxygen atom, while the other is *trans* to Mo=O group. The *trans* influence of the terminal oxo group is reflected in the difference of the two $Mo–O_{ox}$ bond lengths [e.g. 2.02(2) vs. 2.16(2)]. The same phenomenon has also been observed in other reported dimeric molybdenum(V) complexes[20-24]. The bond distances of $Mo–N_{(pyridine)}$ [2.21(3) and 2.22(2) Å] are longer than those of oxalato ligand. This is because the stronger coordination of oxygen atoms of oxalato ligand. In **1**, the short distance [2.549(2) Å] between the Mo1 and Mo2 indicates the formation of metal metal bond.

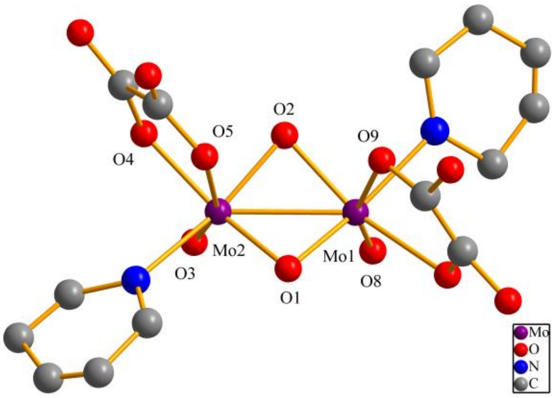


Fig. 1. Perspective view of the anion structure of **1**.

Table 1. Crystal data and structure refinements for **1**.

Compound	**1**
Chemical formula	$C_{22}H_{15}Mo_2N_4O_{12}$
Formula mass	719.25
Crystal system	monoclinic
a/Å	21.1222(2)
b/Å	8.6060(3)
c/Å	14.4913(4)
α/°	90.70(3)
β/°	108.26(2)
γ/°	90.26(3)
Unit cell volume/Å^3	2501.5(4)
Space group	*Cc*
No. of formula units per unit cell, *Z*	1
No. of reflections measured	6676
No. of independent reflections	3650
R_{int}	0.0690
Final R_1 values ($I > 2\sigma(I)$)	0.0751
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2049
Final R_1 values (all data)	0.1430
Final $wR(F^2)$ values (all data)	0.2880
Goodness of fit on F^2	0.853

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

trans-$(PyH)[Mo_2O_4(ox)_2(Py)_2]$ (**1**)			
Mo1–O8	1.70(2)	Mo2–O3	1.65(2)
Mo1–O1	1.96(2)	Mo2–O1	1.92(2)

Mo1–O2	1.97(2)	Mo2–O2	1.93(2)
Mo1–O9	2.15(2)	Mo2–O4	2.02(2)
Mo1–N2	2.21(3)	Mo2–O5	2.16(2)
Mo1–O10	2.26(2)	Mo2–N1	2.22(2)
Mo1–Mo2	2.549(2)		
O8–Mo1–O1	113.3(1)	O3–Mo2–O1	115.6(1)
O8–Mo1–O2	106.4(8)	O3–Mo2–O2	101.4(8)
O1–Mo1–O2	93.1(8)	O1–Mo2–O2	95.4(9)
O8–Mo1–O9	155.9(9)	O3–Mo2–O4	85.2(1)
O1–Mo1–O9	84.1(9)	O1–Mo2–O4	158.9(1)
O2–Mo1–O9	88.3(3)	O2–Mo2–O4	82.6(7)
O8–Mo1–N2	83.3(1)	O3–Mo2–O5	156.6(8)
O1–Mo1–N2	163.2(8)	O1–Mo2–O5	84.7(7)
O2–Mo1–N2	84.1(8)	O2–Mo2–O5	87.2(6)
O9–Mo1–N2	79.3(7)	O4–Mo2–O5	74.3(9)
O8–Mo1–O10	90.4(9)	O3–Mo2–N1	91.3(9)
O1–Mo1–O10	88.7(9)	O1–Mo2–N1	85.8(9)
O2–Mo1–O10	160.7(6)	O2–Mo2–N1	165.2(7)
O9–Mo1–O10	72.8(7)	O4–Mo2–N1	91.0(8)
N2–Mo1–O10	88.6(8)	O5–Mo2–N1	78.2(7)

IV. CONCLUSION

In summary, a pyridine oxalato molybdenum(V) complex *trans*-$(PyH)_2[Mo_2O_4(ox)_2(Py)_2]$ (**1**) was synthesized at high temperature in acidic aqueous solution. Single crystal analysis reveals that its anion contains a dinuclear $[Mo^{V}{}_2O_4]^{2+}$ cores with Mo–Mo bonds. Pyridine acts as the ligand and the cation in the complex. Study of other arrangement pyridine oxalato molybdenum complexes and their applications are ongoing.

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REFERENCES

[1] V. Blanco-Gutierrez, A. Demourgues, M. Gaudon, Sub-micrometric beta-$CoMoO_4$ rods: optical and piezochromic properties, Dalton Trans. vol. 42, 2013, pp. 13622-13627.

[2] Y. Zhu, P. Yin, F. Xiao, D. Li, E. Bitterlich, Z. Xiao, J. Zhang, J. Hao, T. Liu, Y. Wang, Y. Wei, Bottom-up construction of POM-based macrostructures: coordination assembled paddle-wheel macroclusters and their vesicle-like supramolecular aggregation in solution, J. Am. Chem. Soc. vol. 135, 2013, pp. 17155-17160.

[3] Q. Gao, F. Li, Y. Wang, L. Xu, J. Bai, Y. Wang, Organic functionalization of polyoxometalate in aqueous solution: self-assembly of a new building block of $\{VMo_6O_{25}\}$ with triethanolamine, Dalton Trans. vol . 43, 2014, pp. 941-944.

[4] Z. G. Han, X. Q. Chang, J. S. Yan, K. N. Gong, C. Zhao, X. L. Zhai, An unusual metallic oxygen cluster consisting of a $\{AlMo_{12}O_{40}(MoO_2)\}$, Inorg. Chem. vol. 53, 2014, pp. 670-672.

[5] Q. Li, Y. Wei, H. Guo, C. -G. Zhan, Syntheses, structural characterizations and electronic absorption spectra simulation of three phenylimido substituted hexamolybdates incorporating a remote chloro group, Inorg. Chim. Acta. vol. 361, 2008, pp. 2305-2313.

[6] D. Liu, P. Zhang, J. Xu, S. Feng, Z. Shi, Solvothermal synthesis and crystal structure of the Mo(VI)-bridged helical chain containing Mo_2(V) dimers: $(C_4H_{12}N_2)_2[(Mo^{V}{}_2O_4)(Mo^{VI}O_4)(C_2O_4)_2]\cdot 2H_2O$, Solid State Sci. vol. 9, 2007, pp. 16-20.

[7] E. Luévano-Hipólito, A. M.-d.l. Cruz, Q. L. Yu, H. J. H. Brouwers, Photocatalytic removal of nitric oxide by $Bi_2Mo_3O_{12}$ prepared by co-precipitation method, Appl. Cat. A: General. vol. 468, 2013, pp. 322-326.

[8] B. Modec, D. Dolenc, M. Kasunic, Complexation of molybdenum (V) with glycolic acid: an unusual orientation of glycolato ligand in $\{Mo_2O_4\}^{2+}$ complexes‡, Inorg. Chem. vol. 47, 2008, pp. 3625-3633.

[9] B. Modec, M. Šala, R. Clérac, Pyrazine-assisted dimerization of molybdenum(V): synthesis and structural characterization of novel dinuclear and tetranuclear complexes, Eur J. Inorg. Chem. vol. 2010, 2010, pp. 542-553.

[10] M. L. Ramos, L. L. Justino, H. D. Burrows, Structural considerations and reactivity of peroxocomplexes of V(V), Mo(VI) and W(VI), Dalton Trans. vol. 40, 2011, pp. 4374-4383.

[11] M. Tašner, B. Prugovečki, Ž. Soldin, S. Prugovečki, L. Rukavina, D. Matković-Čalogović, Synthesis and characterization of oxomolybdenum(V) dinuclear complexes with β-alanine, l-serine and dl-isoleucine, Polyhedron. vol. 52, 2013, pp. 268-275.

[12] J. -F. Wu, D. -M. Li, L. -F. Cui, C. -F. Zhuang, S. -N. Song, T. -G. Wang, J. -Q. Xu, H. -Q. Jia, N. -H. Hu, Two novel molybdenum complexes containing $[Mo_2O_2S_2]^{2+}$ fragment: synthesis, crystal structures and catalytic studies, Appl. Organomet. Chem. vol. 21, 2007, pp. 1033-1040.

[13] R. Yu, X. -F. Kuang, X. -Y. Wu, C. -Z. Lu, J. P. Donahue, Stabilization and immobilization of polyoxometalates in porous coordination polymers through host–guest interactions, Coord. Chem. Rev. vol. 253, 2009, pp. 2872-2890.

[14] X. -Y. Yu, X. -B. Cui, J. Lu, Y. -H. Luo, H. Zhang, W. -P. Gao, Five inorganic–organic hybrids based on Keggin polyanion $[SiMo_{12}O_{40}]^{4-}$: From 0D to 2D network, J. Solid State Chem. vol. 209, 2014, pp. 97-104.

[15] Q. L. Chen, H. B. Chen, Z. X. Cao, Z. H. Zhou, Synthesis, spectral, and structural characterizations of imidazole oxalato molybdenum(IV/V/VI) complexes, Dalton Trans. vol. 42, 2013, pp. 1627-1636.

[16] Z. M. Zhang, S. Yao, Y. G. Li, H. H. Wu, Y. H. Wang, M. Rouzieres, R. Clerac, Z. M. Su, E. B. Wang, A polyoxometalate-based single-molecule magnet with a mixed-valent $\{Mn(IV)_2Mn(III)_6Mn(II)_4\}$ core, Chem. Comm. vol. 49, 2013, pp. 2515-2517.

[17] Z. Zhao, Y. Ding, J. Bi, Z. Su, Q. Cai, L. Gao, B. Zhou, Molybdenum arsenate crystal: a highly efficient and recyclable catalyst for hydrolysis of ethylene carbonate, Appl. Cat. A: General. vol. 471, 2014, pp. 50-55.

[18] L. Zhu, Y. Zhu, X. Meng, J. Hao, Q. Li, Y. Wei, Y. Lin, DCC-assisted esterification of a polyoxometalate-functionalized phenol with carboxylic acids (DCC: dicyclohexylcarbodiimide), Chemistry, vol. 14, 2008, pp. 10923-10927.

[19] C. -H. Zhang, Y. -G. Chen, Synthesis, characterization and crystal structures of two new compounds of polyoxometalates and diaminocyclohexanetetraacetate–copper complexes, J. Cluster Sci. vol. 25, 2013, pp. 435-444.

[20] M. Grzywa, W. Nitek, W. Łasocha, Synthesis, characterization and crystal structures of three new inorganic dinuclear diperoxo complexes of W(VI) and Mo(VI); $Rb_2\{O[WO(O_2)_2H_2O]_2\}\cdot H_2O$, $Rb_2\{O[MoO(O_2)_2H_2O]_2\}\cdot H_2O$ and $Cs_2\{O[MoO(O_2)_2]_2\}$, J. Mol. Struct. vol. 919, 2009, pp. 59-65.

[21] T. Ueda, K. Machida, M. Shiro, D. Kaneno, Synthesis and characterization of novel polyoxometalates with an inverted-Keggin structure as a new class of building unit, Inorg Chem. Comm. vol. 38, 2013, pp. 123-126.

[22] C. J. Carrasco, F. Montilla, E. Álvarez, M. Herbert, A. Galindo, Molybdenum-catalysed oxidation of cyclohexene with hydrogen peroxide in the presence of alcohols and X-ray structures of octamolybdate $[C_4mim]_4[Mo_8O_{26}]$ and tetraperoxodimolybdate $[Htmpy]_2[\{MoO(O_2)_2\}_2(\mu\text{-}O)]$ complexes, Polyhedron, vol. 54, 2013, pp. 123-130.

[23] X. -Y. Shi, J. -F. Wei, X. -R. Zhang, J. Cao, Propane-1,3-diylbis(triphenylphosphonium) (oxalato)oxodiperoxomolybdate(VI) monohydrate, Acta Cryst. Sect. E Struct. Rep. Online, vol. 63, 2006, pp. m227-m229.

[24] F. Li, L. Xu, Coordination assemblies of polyoxomolybdate cluster framework: from labile building blocks to stable functional materials, Dalton Trans. vol. 40, 2011, pp. 4024-4034.

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