

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[Mo₂O₄(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^V₂O₄]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 counteraction[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.

Quan-Liang Chen, College of Chemistry of Environment Protection Engineering, Southwest University for Nationalities, Chengdu, 610041, China, +86 028-85522269., (e-mail: chql51@xmu.edu.cn).

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[Mo₂O₄(ox)₂(Py)₂] (**1**). Na₂MoO₄·2H₂O (0.48 g, 2.0 mmol), H₂ox·2H₂O (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 hydrochloric 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 C₂₂H₁₅Mo₂N₄O₁₂: C, 36.8; H, 2.2; N, 7.8.

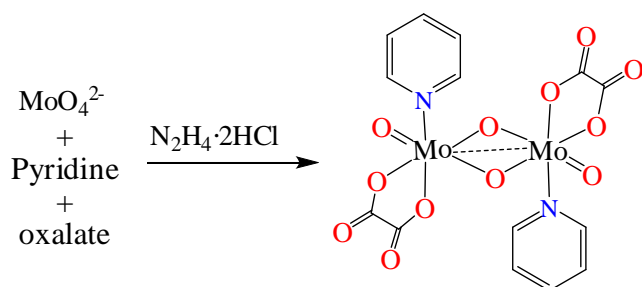
C. X-Ray crystallography

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 K α 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

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, counteractions, 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 hydrazine 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 oxalato 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 cations. The anion structures of **1** contains dinuclear $[\text{Mo}_2\text{O}_4]^{2+}$ 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) $_2$ [$\text{Mo}_2\text{O}_4(\text{ox})_2(\text{H}_2\text{O})_2$] and *trans*-Na(Him)[$\text{Mo}_2\text{O}_4(\text{ox})_2(\text{H}_2\text{O})_2$]. 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.

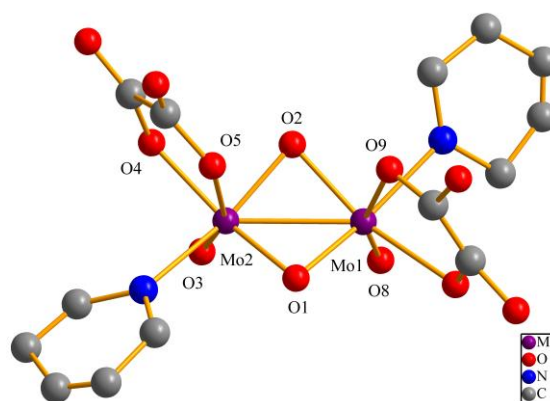


Fig. 1. Perspective view of the anion structure of **1**.

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

Compound	1
Chemical formula	$\text{C}_{22}\text{H}_{15}\text{Mo}_2\text{N}_4\text{O}_{12}$
Formula mass	719.25
Crystal system	monoclinic
$a/\text{Å}$	21.1222(2)
$b/\text{Å}$	8.6060(3)
$c/\text{Å}$	14.4913(4)
$\alpha/^\circ$	90.70(3)
$\beta/^\circ$	108.26(2)
$\gamma/^\circ$	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_I values ($I > 2\sigma(I)$)	0.0751
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2049
Final R_I 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 ($^\circ$) for **1**.

<i>trans</i> -(PyH)[$\text{Mo}_2\text{O}_4(\text{ox})_2(\text{Py})_2$] (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[Mo₂O₄(ox)₂(Py)₂] (**1**) was synthesized at high temperature in acidic aqueous solution. Single crystal analysis reveals that its anion contains a dinuclear [Mo₂O₄]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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Quan-Liang Chen received his bachelor's degree in Chemistry from Fujian Normal University in 2007. Then he obtained his Ph.D. degree in physical chemistry at Xiamen University. In 2014, he took a faculty position in the College of Chemistry and Environment Protection Engineering at Southwest University for Nationalities. His research interests include the synthesis and characterization of molybdenum complexes and photocatalysis.