

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

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.

ACKNOWLEDGMENT

Q.-L Chen thanks the Fundamental Research Funds for the Central Universities (No.2015NZYQN18) in Southwest University for Nationalities.

REFERENCES

- [1] V. Blanco-Gutierrez, A. Demourgues, M. Gaudon, Sub-micrometric beta-CoMoO₄ 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 {VMo₆O₂₅} 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 {AlMo₁₂O₄₀(MoO₂)}, 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 Mo₂(V) dimers: (C₄H₁₂N₂)₂(Mo^V₂O₄)(Mo^{VI}O₄)(C₂O₄)₂·2H₂O, 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 Bi₂Mo₃O₁₂ prepared by co-precipitation method, Appl. Cat. A: General. vol. 468, 2013, pp. 322-326.
- [8] B. Modéc, D. Dolenc, M. Kasunic, Complexation of molybdenum (V) with glycolic acid: an unusual orientation of glycolato ligand in {Mo₂O₄}²⁺ complexes, Inorg. Chem. vol. 47, 2008, pp. 3625-3633.
- [9] B. Modéc, 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 [Mo₂O₂S₂]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 [SiMo₁₂O₄₀]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. Rouziers, 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. Ł. asocha, Synthesis, characterization and crystal structures of three new inorganic dinuclear diperoxo complexes of W(VI) and Mo(VI); Rb₂{O[WO(O₂)₂H₂O]₂·H₂O, Rb₂{O[MoO(O₂)₂H₂O]₂·H₂O and Cs₂{O[MoO(O₂)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 [C₄mim]₄[Mo₈O₂₆] and tetraperoxodimolybdate [Htmpy]₂{[MoO(O₂)₂]₂(μ-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.



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.