Synthesis, Structure, and Catalytic Oxidation of a Molybdenum(VI) Complex [MoO₂(CH₃OH)L]¹

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Abstract—A new molybdenum(VI) complex, [MoO₂(CH₃OH)(L)] (L = N⁻(4-diethylamino-2-hydroxybenzylidene)-4-hydroxybenzohydrazide), was prepared and characterized by spectroscopy methods and single crystal X-ray diffraction (CIF file CCDC no. 1038153). The crystal of the complex, C₁₉H₂₃MoN₃O₆, crystallizes in the triclinic space group $P\overline{1}$ with unit cell dimensions a = 6.9824(9), b = 10.206(1), c = 15.302(2) Å, $\alpha = 94.399(2)^{\circ}$, $\beta = 101.877(2)^{\circ}$, $\gamma = 104.062(2)^{\circ}$, V = 1025.9(2) Å³, Z = 2, $R_1 = 0.0317$, $wR_2 = 100.0000$

0.0796, S = 1.060. The Mo atom in the complex is in an octahedral coordination with phenolate O, imino N, enolate O atoms of the ligand L, and one oxo O in the equatorial plane, and with one methanol O and the other oxo O in the axial sites. Crystals of the complex are stabilized by hydrogen bonds. The complex was studied for its catalytic oxidation property on some olefins, with *tert*-butyl hydrogen peroxide as oxidant.

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INTRODUCTION

The development of processes for oxidation of olefins is a goal that has long been pursued. High-valent molybdenum complexes have attracted continuing attention due to their important practical applications as catalysts in the ammoxidation of propene, the sulfoxidation and epoxidation of olefins, etc. [1-7]. The ability of molybdenum to form stable complexes with oxygen- and nitrogen-containing ligands led to the development of molybdenum Schiff base complexes which are efficient catalysts both in homogeneous and heterogeneous reactions [8-13]. Recently, we have reported some metal complexes with Schiff bases, and their biological aplications [14–16]. As a continuation of the work on the exploration of new catalytic materials based on Schiff base complexes, in this paper, a new molybdenum(VI) complex, $[MoO_2(CH_3OH)(L)]$ (I), where L = N'-(4-diethylamino-2-hydroxybenzylidene)-4-hydroxybenzohydrazide), is described.

EXPERIMENTAL

Materials and instrumentations. $MoO_2(Acac)_2$ was obtained by published method [17]. The remaining reagents were supplied by Merck and Fluka, and were employed without further purification. IR spectra were recorded on a Shimadzu Varian 4300 spectrophotometer. ¹H NMR spectrum of the complex was recorded on a Bruker FT-NMR 300 MHz spectrometer using $(CD_3)_2SO$ as solvent. The electronic spectrum was recorded on a Shimadzu UV–Vis scanning spectrophotometer (Model 2101 PC). Elemental analyses (C, H and N) were performed using a Carlo Erba Model EA 1108 analyzer. GC analyses were performed on a Shimadzu GC-2010 gas chromatograph.

Syntheses of I. To a solution of 4-diethylaminosalicyldehyde (1 mmol) in 25 mL methanol was added a solution of 4-hydroxybenzohydrazide (1 mmol) in 15 mL methanol, and the reaction mixture was heated at reflux for 1 h. Then a solution of $MoO_2(Acac)_2$ (1 mmol) in 15 mL methanol was added dropwise under stirring. The solution color changed immediately to yellow. After the reflux was continued for 30 min, three quarter of the solvent was evaporated. The solid product was filtered and washed with methanol (67% yield). Single crystals, suitable for X-ray diffraction, were obtained by slow evaporation of the methanolic solution of the product.

For C₁₉H₂₃N₃O₆Mo

anal. calcd., %:	C, 47.02;	Н, 4.78;	N, 8.66.
Found, %:	C, 46.86;	H, 4.89;	N, 8.82.

IR frequencies (KBr; v, cm⁻¹): 3276, 2971, 2923, 2857, 1612, 1579, 1507, 1402, 1350, 1245, 1136, 1016, 935, 887, 835, 787, 711, 650. Electronic absorption spectrum in acetonitrile (λ , nm (ϵ , mol⁻¹ L cm⁻¹)): 280 (10232), 346 (13870), 472 (12880). ¹H NMR (300 MHz; DMSO-d₆; δ , ppm): 10.06 (s., 1H), 8.54 (s., 1H), 7.78 (d., 2H), 7.40 (d., 1H), 6.83 (d., 2H),

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Parameter Fw *T* , K Crystal system Space group *a*, Å b, Å *c*, Å α , deg β , deg γ , deg $V. Å^3$ ρ , g cm⁻³ μ , mm⁻¹ $\lambda(MoK_{\alpha}), Å$

6.40 (d.d., J = 8.9, 2.3 Hz, 1H), 6.13 (d., 1H), 4.09 (s., 1H), 3.5–3.1 (m., 6H), 1.13 (t., 6H).

X-ray structure determination. The intensity data were collected on a Bruker SMART 1000 CCD area graphite-monochromatized diffractometer using Mo K_{α} radiation ($\lambda = 0.71063$ Å). The structure was solved by direct methods (SHELXS-97) [18] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97) [18]. The positions of non-hydrogen atoms were located with direct methods. Subsequent Fourier syntheses were used to locate the remaining non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The data collection and refinement processes are summarized in Table 1.

The supplementary crystallographic data for complex I has been deposited with the Cambridge Crystallographic Data 606971; Centre (no. deposit@ccdc.cam.ac.uk or http://www.ccdc.cam. ac.uk).

Catalytic oxidation experiment. Catalytic experiment was carried out in a 50 mL glass round-bottom flask fitted with a reflux condenser and placed in an oil bath at prearranged temperature under continuous stirring. The catalytic oxidation experiment was carried out as follows: molybdenum(VI) complex (0.032 mmol) was dissolved in 10 mL 1,2-dichloroethane. Then 10 mmol alkene was added to the reaction mixture and 30 mmol TBHP was added. The reaction mixture was refluxed for 1 h. The reaction products were monitored at periodic time intervals using gas chromatography. The oxidation products were identified by comparison with authentic samples (retention times in GC).

Value

485.34

273(2)

Triclinic $P\overline{1}$

6.9824(9)

10.206(1)

15.302(2)

94.399(2)

101.877(2)

104.062(2)

1025.9(2)

2

1.571

0.680

0.71073

496

9837 3868

3648

265

1.060

0.0317, 0.0796

0.0341, 0.0811

0.779 and -0.669

RESULTS AND DISCUSSION

The complex was synthesized by the reaction of equimolar quantities of 4-diethylaminosalicylaldehyde, 4-hydroxybenzohydrazide and MoO₂(Acac)₂ in methanol. It was found that the ligand and metal ratio from 1 : 1 to 1 : 3 resulted the same product. Crystals of the complex are stable in open atmosphere.

Ζ

F(000)

Parameters

 $GOOF(F^2)$

Collected reflections

Observed reflections $(I \ge 2\sigma, (I))$

Largest peak and deepest hole, $e \text{ Å}^{-3}$

Unique reflections

 $R_1, wR_2 (I \ge 2\sigma, (I))$

 R_1, wR_2 , all data



Fig. 1. The molecular structure of complex I. Thermal ellipsoids are drawn by 30% probability level.

The oxidoperoxido metal moieties are characterized by v(Mo=O) and v(O-O) vibrations at 935 and 887 cm⁻¹, respectively [19, 20]. Also the IR spectrum of the complex confirms the presence of imine bond (C=N) mode at 1612 cm⁻¹ [21]. In the electronic spectrum of the complex, the lowest energy transition band is observed at 472 nm, which is attributed to LMCT transition as charge transfer from *p*-orbital on the lone-pair of ligands' oxygen atoms to the empty d-orbital of the Mo atom. The bands centered at 280 and 346 nm are attributed to the intra-ligand $\pi \rightarrow \pi^*$ absorption of the ligand. In the ¹H NMR spectrum of the complex, the signals appearing at $\delta = 10.06$ and 4.09 ppm are due to the phenolic and methanol OH groups, respectively. The signal appearing at $\delta =$ 8.54 ppm is assigned to the azomethine (CH=N) proton of the ligand in the complex.

The molecular view of the complex is shown in Fig. 1. The structure of the complex is mononuclear,

with a distorted octahedral arrangement around the center Mo atom. In the octahedral coordination of the complex, ONO donor set of the ligand L and one oxido group are in the equatorial plane, and the other oxido group and methanol molecule oxygen atom occupying the axial positions. In the coordination sphere about the molybdenum atom the oxido ligands are trans respectively to the imino nitrogen atom and the methanol oxygen atom. The selected bond lengths and angles are listed in Table 2, which are consistent with those observed in similar structures [22, 23]. The Schiff base ligand coordinates to the Mo atom in a meridional fashion forming five- and six-membered chelate rings with bite angles of $72.0(1)^{\circ}$ and $81.5(1)^{\circ}$. The displacement of the Mo atom from the equatorial least-squares plane towards the axial oxido group is 0.33 Å. In the crystal structure of the complex, the complex molecules are linked through intermolecular O-H…O hydrogen bonds (Table 3), to form 2D laver structure along the xy plane direction (Fig. 2).

Bond	$d, \mathrm{\AA}$	Bond	d, Å	
Mo(1)-O(1)	1.918(2)	Mo(1)-O(2)	1.972(2)	
Mo(1)–O(4)	2.342(2)	Mo(1)–O(5)	1.719(2)	
Mo(1)-N(2)	2.218(2)	Mo(1)-O(6)	1.690(2)	
Angle	ω, deg	Angle	ω, deg	
O(1)Mo(1)O(2)	149.4(1)	O(1)Mo(1)N(2)	81.5(1)	
O(2)Mo(1)N(2)	72.03(7)	O(1)Mo(1)O(4)	78.1(1)	
O(5)Mo(1)N(2)	158.5(1)	O(5)Mo(1)O(4)	83.3(1)	
O(5)Mo(1)O(1)	102.4(1)	O(5)Mo(1)O(2)	97.1(1)	
O(6)Mo(1)O(1)	98.4(1)	O(6)Mo(1)O(2)	98.7(1)	
O(6)Mo(1)O(5)	105.6(1)	O(6)Mo(1)N(2)	94.6(1)	
O(6)Mo(1)O(4)	171.0(1)	O(2)Mo(1)O(4) 81.1(1)		
N(2)Mo(1)O(4)	76.7(1)			

Table 2. Selected bond lengths (Å) and angles (deg) for complex I

Substrate	Product	Conversion, %**
	<u>o</u>	88.5
	<u> </u>	86.2
CI		93.3
		98.1
		100
		100
		100
CI		100
CI		100
		100

Table 3. Details of the catalytic oxidation of olefins catalyzed by complex I^\ast

* The molar ratio of catalyst : substrate : TBHP is 1 : 300 : 1000. The reaction was performed in mixture of $CH_3OH-CH_2Cl_2$ (*V*: *V* = 3 : 1). ** The GC conversion (%) was measured relative to the starting substrate after 1 h.

····· · · · · · · · · · · · · · · · ·	,	I I		
D–H…A	Distance, Å			D HA
	D-H	Н…А	D…A	D-II A
O(4)-H(4)···O(3) ⁱ	0.93	1.82	2.741(3)	171
O(3)-H(3)···O(5) ⁱⁱ	0.82	1.86	2.679(3)	175

Table 4. Geometric parameters of hydrogen bonds for complex I*

* Symmetry operation used to generate the related atoms: ${}^{i}x, -1 + y, z$; ${}^{ii}1 + x, 1 + y, z$.



Fig. 2. The crystal structure of complex **I**. Hydrogen bonds are drawn as dotted lines.

1-Butene, 1-pentene, 4-chloro-1-butene, phenylene 4-methylphenylene, 3-methylphenylene, 2-methylphenylene, 4-chlorophenylene, 3-chlorophenylene, and 2-chlorophenylene were used as the substrates. The catalytic oxidation results are given in Table 4. The selectivities for both aliphatic and aromatic substrates are 100%. High epoxide yields (86-93%) are obtained for aliphatic substrates. While for aromatic substrates, the epoxide yields (94-100%) are higher than aliphatic substrates. It is easily to find that the methylsubstituted substrates gave lower epoxide yields when compared to the chloro-substituted ones.

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REFERENCES

- 1. Amarante, T.R., Neves, P., Valente, A.A., et al., *Inorg. Chem.*, 2013, vol. 52, no. 8, p. 4618.
- Kokorin, A.I., Kulak, A.I., Tomskii, I.S., et al., *Russ. J. Phys. Chem. B*, 2013, vol. 7, no. 3, p. 255.
- 3. Amarante, T.R., Gomes, A.C., Neves, P., et al., *Inorg. Chem. Commun.*, 2013, vol. 32, p. 59.
- Tagliazucca, V., Schlichte, K., Schuth, F., et al., J. Catal., 2013, vol. 305, p. 277.
- 5. Cao, B.F., Veith, G.M., Diaz, R.E., et al., *Angew. Chem. Int. Ed.*, 2013, vol. 52, no. 41, p. 10753.
- 6. Brussaard, Y., Olbrich, F., and Schaumann, E., *Inorg. Chem.*, 2013, vol. 52, no. 22, p. 13160.
- Amini, M., Khaksar, M., Boghaei, D.M., et al., J. Coord. Chem., 2014, vol. 67, no. 14, p. 2435.
- 8. Elhendawy, A.M., Elkourashy, A.E., and Shnab, M.M., *Polyhedron*, 1992, vol. 11, no. 5, p. 523.
- 9. Zhao, J., Zhou, X.G., Santos, A.M., et al., *Dalton Trans.*, 2003, vol. 19, p. 3736.
- 10. Rao, S.N., Kathale, N., Rao, N.N., et al., *Inorg. Chim. Acta*, 2007, vol. 360, no. 14, p. 4010.
- 11. Sheikhsoaie, I., Rezaeffard, A., Monadi, N., et al., *Polyhedron*, 2009, vol. 28, no. 4, p. 733.
- 12. Aziz, A.A.A., J. Mol. Struct., 2010, vol. 979, nos. 1–3, p. 77.
- 13. Rayati, S., Rafiee, N., and Wojtczak, A., *Inorg. Chim. Acta*, 2012, vol. 386, p. 27.
- 14. Liu, H.-Y., Russ. J. Coord. Chem., 2013, vol. 39, no. 8, p. 583.
- 15. Liu, H.Y., Li, G.W., Li, Z.L., et al., *Russ. J. Coord. Chem.*, 2011, vol. 37, no. 9, p. 668.
- 16. Liu, H.-Y., J. Struct. Chem., 2014, vol. 55, no. 1, p. 134.
- 17. Chen, G.J.J., McDonald, J.W., and Newton, W.E., Inorg. Chem., 1976, vol. 15, no. 11, p. 2612.
- 18. Sheldrik, G.M., *SHELXL-97 and SHELXS-97*, Göttingen (Germany): Univ. of Göttingen, 1997.
- 19. Rao, S.N., Munshi, K.N., Rao, N.N., et al., *Polyhedron*, 1999, vol. 18, no. 19, p. 2491.
- 20. Bagherzadeh, M., Amini, M., Parastar, H., et al., *Inorg. Chem. Commun.*, 2012, vol. 20, no. 1, p. 86.
- 21. Ngan, N.K., Lo, K.M., and Wong, C.S.R., *Polyhedron*, 2011, vol. 30, no. 17, p. 2922.
- 22. Vrdoljak, V., Prugovečki, B., Matkovic-Čalogovic, et al., *Cryst. Growth Des.*, 2011, vol. 11, no. 4, p. 1244.
- 23. Dinda, R., Sengupta, P., Ghosh, S., et al., *Dalton Trans.*, 2002, no. 23, p. 4434.

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