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Synthesis, Structure, and Catalytic Property of a Mononuclear Dioxomolybdenum(VI) Complex Containing MoON Core[1]

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Abstract—Reaction of molybdenyl(IV) oxide bis(2,4-pentanedionate) with *N*'-(3-ethoxy-2-hydroxybenzylidene)-2-methoxybenzohydrazide in methanol affords a mononuclear dioxomolybdenum(VI) complex containing MoO_5N basic core. The complex has been characterized by various physicochemical techniques (IR and elemental analysis), and single crystal X-ray diffraction. X-ray crystal structure determination reveals that the complex crystallizes as monoclinic space group $P2_1/c$, with unit cell dimensions $a = 9.251(1)$, $b = 11.910(2)$, $c = 17.636(3)$ Å, $\beta = 103.220(2)°$, $V = 1891.7(5)$ Å^3, $Z = 4$, $R_1 = 0.0693$, $wR_2 = 0.1691$. The Mo atom in the complex is octahedrally coordinated, with the tridentate ONO ligand occupying the meridional sites. Thermal stability analysis was performed. The complex shows high catalytic property for the oxidation of various olefins.

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INTRODUCTION

Molybdenum is an essential transition metal that of great importance in life sciences. Enzymes containing molybdenum at their active sites catalyze a wide range of reactions in carbon, sulfur, and nitrogen metabolism [1–3]. In particular the molybdenum mediated oxo transfer in enzymatic systems has attracted much attention in reactivity and coordination chemistry of *cis*-dioxomolybdenum(VI) complexes [4–6]. In recent years, a number of molybdenum complexes have been used as catalysts for the epoxidation and hydroxylation of olefines [7–9], oxidation of alcohols [10], and oxo-transfer reactions [11]. Hydrazone ligands are widely used to prepare complexes with various metal salts. Molybdenum complexes with such ligands are also reported, but the number is still less when compared to other metals. In the present work, we report the synthesis, structure, and catalytic property of a new dioxomolybdenum(VI) complex, $[MoO_2L(OH_2)]$, derived from a new hydrazone ligand *N*'-(3-ethoxy-2-hydroxybenzylidene)-2-methoxybenzohydrazide (H_2L).

EXPERIMENTAL

Materials and physical measurements. Reagent grade solvents were used as received. All other chemicals were of AR grade, obtained from commercial sources and used as received. The ligand H_2L was prepared by using a reported procedure [12]. Elemental analyses (C, H, and N) were done with a PerkinElmer 2400 analyzer. IR spectra (as KBr pellet) were recorded using a PerkinElmer RXI FT-IR spectrophotometer. Solution electrical conductivity was measured with a DDS-11A conductivity meter. Thermal analysis of the complex was carried out by heating at a rate of 10°C per minute on a PerkinElmer TGA-4000 thermo balance. The oxidation products were analyzed with a gas chromatograph (Shimadzu, GC-14B) equipped with a SAB-5 capillary column (phenyl methyl siloxane 30 × 320 × 0.25 mm) and a flame ionization detector.

Synthesis of the complex. The ligand H_2L (0.31 g, 1.0 mmol) was dissolved in 30 mL methanol and $[MoO_2(Acac)_2]$ (0.33 g, 1.0 mmol) was added to the solution and the mixture was refluxed for 1 h at room temperature. The color of the solution changed from colorless to yellow. The solution was filtered and allowed to evaporate slowly at room temperature. After a week, yellow single crystals, suitable for X-ray diffraction analysis, were obtained by filtration. The yield was 55%.

For $C_{17}H_{18}N_2O_7Mo$

anal. calcd., %:	C, 44.55;	H, 3.96;	N, 6.11.
Found, %:	C, 44.32;	H, 4.10;	N, 6.27.

IR (KBr; ν, cm^{-1}): 3443 and 3341 ν(O–H), 1609 ν(C7=N1), 1670 ν(C–N), 1262r ν(C–O), 941 and 893 ν(MoO_2), 500–800 ν(Mo–O/N).

X-ray crystallography. A suitable single crystal of the complex was mounted on a thin glass fiber without

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protection. Cell dimensions were determined at 298(2) K from the setting angles of a Bruker SMART 1K CCD diffractometer using a graphite monochromated MoK_α (λ = 0.71073 Å) radiation source. Data collection was completed using the $\omega/2\theta$ scan techniques. Structure of the complex was solved by direct method, developed by successive difference Fourier synthesis and refined on F^2 by a full-matrix least-squares procedure using SHELXL-97 [13]. The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. The water hydrogen atoms were located from a difference map, and with O–H and H···H distances of 0.85(1) and 1.37(2) Å, respectively. The remaining hydrogen atoms were geometrically calculated and isotropically fixed at positions recalculated after each cycle of refinement (C–H 0.93–0.97 Å with the isotropic thermal parameters of $U_{iso}(H) = 1.2\ U_{iso}(C)$ and $1.5\ U_{iso}(C_{methyl})$). Absorption corrections based on multi-scan using SADABS were applied [14]. Data reduction was accomplished using the SAINT plus [15].

Pertinent cell parameters, data collection conditions, and refinement details are provided in Table 1. The important bond lengths and angles are provided in Table 2. Supplementary material for the complex has been deposited with the Cambridge Crystallographic Data Centre (no. 9506932; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Catalytic oxidation procedure. Catalytic experiment was carried out in a 50 mL glass reaction flask fitted with a water condenser. 0.032 mmol dioxo-molybdenum(VI) complexes were dissolved in 10 mL 1,2-dichloroethane. Then 10 mmol alkene was added to the reaction mixture and 30 mmol *tert*-butyl hydroperoxide (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.

RESULTS AND DISCUSSION

The synthesis of the hydrazone ligand requires a two step reaction. In the first step the 2-methoxybenzohydrazide was synthesized by reaction of the methyl 2-methoxybenzoate with 1.3 equivalent of hydrazine hydrate under reflux and continuous stirring for 6 h. Subsequently the hydrazone ligand was obtained via condensation reaction of 2-methoxybenzohydrazide with 3-ethoxysalicylaldehyde in methanol solution at room temperature. Stoichiometric reaction of the hydrazone ligand with $MoO_2(Acac)_2$ as molybdenum source in refluxing methanol yields the corresponding *cis*-dioxomolybdenum(VI) complex. The reaction progress is accompanied by an immediate color change of the solution from colorless to yellow. The complex is soluble in methanol, ethanol, acetonitrile, DMF, and DMSO. The molar conductance of a ~0.10 mmol dm^{-3} solution of the complex in acetonitrile at 25°C is 21.5 Ω^{-1} cm^2 mol^{-1}. The data indicates non-electrolytic behavior in the solution [16].

Table 1. Crystal data and structure refinement for the complex

Parameter	Value
Formula weight	458.3
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions:	
a, Å	9.215(1)
b, Å	11.910(2)
c, Å	17.636(3)
β, deg	103.220(2)
Volume, Å^3	1891.7(5)
Z	4
ρ_{calcd}, g cm^{-3}	1.609
Absorption coefficient, mm^{-1}	0.734
F(000)	928
Crystal size, mm	0.18 × 0.18 × 0.16
Limiting indices	$-10 \le h \le 9$, $-9 \le k \le 14$, $-17 \le l \le 20$
Reflections collected/unique	4433/2332
Observed reflections, ($I > 2\sigma(I)$)	1975
Parameters	252
Restraints	3
Goodness-of-fit on F^2	1.307
Final *R* indices, ($I > 2\sigma(I)$)	$R_1 = 0.0693$, $Rw_2 = 0.1691$
R indices (all data)	$R_1 = 0.0796$, $Rw_2 = 0.1735$
Largest difference in peak and hole, *e* Å^{-3}	1.031 and –0.517

An ORTEP diagram of the complex is illustrated in Fig. 1. In the complex a distorted octahedral geometry is observed for the molybdenum atom, with an [ONO] donor set from the hydrazone ligand, a complementing water O donor, and the two oxo groups of the MoO_2 moiety. For the latter Mo–O bond lengths of 1.700(7) and 1.726(7) Å and OMoO bond angle of 105.7(4)° are found, which are in excellent agreement with the corresponding values observed in similar dioxomolybdenum complexes [17, 18]. The equatorial plane at the molybdenum atom is given by the tridentate hydrazone ligand (O(1), N(1), and O(2)) and one of the oxo groups (O(7)). The ligand coordinates in a meridional fashion forming five- and six-membered chelate rings at the MoO_2 moiety with bite angles of 71.6(3)° and 82.1(3)°, respectively. The hydrazone ligand is coordinated in its dianionic form. This is evident from the N(2)–C(8) and O(2)–C(8) bond lengths with values of 1.315(13) and 1.324(12) Å, re-

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

Bond	d, Å	Bond	d, Å
Mo(1)–O(1)	1.915(7)	Mo(1)–O(2)	1.998(6)
Mo(1)–N(1)	2.215(9)	Mo(1)–O(5)	2.340(7)
Mo(1)–O(6)	1.700(7)	Mo(1)–O(7)	1.726(7)
Angles	ω, deg	Angles	ω, deg
O(1)Mo(1)O(2)	150.9(3)	O(1)Mo(1)N(1)	82.1(3)
O(2)Mo(1)N(1)	71.6(3)	O(6)Mo(1)O(5)	170.8(3)
O(1)Mo(1)O(5)	82.3(3)	O(2)Mo(1)O(5)	79.3(3)
O(6)Mo(1)O(1)	99.2(4)	O(6)Mo(1)O(2)	95.7(3)
O(6)Mo(1)O(7)	105.7(4)	O(6)Mo(1)N(1)	96.0(3)
O(7)Mo(1)O(1)	103.1(3)	O(7)Mo(1)O(2)	96.6(3)
O(7)Mo(1)N(1)	156.3(3)	O(7)Mo(1)O(5)	82.6(3)
N(1)Mo(1)O(5)	75.2(3)		

Table 3. Geometric parameters of hydrogen bonds of the complex*

Contact D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
O(5)–H(5*A*)···O(7)^{i}	0.85(1)	2.45(12)	2.758(10)	102(9)
O(5)–H(5*B*)···O(4)^{ii}	0.85(1)	2.39(10)	2.967(11)	126(11)
O(5)–H(5*B*)···O(2)^{ii}	0.90(1)	2.11(5)	2.903(11)	155(10)

* Symmetry codes: $^{i}\ 2 - x, 2 - y, -z$; $^{ii}\ 1 - x, 2 - y, -z$.

spectively, which are indicative for the presence of the enolate form of the ligand amide group. The two axial positions are occupied by the second oxo group O(6) of the MoO_2 unit and an oxygen atom of a water molecule (O(5)). The rather long Mo(1)–O(5) bond and consequently weak bonding is due to the *trans* effect of the oxo group O(6). This is accompanied by a significant displacement of the Mo atom from the equatorial mean plane towards the axial oxygen atom O(6) by 0.324(1) Å. The coordinate bond lengths are comparable with those observed in similar dioxomolybdenum(VI) complexes [17–19]. The crystal packing of the complex is depicted in Fig. 2. The complex molecules are linked by water molecules through intermolecular O–H···O hydrogen bonds (Table 3), to form chains running down the *x* axis.

The ligand showed stretching bands attributed to C=O, C=N, C–OH, and NH at 1658, 1636, 1155 and 1227, and 3317 cm^{-1}, respectively. In addition, a strong band found at 1621 cm^{-1} is attributed to C=N–N=C group. This IR evidence has been registered earlier for the similar class of ligands that behave as tridentate dibasic ligands upon enolization [20]. The dioxomolybdenum complex showed two prominent bands at 941 and 893 cm^{-1} attributed to *cis*-dioxomolybdenum (MoO_2) group. The bands due to ν(C=O) and ν(NH) were absent in the complex, but a new C–O stretch appeared at 1262 cm^{-1}. This suggests occurrence of keto-imine tautomerization of the ligand during complexation. The C=N–N=C framework seen at 1621 cm^{-1} in the ligand shifted to 1609 cm^{-1} upon coordination to Mo atom. Bands have also appeared in the range 3200–3600 cm^{-1} that may be attributed to coordinated water. Three new peaks found at 777, 586, and 519 cm^{-1} may be attributed to Mo–O and Mo–N linkages in the complex. The doubly ν(C=N) found at 1609 and 1670 cm^{-1} in the complex may be due to different C(7)–N(1) and C(8)–N(2) bond distances.

Thermo analysis of the complex was carried out in the temperature range 50–1000°C at a heating rate of 10°C min^{-1}. The TG and DTA curves of the complex are shown in Fig. 3. The complex is stable up to 187°C. Above this temperature, the TG curve show three steps of weigh losses. The first step of decomposition in the temperature range 187–237°C involved the removal of the coordinated water molecule and the ethoxy and methoxy groups of the ligand. The second step of decomposition in the temperature range 238–603°C involved the removal of the remaining moiety of the

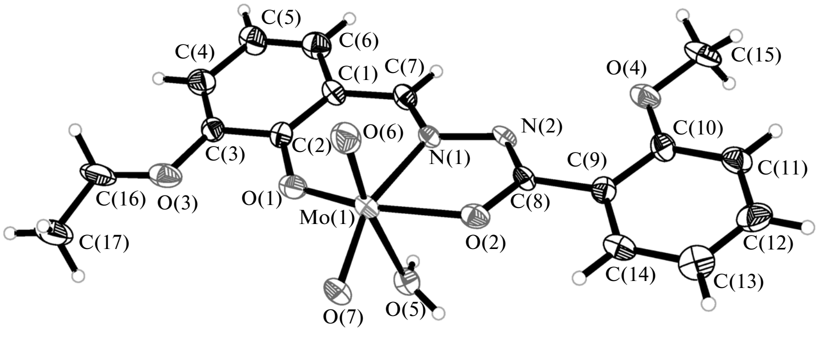


Fig. 1. An ORTEP drawing at 30% thermal ellipsoid of the crystal structure of the complex, with the atomic numbering scheme.

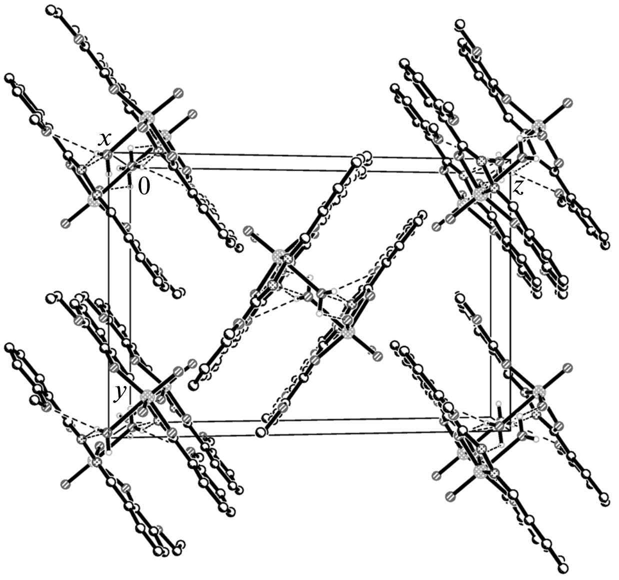


Fig. 2. The molecular packing of the complex, viewed along the *x* axis. H atoms, except those related to hydrogen bonding, are omitted for clarity. Hydrogen bonds are indicated by dashed lines.

ligand. With further elevation in temperature until 880°C, the MoO_2 residue was volatilized.

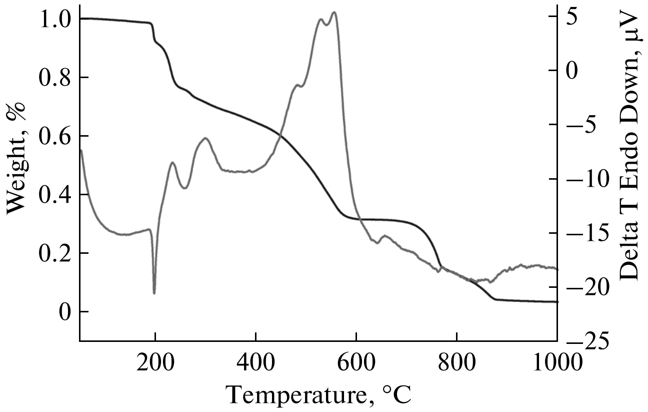
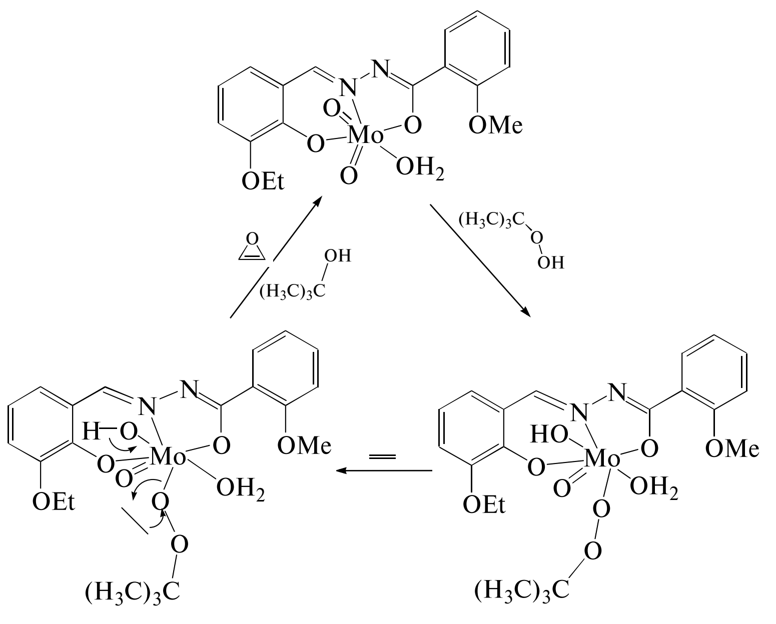


Fig. 3. TG–DTA curves of the complex.

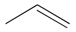
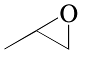
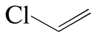
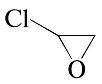
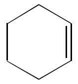
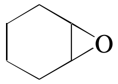
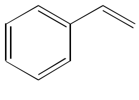
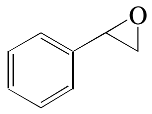
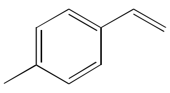
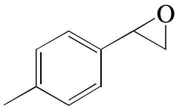
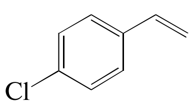
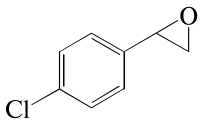
The catalytic results are listed in Table 4. Generally speaking, excellent epoxide yields and selectivity were observed for both aliphatic and aromatic substrates. Oxidation of aromatic substrates gave the corresponding epoxides in 100% yields, while in the oxidation of aliphatic substrates, the conversions are less than 100%. This is in accordance with those reported in the literature [21]. The possible catalytic procedure is is illustrated below:



To start with, TBHP was activated by coordination to the Mo atom and formation of hepta-coordinated molybdenum intermediate. Then a molecule of an olefin as a nucleophile attacks the electrophilic oxygen atom of the coordinated TBHP. As a result, the corresponding epoxides were formed, and TBHP was reduced to *tert*-butyl alcohol.

Thus, a new mononuclear dioxomolybdenum(VI) complex containing MoO_5N basic core derived from *N*'-(3-ethoxy-2-hydroxybenzylidene)-2-methoxybenzohydrazide in methanol has been prepared and characterized. The Mo atom is six-coordinated in octahedral geometry. The molecular structure of the complex is stabilized by hydrogen bonds. Thermal analysis was al-

Table 4. Catalytic oxidation results*

Substrate	Product	Conversion, % (TON)**	Selectivity, %
		95 (251)	100
		97 (272)	100
		100 (275)	100
		100 (295)	100
		100 (266)	100
		100 (287)	100

* The molar ratio of catalyst : substrate : TBHP is 1 : 300 : 1000. The reactions were performed in mixture of $CH_3OH{-}CH_2Cl_2$ (V: V = 1 : 1; 1.5 mL).

** The GC conversion (%) was measured relative to the starting substrate after 60 min; TON = (mmol of product)/(mmol of catalyst).

so performed to understand the stability of the complex. The complex shows high catalytic property for the oxidation of various olefins.

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