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Synthesis, Crystal Structure, and Catalytic Property of a Dioxomolybdenum(VI) Complex Derived from *N'*-(3-Bromo-5-Chloro-2-Hydroxybenzylidene)-4-Nitrobenzohydrazide[1]

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Abstract—New dioxomolybdenum(VI) complex $[MoO_2(L)(CH_3OH)]$, where L is the dianionic form of *N'*-(3-bromo-5-chloro-2-hydroxybenzylidene)-4-nitrobenzohydrazide (H_2L), was prepared and characterized by IR and UV-Vis spectra, as well as single crystal X-ray diffraction (CIF file CCDC no. 1567063). The complex crystallizes as the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 13.8471(10)$, $b = 7.5618(6)$, $c = 17.9445(12)$ Å, $\beta = 90.107(2)°$, $V = 1878.9(2)$ Å^3, $Z = 4$, $R_1 = 0.0821$, $wR_2 = 0.0907$, GOOF = 1.024. X-ray analysis indicates that the complex is a dioxomolybdenum(VI) species with the Mo atom in octahedral coordination. The catalytic oxidation property of the complex with *tert*-butylhydroperoxide in CH_2Cl_2 was studied.

Keywords: hydrazone, dioxomolybdenum complex, crystal structure, catalytic property

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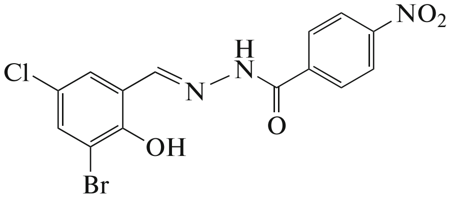
INTRODUCTION

Schiff bases are readily synthesized and form various complexes with most metal ions. Many Schiff base complexes show excellent catalytic properties, such as ring opening polymerization of cycloalkenes [1], oxidation of hydrocarbons [2, 3], ring opening of large cycloalkanes [4–6], reduction of ketones to alcohols [7], alkylation of allylic substrates [8], improve enantioselectivity in the cyclopropanation reactions [9, 10], and so on. The ability of molybdenum to formation of stable complexes with oxygen-, nitrogen-, and sulfur-containing ligands led to development of molybdenum Schiff base complexes which are efficient catalysts both in homogeneous and heterogeneous reactions [11–16]. The activity of these complexes varied obviously with the type of ligands and coordination sites. Thus, herein we synthesized a new dioxomolybdenum(VI) complex $[MoO_2(L)(CH_3OH)]$ with hydrazone ligand and evaluated its catalytic property in the oxidation of various olefins.



(H_2L)

EXPERIMENTAL

Materials and methods. 3-Bromo-5-chloro-2-hydroxybenzaldehyde, 4-nitrobenzohydrazide, and $MoO_2(Acac)_2$ were purchased from Sigma-Aldrich and used as received. All other reagents were of analytical reagent grade. Elemental analyses of C, H, and N were carried out in a Perkin-Elmer automated model 2400 Series II CHNS/O analyzer. FT-IR spectra were obtained on a Perkin-Elmer 377 FT-IR spectrometer with samples prepared as KBr pellets. UV-Vis spectra were obtained on a Lambda 900 spectrometer. X-ray diffraction was carried out on a Bruker APEX II CCD diffractometer.

Synthesis of the complex. 3-Bromo-5-chloro-2-hydroxybenzaldehyde (0.01 mol, 2.35 g) and 4-nitro-

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[1] The article is published in the original.

Table 1. Crystallographic and refinement data for the complex

Parameter	Value
Formula weight	556.6
Crystal shape/color	Block/yellow
T, K	298(2)
Crystal dimensions, mm	0.27 × 0.25 × 0.23
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	13.847(1)
b, Å	7.5618(6)
c, Å	17.945(1)
β, deg	90.107(2)
V, Å^3	1878.9(2)
Z	4
ρ_{calcd}, g cm^{-3}	1.967
$\mu(MoK_\alpha)$, mm^{-1}	3.011
F(000)	1088
Measured reflections	17251
Unique reflections	3487
Observed reflections ($I \geq 2\sigma(I)$)	2770
Min and max transmission	0.4969 and 0.5443
Restraints/parameters	3/257
Goodness of fit on F^2	1.028
R_1, wR_2 ($I \geq 2\sigma(I)$)*	0.0369, 0.0819
R_1, wR_2 (all data)*	0.0532, 0.0904

* $R_1 = F_o - F_c/F_o$, $wR_2 = [\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2]^{1/2}$.

benzohydrazide (0.01 mol, 1.81 g) were dissolved in methanol. Then, $MoO_2(Acac)_2$ (0.01 mol, 2.65 g) was added and stirred for 1 h to give yellow solution. Single crystals of the complex, suitable for X-ray diffraction, were grown from the solution upon slowly evaporation for a few days. The yield was 2.38 g (43%).

IR data (ν, cm^{-1}): 3445 w ν(O–H); 1608 s ν(C=N); 936 m, 913 m ν(Mo=O). UV-Vis data (CH_3OH, λ_{max}, nm): 273, 335.

For $C_{15}H_{11}N_3O_7ClBrMo$

Anal. calcd., %	C, 32.37	H, 1.99	N, 7.55
Found, %	C, 32.12	H, 2.13	N, 7.67

X-ray crystallography. X-ray diffraction was carried out at a Bruker APEX II CCD area diffractometer equipped with MoK_α radiation (λ = 0.71073 Å). The collected data were reduced with SAINT [17], and multiscan absorption correction was performed using SADABS [18]. The structure of the complex was solved by direct method and refined against F^2 by full-matrix least-squares method using SHELXTL [19]. All of the non-hydrogen atoms were refined anisotropically. The methanol hydrogen atom was located from an electronic density map and refined isotropically with O–H distance restrained to 0.85(1) Å. The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data and refinement parameters for the complex are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1567063; deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk/const/retrieving.html).

Catalytic epoxidation of olefins. Epoxidation of cyclooctene, cyclohexene, 1-octene and 1-hexene catalyzed by the complex with *tert*-butylhydroperoxide (TBHP) in CH_2Cl_2 was carried out according to the following general procedure. To a 25 mL round bottomed flask equipped with a magnetic stirring bar and immersed into water thermo-stated bath, was added 10 mL CH_2Cl_2, 1.0 mmol TBHP, 0.01 mmol catalyst and 1.0 mmol olefin. The mixture was refluxed with vigorous stirring for 2 h at an appropriately chosen temperature. The progress of the reaction was monitored by carefully withdrawing aliquots of the sample at different time intervals to determine concentrations of the products by gas chromatography analysis, using *n*-hexane as an internal standard and was left to proceed until near complete conversion of TBHP. The concentration of the TBHP was determined by iodometric titration method [20]. The yield of epoxide (%) was calculated according to the starting amount of olefin. Assignments of the products were made by comparison with authentic samples. All the reactions were run in triplicates. Control experiments showed that no epoxide was formed in a measurable extent in the absence of catalyst.

RESULTS AND DISCUSSION

The ligand H_2L was readily prepared by the condensation reaction of 3-bromo-5-chloro-2-hydroxybenzaldehyde with 4-nitrobenzohydrazide in methanol. The molybdenum(VI) complex was synthesized by stirring equimolar quantities of H_2L with $MoO_2(Acac)_2$ in methanol at room temperature. The chemical formula of the complex has been confirmed by elemental analyses, IR spectra, and single crystal X-ray diffraction.

The band at 1617 cm^{-1} characteristic of the azomethine nitrogen atom present in the free ligand, was shifted to lower wave number at 1608 cm^{-1} after complexation, indicating that the involvement the azomethine nitrogen atom in coordination. The band at 1277 cm^{-1} in the spectrum of H_2L is ascribed to the phenolic C–O stretching vibration. This band is found at 1287 cm^{-1} in the spectrum of the complex. These changes suggest that the hydroxyl group of this Schiff base moiety has taken part in complex formation. H_2L and the complex exhibit broad bands at 3450 and 3445 cm^{-1}, respectively, which may be assigned to the ν(OH). Further evidence of the bonding is also shown by the observation that new bands in the IR spectrum of the metal complex appear at 400–470 and 500–550 cm^{-1} assigned to Mo–N and Mo–O stretching vibrations that are not observed in the spectrum of the ligand. The Mo=O stretching mode occur as double bands at 936 and 913 cm^{-1}, assigned to the symmetric and asymmetric stretching modes of the MoO_2 moieties [21, 22].

Electronic absorption spectra of the ligand and the complex were obtained in methanol solutions. The electronic absorption spectrum of H_2L displayed two bands at 275 and 370 nm, which are assigned for the $\pi \to \pi^*$ and $n \to \pi^*$ transitions, respectively. In the electronic spectrum of the complex, the strong band centered at 335 nm is attributed to the intraligand $\pi \to \pi^*$ absorption band of the hydrazone ligand. The LMCT and to some extent $\pi \to \pi^*$ band appears at 273 nm.

The molecular structure of the complex is shown in Fig. 1. The coordination geometry around the Mo atom can be described as distorted octahedron with the phenolate-O, imino-N, and enolate-O of the hydrazone ligand, and one oxo-group defining the equatorial plane, and with the other oxo-group and one methanol oxygen occupying the axial positions. The hydrazone ligand coordinates to the Mo atom in a meridional fashion forming five- and six-membered chelate rings with bite angles of 71.07(11)° and 81.17(11)°. The dihedral angle between the two benzene rings of the hydrazone ligand are 1.3(5)°. The displacement of the Mo atom in the complex from the equatorial mean planes toward the apical oxo-group is 0.322(1) Å. The hydrazone ligand is coordinated in its dianionic form, which is evident from the N(2)–C(8) and O(2)–C(8) bond lengths. The abnormal bond values indicate the presence of the enolate form of the ligand amide groups. The Mo–O, Mo–N, and Mo=O bonds are within normal ranges and are similar to those observed in similar molybdenum(VI) complexes [11–16].

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

Bond	*d*, Å	Bond	*d*, Å
Mo(1)–O(1)	1.926(3)	Mo(1)–O(2)	1.995(3)
Mo(1)–O(5)	1.683(4)	Mo(1)–O(6)	1.683(4)
Mo(1)–O(7)	1.687(3)	Mo(1)–N(1)	2.263(3)
Angle	ω, deg	Angle	ω, deg
O(6)Mo(1)O(7)	106.3(2)	O(6)Mo(1)O(1)	98.3(2)
O(7)Mo(1)O(1)	102.5(1)	O(6)Mo(1)O(2)	97.7(2)
O(7)Mo(1)O(2)	98.6(1)	O(1)Mo(1)O(2)	148.7(1)
O(6)Mo(1)N(1)	93.6(1)	O(7)Mo(1)N(1)	158.8(2)
O(1)Mo(1)N(1)	81.2(1)	O(2)Mo(1)N(1)	71.1(1)
O(6)Mo(1)O(5)	169.6(1)	O(7)Mo(1)O(5)	84.0(1)
O(1)Mo(1)O(5)	79.8(1)	O(2)Mo(1)O(5)	79.7(1)
N(1)Mo(1)O(5)	76.1(1)		

In the crystal structure of the complex, adjacent two $[MoO_2(L)(CH_3OH)]$ molecules are linked through two intermolecular O–H···N hydrogen bonds (O(5)–H(5) 0.85(1), H(5)···$N(2)^i$ 1.98(1), O(5)···$N(2)^i$ 2.833(4) Å, O(5)–H(5)···$N(2)^i$ 174(5)°; symmetry code: ^{i} 1 – *x*, –*y*, –*z*), to form dimers (Fig. 2).

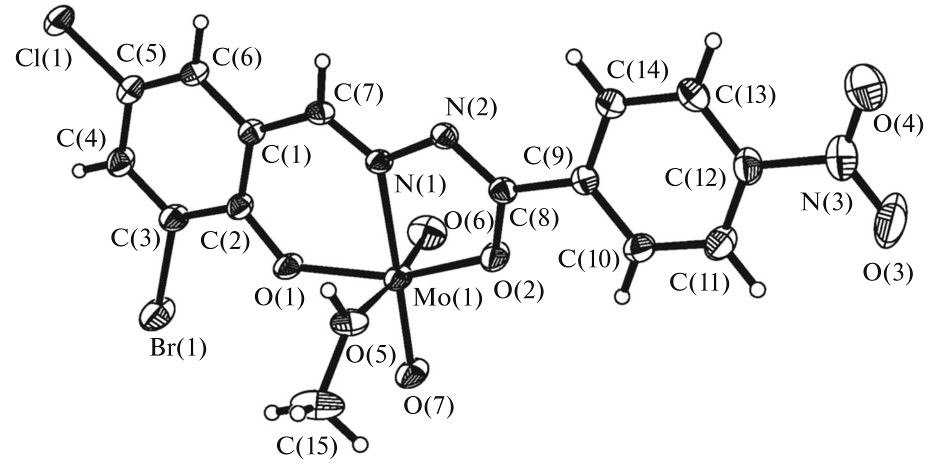

Fig. 1. A perspective view of the complex with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

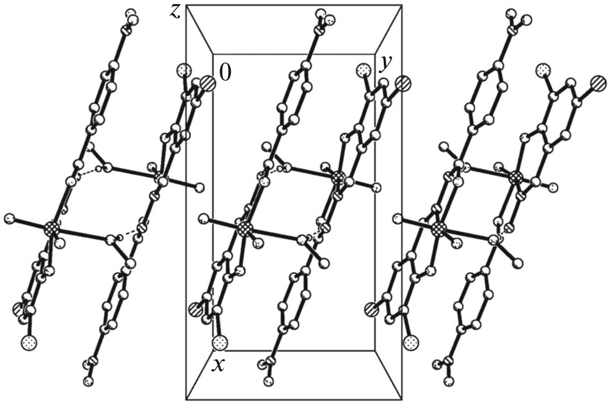

Fig. 2. The hydrogen bonds (dashed lines) linked dimers of the complex.

Table 3. Catalytic results of the complex at different temperatures

Substrate	Epoxide yield, %		
	25°C	45°C	65°C
Cyclooctene	79	92	97
Cyclohexene	61	85	92
1-Hexene	50	73	86
1-Octene	42	58	81

Catalytic activity of the complex was investigated in the epoxidation of cyclooctene, cyclohexene, 1-octene and 1-hexene with TBHP and CH_2Cl_2 as a solvent at different temperatures 25, 45 and 65°C. The catalytic reactions were initially performed in common atmosphere in order to test the performance of the system under the easiest possible reaction conditions. A substrate : oxidant : catalyst ratio of 100 : 100 : 1 was used. In general, the epoxide yield was higher for cyclic olefins than those for terminal olefins. As seen in Table 3, the order of increasing reactivity based on yield % are as cyclooctene > cyclohexene > 1-hexene > 1-octene. In addition, the epoxide yield increase with the rise in temperature.

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