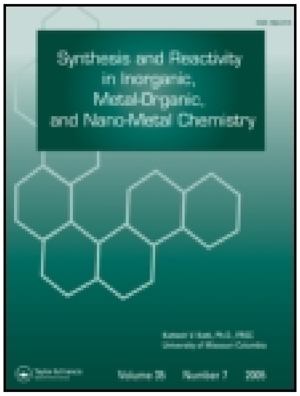

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Synthesis, X-Ray Crystal Structure, and Oxidation Catalytic Property of a Dioxomolybdenum(VI) Complex Derived From 5-Diethylamino-2-[(2-hydroxyethylimino)methyl]phenol

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Synthesis, X-Ray Crystal Structure, and Oxidation Catalytic Property of a Dioxomolybdenum(VI) Complex Derived From 5-Diethylamino-2-[(2-hydroxyethylimino)methyl]phenol

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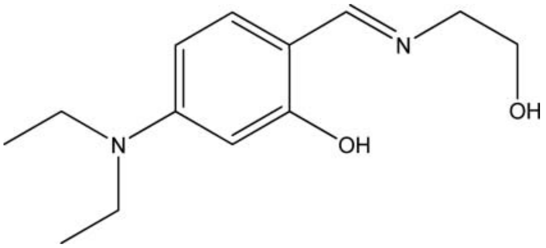
A new dioxomolybdenum(VI) complex, $[MoO_2L(CH_3OH)]$, where L is the dianion of 5-diethylamino-2-[(2-hydroxyethylimino) methyl]phenol, was prepared and structurally characterized by physicochemical and spectroscopic methods and single-crystal X-ray determination. The Mo atom in the complex is in octahedral coordination. The crystal of the complex is stabilized by hydrogen bonds. The complex functions as an effective olefin epoxidation catalyst with hydrogen peroxide as terminal oxidant and sodium hydrogen carbonate as a cocatalyst under air atmosphere at room temperature.

Keywords catalytic property, crystal structure, molybdenum complex, Schiff base, synthesis

INTRODUCTION

Selective oxidation of hydrocarbons has attracted considerable attention in organic industry.[1–3] The synthesis, characterization, and reactivity studies of a number of dioxomolybdenum complexes with Schiff bases have been reported.[4–7] Some of the complexes have been shown to possess oxygen atom transfer properties as they were found to oxidize thiols, hydrazine, polyketones, tertiary phosphines, and olefins, etc.[8–11] However, the number of reported dioxomolybdenum complexes used as catalysts is still very limited. I report herein the synthesis, X-ray crystal structure, and catalytic property of a new dioxomolybdenum(VI) complex, $[MoO_2L(CH_3OH)]$, where L is the dianion of 5-diethylamino-2-[(2-hydroxyethylimino)methyl]phenol (H_2L; Scheme 1). The search in Cambridge Crystallographic Database (version 5.31 with addenda up to August 2012) revealed that no complexes derived from H_2L have reported so far.



SCH. 1. H_2L.

EXPERIMENTAL

All chemical reagents were of analytical reagent grade, and purchased from Xiya Chemical Reagent Company (Chengdu, P. R. China). Microanalyses (C, H, N) were performed using Perkin-Elmer 2400 elemental analyzer (Jingchu University of Technology, P. R. China). Infrared spectra were carried out using JASCO FT-IR model 420 spectrophotometer (Jingchu University of Technology, P. R. China) with KBr disk in the region 4000–200 cm^{-1}. Electronic spectra were recorded on Shimadzu UV 3101 spectrophotometer (Jingchu University of Technology, P. R. China). GC analyses were carried out using a Shimadzu GC-2014C gas chromatograph (Jingchu University of Technology, P. R. China).

Synthesis of H_2L

A hot methanol solution (20 mL) of 4-diethylaminosa licylaldehyde (1.93 g, 10 mmol) was added to a hot methanol solution (20 mL) of 2-aminoethanol (0.61 g, 10 mmol). The mixture was stirred for 30 min at reflux, and the solvent was evaporated to dry, to give yellow gummy product of H_2L. Anal. Calcd. for $C_{13}H_{20}N_2O_2$: C, 66.1; H, 8.5; N, 11.8. Found: C, 65.9; H, 8.6; N, 11.9%.

Synthesis of the Complex

A hot methanol solution (15 mL) of $MoO_2(acac)_2$ (0.33 g, 1 mmol) was added to a hot methanol solution (15 mL) of H_2L (0.24 g, 1 mmol). The mixture was stirred for 30 min at reflux, and then cooled to room temperature, to give yellow solution. Single crystals of the complex, suitable for X-ray diffraction, were formed by slow evaporation of the methanol solution

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containing the complex in air for a week. Yield: 53%. Anal. Calcd. for $C_{14}H_{22}MoN_2O_5$: C, 42.6; H, 5.6; N, 7.1. Found: C, 42.5; H, 5.7; N, 7.1%.

X-Ray Diffraction

X-ray diffraction was performed using a Bruker Smart 1000 CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using the ω-scan technique. Determination of the Laue class, orientation matrix, and cell dimensions were performed according to the established procedures where Lorentz polarization and absorption corrections were applied. Absorption corrections were applied by fitting a pseudoellipsoid to the ψ-scan data of selected strong reflections over a wide range of 2θ angles. The positions of non-hydrogen atoms were located with direct methods. Subsequent Fourier syntheses were used to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. H5A attached to O5 in the complex was located from a difference Fourier map and refined isotropically, with O–H distance restrained to 0.85(1) Å and U_{iso} fix at 0.08 Å^2. The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The analysis was performed with the aid of the SHELXS-97 and SHELXL-97 suite of codes.[12,13] Crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

TABLE 1
Crystal data for the complex

Chemical formula	$C_{14}H_{22}MoN_2O_5$
Fw	394.3
Crystal shape/colour	Block/yellow
Crystal size (mm)	0.20 × 0.18 × 0.18
T (K)	298(2)
λ (MoKα) (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	16.422(3)
b (Å)	7.898(1)
c (Å)	14.142(2)
β (°)	114.831(2)
V (Å^3)	1664.6(4)
Z	4
μ (MoKα) (cm^{-1})	0.811
T (min)	0.8546
T (max)	0.8677
D_c (g cm^{-3})	1.573
Reflections/parameters	3602/205
Restraints	1
Unique reflections	2876
Goodness of fit on F^2	1.044
R_{int}	0.0251
R_1 [$I \geq 2\sigma(I)$]	0.0329
wR_2 [$I \geq 2\sigma(I)$]	0.0781
R_1 (all data)	0.0453
wR_2 (all data)	0.0857
$\Delta\rho_{\max}$	0.576
$\Delta\rho_{\min}$	–0.381

TABLE 2
Selected bond lengths (Å) and angles (°) for the complex

1			
Bond lengths			
Mo1-O1	1.9510(19)	Mo1-O2	1.956(2)
Mo1-O3	1.690(2)	Mo1-O4	1.707(2)
Mo1-O5	2.387(2)	Mo1-N1	2.229(3)
Bond angles			
O3-Mo1-O4	106.35(12)	O3-Mo1-O1	96.78(10)
O4-Mo1-O1	101.23(9)	O3-Mo1-O2	98.99(11)
O4-Mo1-O2	95.31(10)	O1-Mo1-O2	152.89(9)
O3-Mo1-N1	97.54(12)	O4-Mo1-N1	155.46(10)
O1-Mo1-N1	81.09(8)	O2-Mo1-N1	75.10(9)
O3-Mo1-O5	171.84(11)	O4-Mo1-O5	81.68(10)
O1-Mo1-O5	79.89(8)	O2-Mo1-O5	81.45(9)
N1-Mo1-O5	74.65(9)		

Catalytic Epoxidation of Olefins

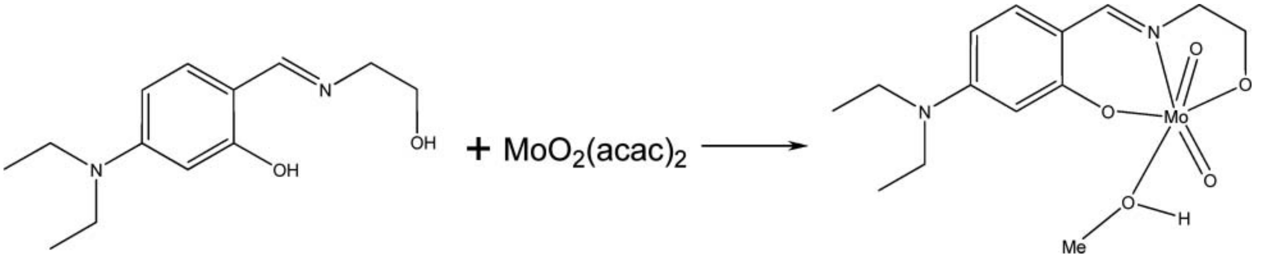
To a solution of olefins (0.28 mmol), $NaHCO_3$ (0.11 mmol), and catalyst (9.4×10^{-4} mmol) in MeCN (0.5 mL) was added H_2O_2 (1.1 mmol, 30% H_2O solution) as oxidant. After the reaction was over, for the products analysis, the solution was subjected to multiple ether extraction, and the extract was also concentrated down to 0.5 cm^3 by distillation in a rotary evaporator at room temperature and then a sample (2 μL) was taken from the solution and analyzed by GC. The retention times of the peaks were compared with those of commercial standards, and chlorobenzene was used as an internal standard for GC yield calculation.

RESULTS AND DISCUSSION

The Schiff base ligand H_2L was readily prepared by the condensation reaction of equimolar quantities of 4-diethylaminosalicylaldehyde with 2-aminoethanol in methanol. The complex was synthesized by reaction of $MoO_2(acac)_2$ with H_2L in methanol in a 1:1 mole proportion at reflux. The reaction progress is shown in Scheme 2. Chemical formula of the complex has been confirmed by elemental analyses, IR spectra, and X-ray single-crystal structure determination.

Structure Description of the Complex

The molecular structure of the complex is shown in Figure 1. The coordination geometry around the Mo atom can be described as slightly distorted octahedral, with one phenolate O, one imino N, and one amino N atoms of the dianionic Schiff base ligand, and with one oxo O atom defining the equatorial plane, and with one O atom of a methanol ligand and the other oxo O atom occupying the axial positions. The Schiff base ligand coordinates to the Mo atom in a meridional fashion forming



SCH. 2. The synthesis procedure of the complex.

five- and six-membered chelate rings with bite angles of 75.10(9)° and 81.09(8)°, respectively. The displacement of the Mo atom from the equatorial mean plane towards the axial oxo atom O3 is 0.342(2) Å. The Schiff base ligand is coordinated in its dianionic form, which are evident from the absence of the H atoms of the hydroxyl groups. The Mo–O, Mo–N, and Mo═O bonds are within normal ranges and are similar to those observed in similar dioxomolybdenum(VI) complexes with Schiff bases.[14–16]

In the crystal structure of the complex, adjacent two complex molecules are linked through intermolecular O5—H5A···O2 hydrogen bonds [O5—H5A = 0.85(1) Å, H5A···O2 = 1.787(11) Å, O5···O2 = 2.625(3) Å, O5—H5A···O2 = 177(4)°; symmetry code for A: $-x, 1-y, -z$], to form a dimer, as shown in Figure 2.

IR Spectra

The weak and broad band centered at 3447 cm^{-1} in the IR spectrum of the complex can be assigned to the ν_{OH} vibrations of the methanol ligand. The Mo═O stretching modes occur as a pair of sharp strong bands at 928 and 905 cm^{-1}, assigned to the antisymmetric and symmetric stretching modes of the dioxomolybdenum(VI) moieties.[17] The intense band indicative of the –C═N– group is shifted to 1597 cm^{-1} for the complex, which is much lower than that of the free Schiff base ligand. The new weak peaks observed at 637, 535, and 435 cm^{-1} may be attributed to the Mo–O and Mo–N vibrations in the complex.

Catalytic Property

The complex shows effective catalytic property in the oxidation of several olefins, including cyclohexene, vinylbenzene, 1-butylene, and 1-pentene, to their corresponding epoxides. The detailed information of catalytic property with respect to epoxidation of olefins with the complex as a catalyst is given in Table 3. In general, high epoxide yields and selectivity were observed for all aliphatic and aromatic substrates. The results of catalytic studies using the complex reveal that the efficiency of catalysts toward all the substrates are similar with maximum conversion, TON, and selectivity. The mechanism (Scheme 3) for the epoxidation of various olefins to epoxides using the complex as a catalyst has been proposed by comparison with the literature report.[18] When H_2O_2 was used as a sole oxidant the catalytic efficiency is not high, but when $NaHCO_3$ was added as a cocatalyst the efficiency of the system increases many fold. The key aspect of such a reaction is that H_2O_2 and hydrogen carbonate react in an equilibrium process to produce

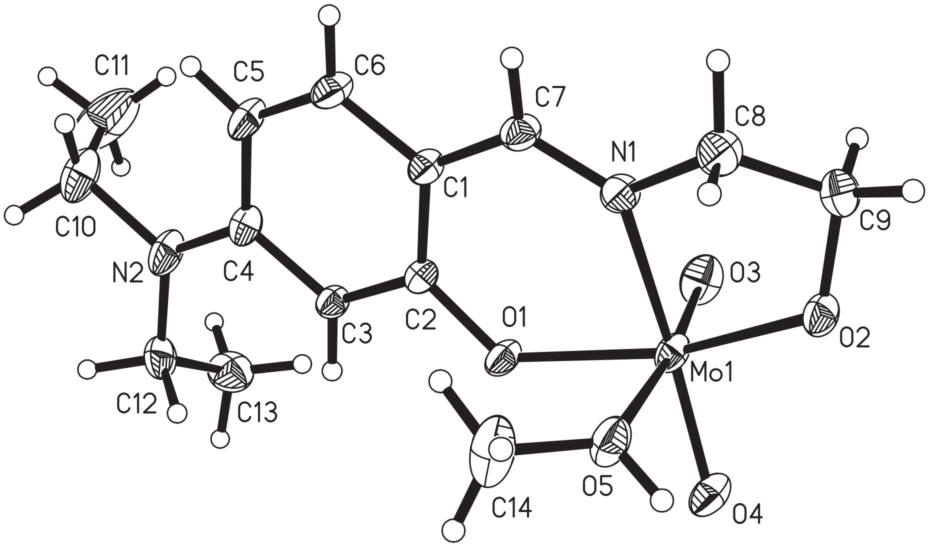


FIG. 1. Molecular structure of the complex with 30% probability thermal ellipsoids.

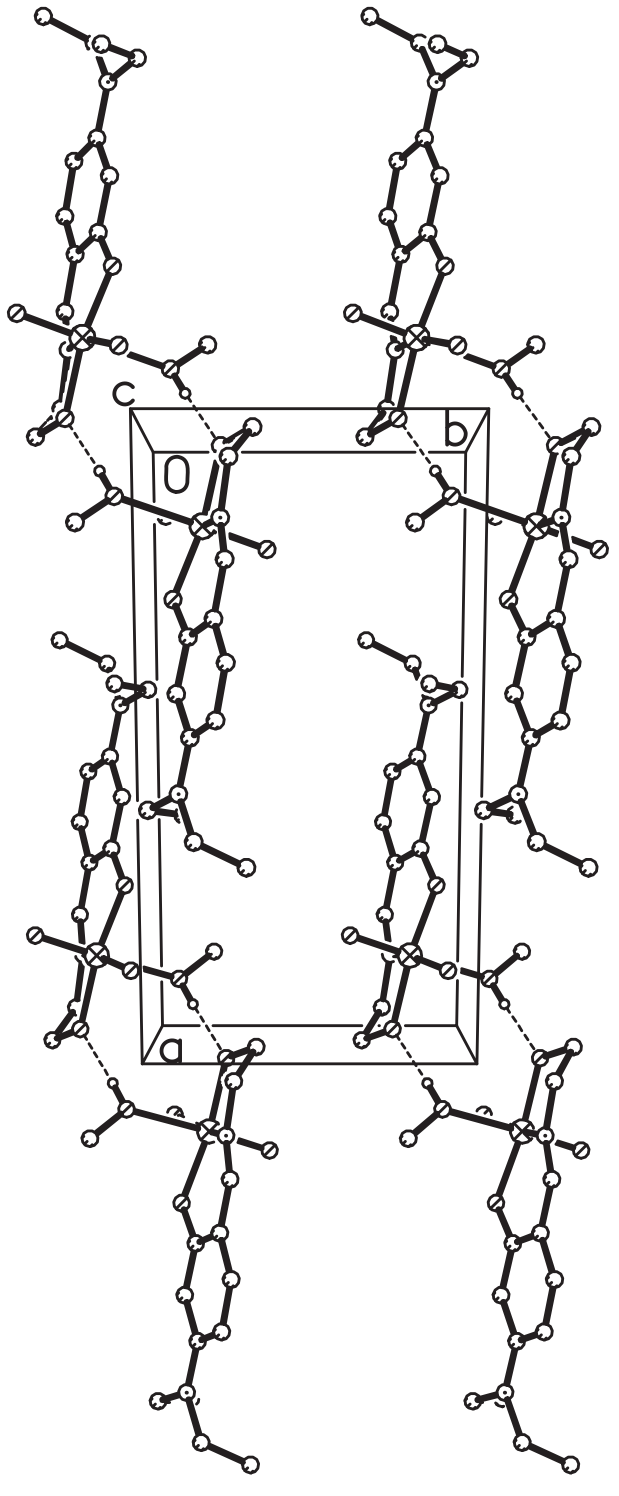
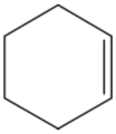
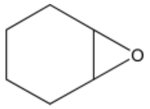
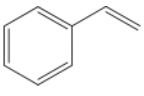
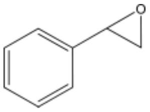
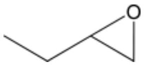
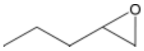


FIG. 2. Molecular packing of the complex, viewed along the *c*-axis. Hydrogen bonds are drawn as thin dashed lines.

peroxymonocarbonate, HCO_4^-, which is a more reactive nucleophile than H_2O_2 and speeds up the epoxidation reaction.[18]

TABLE 3
Detailed information of the catalytic oxidation of olefins catalyzed by the complex[a]

Substrate	Product	Conversion (%)[b] (TON)[c]	Selectivity (%)[d]
		91 (267)	100
		94 (283)	100
		97 (295)	100
		97 (302)	100

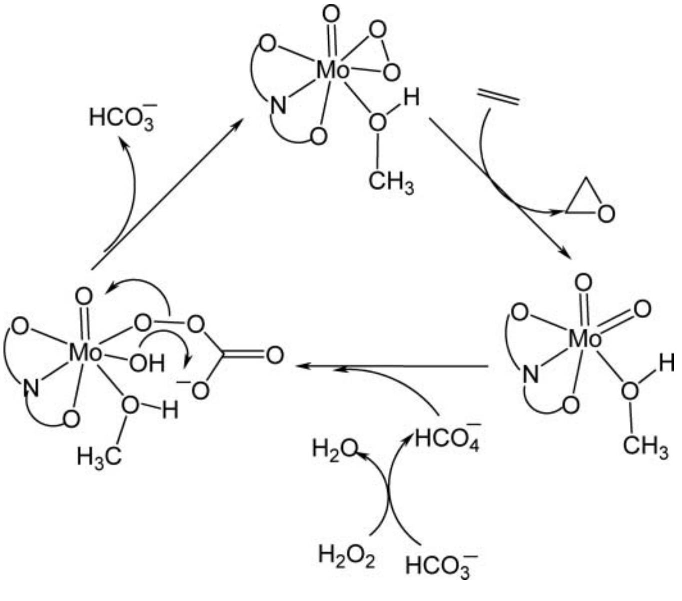
[a] The molar ratios for catalyst: substrate:$NaHCO_3$:H_2O_2 are 1:298:117:1170. The reactions were performed in (70:30) mixture of CH_3OH/CH_2Cl_2 (1.2 mL) under air atmosphere at room temperature.

[b] The GC conversion (%) are measured relative to the starting olefin after 75 min.

[c] TON = (mmol of product)/mmol of catalyst.

[d] Selectivity to epoxide = [epoxide%/(epoxide% + aldehyde%)] × 100.

The basic principle of the catalytic reaction is the conversion of oxoperoxo-complex to dioxo-complex transferring oxo species to the olfins and the conversion of dioxo complex to the oxoperoxo complex reacting with HCO_4^- to regain the catalytic activity.



SCH. 3. Probable mechanism of catalytic oxidation of olefins to epoxides.

CONCLUSION

A new dioxomolydenum(VI) complex derived from the Schiff base ligand 5-diethylamino-2-[(2-hydroxyethylimino) methyl]phenol, has been prepared and structurally characterized. The Schiff base ligand coordinates to the Mo atom through phenolate O, imino N and amino N atoms. The Mo atom in the complex is in octahedral coordination. The complex shows effective catalytic property in the oxidation of several olefins to their corresponding epoxides.

SUPPLEMENTARY MATERIALS

CCDC 909613 contains the supplementary crystallographic data for the complexes. These data can be obtained free of charge *via* http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223–336-033; or email: deposit@ccdc.cam.ac.uk.

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