Scientific paper

## Ethanol-Coordinated Dioxidomolybdenum(VI) Complexes with Aroylhyrazone Ligands: Synthesis, Spectroscopic Characterization, Crystal structures and Catalytic Oxidation Property

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### Abstract

Two new dioxidomolybdenum(VI) complexes, [MoO<sub>2</sub>L<sup>1</sup>(EtOH)] (1) and [MoO<sub>2</sub>L<sup>2</sup>(EtOH)] (2), derived from the aroylhydrazone ligands N'-(2-hydroxyl-3-methoxybenzylidene)-3-methylbenzohydrazide (H<sub>2</sub>L<sup>1</sup>) and 4-fluoro-N'-(2-hydroxylbenzylidene)benzohydrazide (H<sub>2</sub>L<sup>2</sup>), respectively, were prepared in ethanol under ambient temperature. Both complexes were characterized by elemental analysis, IR and UV-Vis spectroscopy, as well as single crystal X-ray determination. The Mo atoms in the complexes are in octahedral coordination. Crystal structures of the complexes are stabilized by hydrogen bonds. The catalytic property for epoxidation of styrene by both complexes was studied.

Keywords: Molybdenum complex; aroylhydrazone; crystal structure; catalytic property

### 1. Introduction

The petrochemical and pharmaceutical industries are inevitably causing serious environmental problems followed by the organic synthesis. To solve this problem, the application of catalysts is an efficient way to reduce the energy consumption. Schiff bases and their complexes with various metal atoms have received particular attention in many aspects like catalysts,1 magnetism2 and biological applications.3 Aroylhydrazones bearing the functional group -CH=N-NH-C(O)- are a kind of special Schiff bases having donor atoms around the metal ions that can adopt both keto and enol forms during coordination.4 Complexes with aroyhydrazone ligands have wide applications as catalysts for the oxidation of sulfides, polymerization and asymmetric epoxidation.<sup>5</sup> The oxidation of alkenes to their corresponding epoxides is of great industrial and academic interest. Among the epoxides, cyclooctene and cyclohexene oxides are the most important intermediates used in the preparation of a great number of organic products. Molybdenum complexes are reported to have fascinating catalytic properties on epoxidation reactions.<sup>6</sup> Tridentate dianionic Schiff base complexes such as cis-MoO<sub>2</sub>LL' (L' = solvent) are good substrates for redox reactions because of the ability of L' replacement with other solvents.<sup>7</sup> There are several crystal structures of molybdenum(VI) complexes with methanol acting as L'. However, those with ethanol as co-ligands are rare. The reason might be that the size of methanol molecule is smaller than ethanol, which leads to easier coordination of methanol to Mo in respect with ethanol. In pursuit of new catalysts for epoxidation reactions, we report herein two new ethanol-coordinated dioxidomolybdenum(VI) complexes,  $MoO_2L^1(EtOH)$ ] (1) and  $MoO_2L^2(EtOH)$ ] (2), where  $L^1$  and  $L^2$  are the dianionic form of N'-(2-hydroxyl-3-methoxybenzylidene)-3-methylbenzohydrazide ( $H_2L^1$ ) and 4-fluoro-N'-(2-hydroxylbenzylidene)benzohydrazide ( $H_2L^2$ ), respectively (Scheme 1).

H<sub>2</sub>L<sup>2</sup>

**Scheme 1.** The aroylhydrazone ligands.

### 2. Experimental

### 2. 1. Reagents

 ${\rm MoO_2(acac)_2},~3$ -methoxysalicylaldehyde, salicylaldehyde, 3-methylbenzohydrazide and 4-fluorobenzohydrazide were purchased from Aldrich. All other reagents with AR grade were used as received without further purification.

#### 2. 2. Instruments

Elemental analyses were carried out on a Perkin-Elmer 2400 CHN elemental analyzer. Infrared spectra (4000–400 cm<sup>-1</sup>) were recorded as KBr discs with a FTS-40 BioRad FT-IR spectrophotometer. Electronic spectra were recorded on a Lambda 35 spectrometer. Solution electrical conductivity was measured at 298 K using a DDS-11 conductivity meter. GC analyses were performed on a Shimadzu GC-2010 gas chromatograph.

### 2. 3. Syntheses

### 2. 3. 1. Synthesis of [MoO<sub>2</sub>L<sup>1</sup>(EtOH)] (1)

 $\rm H_2L^1$  (1.0 mmol, 0.28 g) and [MoO<sub>2</sub>(acac)<sub>2</sub>] (1.0 mmol, 0.33 g) were mixed and stirred in ethanol (40 mL) for 30 min at room temperature. The yellow solution was evaporated to remove three quarters of the solvents under reduced pressure, yielding orange solid product. Yield: 87%. Well-shaped single crystals suitable for X-ray diffraction were obtained by re-crystallization of the solid from ethanol. Analysis calculated for  $\rm C_{18}H_{20}MoN_2O_6$ : C, 47.38; H, 4.42; N, 6.14%; found: C, 47.23; H, 4.51; N, 6.08%. IR data (KBr, cm<sup>-1</sup>): 3420 (w,  $\rm v_{OH}$ ), 1605 (s,  $\rm v_{C=N}$ ), 945 (m,  $\rm v_{Mo=O}$ ). UV-Vis data ( $\rm \lambda_{max}$ , nm): 220, 303, 370.

### 2. 3. 2. Synthesis of MoO<sub>2</sub>L<sup>1</sup>(EtOH)] (2)

 $\rm H_2L^2$  (1.0 mmol, 0.26 g) and [MoO<sub>2</sub>(acac)<sub>2</sub>] (1.0 mmol, 0.33 g) were mixed and stirred in ethanol (40 mL) for 30 min at room temperature. The yellow solution was evaporated to remove three quarters of the solvents under reduced pressure, yielding orange solid product. Yield: 83%. Well-shaped single crystals suitable for X-ray diffraction were obtained by re-crystallization of the solid from ethanol. Analysis calculated for  $\rm C_{16}H_{15}FMoN_2O_5$ : C, 44.67; H, 3.51; N, 6.51%; found: C, 44.53; H, 3.45; N, 6.60%. IR data (KBr, cm $^{-1}$ ): 3407 (w, v<sub>OH</sub>), 1608 (s, v<sub>C=N</sub>), 945 (m, v<sub>Mo=O</sub>). UV-Vis data ( $\lambda_{max}$ , nm): 230, 305, 400.

### 2. 4. X-ray Crystallography

Crystallographic data of the complexes were collected on a Bruker SMART CCD area diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 298(2) K. Absorption corrections were applied by using the multi-scan program.<sup>8</sup> Structures of the two com-

plexes were solved by direct methods and successive Fourier difference syntheses, and anisotropic thermal parameters for all non-hydrogen atoms were refined by full-matrix least-squares procedure against  $F^2$ . All non-hydrogen atoms were refined anisotropically. The ethanol H atoms of both complexes were located from difference Fourier maps and refined isotropically, with O-H distances restrained to 0.85(1) Å. The remaining hydrogen atoms were located at calculated positions, and refined isotropically with  $U_{\rm iso}({\rm H})$  values constrained to 1.2  $U_{\rm iso}({\rm C})$  and 1.5  $U_{\rm iso}({\rm C}_{\rm methyl})$ . The crystallographic data and experimental details for the complexes are listed in Table 1.

Table 1. Crystallographic data for the complexes

	1	2
Empirical formula	$C_{18}H_{20}MoN_2O_6$	$C_{16}H_{15}FMoN_2O_5$
Formula weight	456.30	430.24
Temperature (K)	298(2)	298(2)
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2_1/c$
a (Å)	7.993(2)	7.987(2)
b (Å)	10.371(2)	16.023(2)
c (Å)	11.475(2)	15.515(2)
α (°)	95.413(2)	90
β (°)	94.189(2)	120.973(2)
γ (°)	101.323(2)	90
$V(Å^3)$	924.5(3)	1702.4(5)
Z	2	4
F(000)	464	864
M (mm <sup>-1</sup> )	0.747	0.810
$R_{ m int}$	0.0297	0.0374
Collected data	5511	7165
Unique data	3433	2351
Observed data $[I > 2\sigma(I)]$	3118	1830
Restraints	1	1
Parameters	250	230
Goodness-of-fit on $F^2$	1.054	0.935
$R_1$ , $wR_2$ indices $[I > 2\sigma(I)]$	0.0385, 0.1020	0.0333, 0.0846
$R_1$ , $wR_2$ indices (all data)	0.0428, 0.1061	0.0456, 0.0883
Large diff. peak and hole, $e \ {\rm \AA}^{-3}$	0.880, -0.790	0.409, -0.354

# 2. 5. General Procedure for Catalytic Epoxidation of Styrene

The epoxidation reaction was carried out at room temperature in acetonitrile under  $N_2$  atmosphere with constant stirring. The composition of the reaction mixture was 2.00 mmol of styrene, 2.00 mmol of chlorobenzene (internal standard), 0.10 mmol of the complexes (catalyst) and 2.00 mmol iodosylbenzene or sodium hypochlorite (oxidant) in 5.00 mL freshly distilled acetonitrile. When the oxidant was sodium hypochlorite, the solution was buffered to pH = 11.2 with  $NaH_2PO_4$  and NaOH. The composition of reaction medium was determined by GC

with styrene and styrene epoxide quantified by the internal standard method (chlorobenzene). All other products detected by GC were mentioned as others. For each complex the reaction time for maximum epoxide yield was determined by withdrawing periodically 0.1 mL aliquots from the reaction mixture and this time was used to monitor the efficiency of the catalyst on performing at least two independent experiments. Blank experiments with each oxidant and using the same experimental conditions except catalyst were also performed.

### 3. Results and Discussion

### 3. 1. Chemistry

By using the aroylhydrazone compounds H<sub>2</sub>L<sup>1</sup> and H<sub>2</sub>L<sup>2</sup> as ligands to react with dioxomolybdenum(VI) acetylacetonate in ethanol, two new dioxidomolybdenum complexes were obtained (Scheme 2). The progress of the reaction was accompanied by an immediate color change of the solution from colorless to yellow. The hydrazones were deprotonated during the coordination. The hydrazones are in dianionic form with no base used during the synthesis. This is not uncommon for the preparation of such type complexes. The two H atoms of the hydrazone ligands may transfer to acetylacetone. The analytical data are in good agreement with the proposed molecular formulae. Both complexes are insoluble in water but soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CH<sub>3</sub>CN, MeOH, EtOH, DMF and DMSO. The molar conductivity of the complexes at concentration of 1.0×10<sup>-3</sup> M in DMSO and water solution  $(\Lambda_{\rm M} = 23~\Omega^{-1}~{\rm cm^2~mol^{-1}}~{\rm for}~{\rm 1}~{\rm and}~31~\Omega^{-1}~{\rm cm^2~mol^{-1}}~{\rm for}~{\rm 2})$ is in agreement with non-electrolyte behavior. 10

and angles are given in Table 2. Single crystal X-ray analysis indicates that the complexes are mononuclear dioxidomolybdenum(VI) compounds. The Mo atoms in the complexes are in octahedral geometry, with the equatorial plane defined by the enolate oxygen (O1), phenolate oxygen (O2), imino nitrogen (N2) of the aroylhydrazone ligand, and one oxido oxygen (O3). The axial positions are occupied by the other oxido oxygen (O4) and ethanol oxygen (O5). The Mo atoms displaced toward the axial oxido O4 atoms by 0.322(1) Å for 1, and 0.338(1) Å for 2, from the equatorial planes of the octahedral coordination. The distortion of the coordination of both complexes can be observed from the bond angles related to the Mo atoms. The cis- and trans-angles at the equatorial planes are in the ranges of 71.18(9)-103.97(11)° and 149.69(10)-156.72(11)° for 1 and 71.29(10)-102.55(14)° and 149.74(13)-156.38(16)° for 2. The angles among the axial and basal bonds are in the ranges of 75.94(9)–105.30(13)° for 1 and 75.31(11)-105.57(18)° for 2. The bond lengths of Mo-O and Mo-N of both complexes are similar to each other, and comparable to those in other Mo complexes reported in literature. 11 The terminal Mo=O [1.68-1.70 Å] bond distances of both complexes agree well with the corresponding values reported for related systems. 11 Because of the trans influence of the oxido groups (O4), the bond distances of Mo1-O5 (2.36 Å) are considerably elongated, making the O5 atoms weakly coordinated to the Mo atoms. Such elongation has previously been observed in other complexes with similar structures. The aroylhydrazone ligands coordinate to the Mo atoms through dianionic form, which can be observed from the bond lengths of C7-O1 and C7-N1. The bonds C7-O1 are obviously longer than typical double bonds, while the bonds C7-N1

Scheme 2. The synthesis of the dioxidomolybdenum(VI) complexes.

# 3. 2. Crystal Structure Description of the Complexes

The ORTEP plots of the complexes 1 and 2 are shown in Figs. 1 and 2, respectively. Selected bond lengths

are shorter than typical single bonds. This phenomenon is not uncommon for metal complexes with hydrazone ligands.

In the crystal structure of complex 1 (Fig. 3), the molecules are linked by C15-H15B···O4 hydrogen

bonds (Table 3) to form chains along the *a* axis. The chains are linked through C16-H16B···O6 and O5-H5···N1 hydrogen bonds along the *c* axis, to generate a two dimensional network parallel to the *ac* plane. In the crystal structure of complex **2** (Fig. 4), the molecules are linked by C5-H5A···O3 and C12-H12···O3 hydrogen bonds (Table 3) to form two dimensional network along parallel to the *bc* plane. The layers are further linked through C10-H10···O4 and O5-H5···N1 hydrogen bonds along the *a* axis, to generate a three dimensional network.

Table 2. Selected bond distances (Å) and bond angles (°) for the complexes

	1	2
Mo1-O1	2.018(2)	2.019(3)
Mo1-O2	1.924(2)	1.923(3)
Mo1-O3	1.700(2)	1.694(3)
Mo1-O4	1.686(3)	1.683(4)
Mo1-O5	2.360(2)	2.362(4)
Mo1-N2	2.249(3)	2.243(3)
O4-Mo1-O3	105.30(13)	105.57(18)
O4-Mo1-O2	98.57(13)	99.27(17)
O3-Mo1-O2	103.97(11)	102.55(14)
O4-Mo1-O1	96.34(12)	97.17(16)
O3-Mo1-O1	97.28(11)	97.23(13)
O2-Mo1-O1	149.69(10)	149.74(13)
O4-Mo1-N2	96.22(12)	96.48(14)
O3-Mo1-N2	156.72(11)	156.38(16)
O2-Mo1-N2	81.06(9)	81.72(11)
O1-Mo1-N2	71.18(9)	71.29(10)
O4-Mo1-O5	171.75(11)	171.56(13)
O3-Mo1-O5	82.09(11)	82.29(15)
O2-Mo1-O5	82.90(10)	81.69(15)
O1-Mo1-O5	78.84(9)	78.51(13)
N2-Mo1-O5	75.94(9)	75.31(11)

Table 3. Hydrogen bond distances (Å) and bond angles (°) for the complexes

D-H···A	d(D-H)	<i>d</i> (H··· <i>A</i> )	d(D···A)	Angle (D-H···A)
1				
O5-H5···N1 <sup>#1</sup>	0.85	2.04(3)	2.885(4)	176(5)
C15-H15B···O4 <sup>#2</sup>	0.97	2.50(3)	3.441(5)	163(5)
C16-H16B···O6 <sup>#3</sup>	0.96	2.56(3)	3.456(5)	156(5)
2				
O5-H5···N1 <sup>#4</sup>	0.85	2.01(3)	2.847(5)	167(4)
C5-H5A···O3 <sup>#5</sup>	0.93	2.48(4)	3.404(5)	171(5)
C10-H10···O4 <sup>#6</sup>	0.93	2.55(4)	3.283(5)	136(5)
C12-H12···O3 <sup>#7</sup>	0.93	2.39(4)	3.176(5)	142(5)

Symmetry codes: #1: 1-x, 1-y, 1-z; #2: 1+x, y, z; #3: 1-x, 1-y, 2-z; #4: -x, -y, -z; #5: -1+x,  $\frac{1}{2}-y$ ,  $-\frac{1}{2}+z$ . #6: 1-x, -y, 1-z; #7: 1+x,  $\frac{1}{2}-y$ ,  $\frac{1}{2}+z$ .

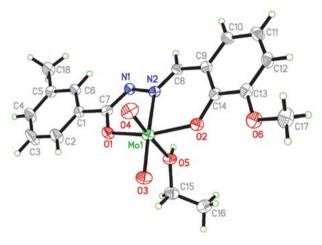


Fig. 1. ORTEP diagram of complex 1 with 30% thermal ellipsoid.

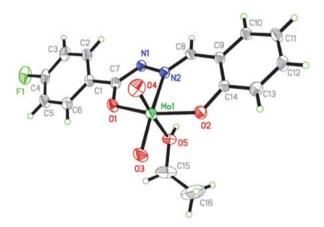
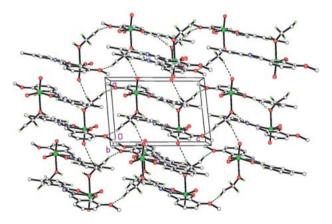


Fig. 2. ORTEP diagram of complex 2 with 30% thermal ellipsoid.



**Fig. 3.** Molecular packing structure of complex 1 linked by hydrogen bonds (dashed lines).

### 3. 3. IR Spectra of the Complexes

The weak and broad absorptions centered at 3420 cm<sup>-1</sup> for complex **1** and 3407 cm<sup>-1</sup> for complex **2** are attributed to the O-H bonds of the ethanol ligands. The in-

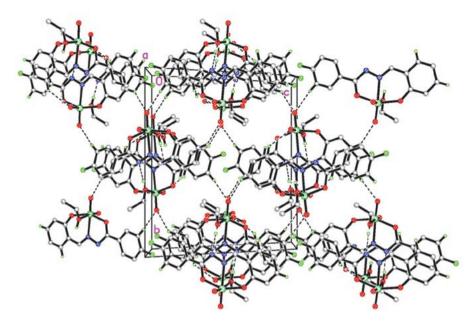


Fig. 4. Molecular packing structure of complex 2 linked by hydrogen bonds (dashed lines).

tense bands at 1605 cm<sup>-1</sup> for complex 1 and 1608 cm<sup>-1</sup> for complex 2 are assigned to the vibrations of the azomethine groups, v(C=N).<sup>12</sup> The characteristic of the spectra of both complexes is the exhibition of sharp bands at 945 cm<sup>-1</sup>, corresponding to the Mo=O stretching vibration.<sup>13</sup> Further evidence of the bonding is also shown by the observation that new bands in the IR spectra of the metal complexes appear at 450–470 cm<sup>-1</sup> and 520–550 cm<sup>-1</sup> assigned to M-N and M-O stretching vibrations.

### 3. 4. Catalytic Properties of the Complexes

The percentage of conversion of styrene, selectivity for styrene oxide, yield of styrene oxide and reaction time to obtain maximum yield using both the oxidants are presented in Table 4. The data reveals that both complexes as catalysts convert styrene most efficiently in the presence of the oxidants. Nevertheless, the catalysts are selective towards the formation of styrene epoxides despite of the formation of by-products which have been identified by GC-MS as benzaldehyde, phenylacetaldehyde, styrene epoxides derivative, alcohols etc. From the data it is also clear that the complexes exhibit excellent efficiency for styrene epoxide yield. When the reactions are carried out with PhIO and NaOCl, styrene conversions of complexes 1 and 2 were about 89% and 85%, and 91% and 86%, respectively. It is evident that between PhIO and NaOCl, the former acts as a better oxidant with respect to both styrene conversion and styrene epoxide selectivity. The epoxide yields for the complexes 1 and 2 using PhIO and NaOCl as oxidants are 79% and 88%, and 80% and 91%, respectively. The two complexes have similar catalytic oxidation behavior with the molybdenum(VI) complex with 2-bromo-N'-(3,5-dichloro-2-hydroxybenzylidene)benzohydrazide as ligand,<sup>14</sup> and better activity than the copper(II) and manganese(II) complexes with hydrazones.<sup>15</sup>

Table 4. Catalytic epoxidation results of complexes 1 and 2<sup>a</sup>

	1		2	2
Oxidant	PhIO	NaOCl	PhIO	NaOCl
Conversion (%)	89	85	91	86
Epoxide yield (%)	79	88	80	91
Selectivity (%)	95	93	92	88

<sup>&</sup>lt;sup>a</sup> The time is 2 h for PhIO, and 3 h for NaOCl.

### 4. Conclusion

We have successful synthesized two new mononuclear dioxidomolybdenum(VI) complexes with the aroylhydrazone ligands N'-(2-hydroxyl-3-methoxybenzylidene)-3-methylbenzohydrazide and 4-fluoro-N'-(2-hydroxylbenzylidene)benzohydrazide. Single crystal X-ray analysis indicates that the Mo atoms in both complexes are in distorted octahedral coordination. The aroylhydrazone ligands are in dianionic chelate form and coordinate to the metal through the enolate oxygen, phenolate oxygen and imino nitrogen. Two oxo ligands and an ethanol furnish the remaining coordination sites. The complexes have effective catalytic property for the epoxidation of styrene, with conversions over 85% and selectivity over 88%. The resulting epoxides are both of academic and industrial interest.

#### Supplementary Material

CCDC 2256616 for 1 and 2256617 for 2 contain the supplementary crystallographic data for this paper. These

data can be obtained free of charge *via* http://www.ccdc.cam.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 e-mail: deposit@ccdc.cam.ac.uk.

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### **Povzetek**

Sintetizirali smo dva nova dioksidomolibdenova(VI) kompleksa, [MoO<sub>2</sub>L<sup>1</sup>(EtOH)] (1) in [MoO<sub>2</sub>L<sup>2</sup>(EtOH)] (2), pridobljena iz aroilhidrazonskih ligandov  $N^*$ -(2-hidroksil-3-metoksibenziliden)-3-metilbenzohidrazida (H<sub>2</sub>L<sup>1</sup>) oziroma 4-fluoro- $N^*$ -(2-hidroksilbenziliden)benzohidrazida (H<sub>2</sub>L<sup>2</sup>), v etanolu pri sobni temperaturi. Oba kompleksa smo okarakterizirali z elementno analizo, IR in UV-Vis spektroskopijo ter z rentgensko monokristalno analizo. Mo atomi v kompleksih so koordinirani oktaedrično. Kristalne strukture kompleksov so stabilizirane z vodikovimi vezmi. Preučevali smo katalitične lastnosti obeh kompleksov pri epoksidaciji stirena.



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