# Synthesis, Crystal Structures, and Catalytic Oxidation of Olefins of Dioxomolybdenum(VI) Complexes with Aroylhydrazone Ligands<sup>1</sup>

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Abstract—Two Mo(VI) aroylhydrazone complexes, *cis*-[MoO<sub>2</sub>(L<sup>1</sup>)(CH<sub>3</sub>OH)] (I) and *cis*-[MoO<sub>2</sub>(L<sup>2</sup>)(CH<sub>3</sub>OH)] (II), derived from 2-bromo-*N'*-(3,5-dibromo-2-hydroxybenzylidene)benzohydrazide (H<sub>2</sub>L<sup>1</sup>) and 2-bromo-*N'*-(2-hydroxy-4-methoxybenzylidene)benzohydrazide (H<sub>2</sub>L<sup>2</sup>), respectively, are reported. The complexes were characterized by elemental analyses, infrared and electronic spectroscopy, and single crystal structure analysis (CIF files CCDC nos. 1443679 (I) and 1443678 (II)). The Mo atoms are coordinated by two *cis* terminal oxygen, ONO from the aroylhydrazone ligand, and methanol oxygen. Complex I crystallized as monoclinic space group *P*2<sub>1</sub>/*c* with unit cell dimensions *a* = 8.075(2), *b* = 13.905(1), *c* = 16.448(1) Å,  $\beta$  = 91.282(2)°, *V* = 1846.5(4) Å<sup>3</sup>, *Z* = 4, *R*<sub>1</sub> = 0.0859, *wR*<sub>2</sub> = 0.2066. Complex II crystallized as triclinic space group *P*1, with unit cell dimensions *a* = 8.0824(6), *b* = 10.5919(8), *c* = 10.7697(8),  $\alpha$  = 96.432(2)°,  $\beta$  = 97.438(2)°,  $\gamma$  = 103.119(2)°, *V* = 880.8(1) Å<sup>3</sup>, *Z* = 2, *R*<sub>1</sub> = 0.0271, *wR*<sub>2</sub> = 0.0571. The complexes were tested as catalyst for the oxidation of olefins and showed effective activity.

**Keywords**: *cis*-dioxomolybdenum(VI) complexes, aroylhydrazone ligands, catalysis, oxidation, olefins **DOI**: 10.1134/S1070328417030058

## **INTRODUCTION**

Molybdenum is an essential metal that is capable of forming metal complexes with various ligands [1-5]. Molybdenum is not only much less toxic than many other metals of industrial importance but it is also an essential constituent of certain enzymes that catalyze reduction of molecular nitrogen and nitrate in plants and oxidation (hydroxylation) of xanthine and other purines and aldehvdes in animals [6]. Epoxides are very important chemicals for manufacturing a range of important commercial products such as pharmaceuticals and polymers. Many transition metal complexes have been reported for oxidation of olefins [7-13]. Molybdenum complexes are known for considerable use in organic chemistry, in particular for the various oxidations of organic compounds [2, 4, 14]. Oxido-peroxido molybdenum complexes have been intensively investigated as oxidation catalysts for variety of organic substrates, particularly for sulfoxidation and epoxidation of olefins [15–18]. In order to further study the catalytic potentiality of the oxido-peroxido complexes of molybdenum, in this paper, the synthesis, crystal structures and catalytic activity of Mo(VI) hydrazone complexes, *cis*-[MoO<sub>2</sub>(L<sup>1</sup>)(CH<sub>3</sub>OH)] (I) and *cis*-[MoO<sub>2</sub>(L<sup>2</sup>)(CH<sub>3</sub>OH)] (II), derived from 2- bromo-*N*'-(3,5-dibromo-2-hydroxybenzylidene)benzohydrazide (H<sub>2</sub>L<sup>1</sup>) and 2-bromo-*N*'-(2-hydroxy-4-methoxybenzylidene)benzohydrazide (H<sub>2</sub>L<sup>2</sup>), respectively, are reported.

#### EXPERIMENTAL

**Materials and methods.** All the reagents and solvents used in the synthesis were procured commercially and used without subsequent purification. The starting material, bis(acetylacetonato) dioxomolybdenum(VI), [MoO<sub>2</sub>(Acac)<sub>2</sub>] was prepared as described in the literature [19]. Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 elemental analyzer. Infrared spectra were carried out using the JASCO FT-IR model 420 spectrophotometer with KBr disk in the region 4000–400 cm<sup>-1</sup>. Electronic absorption spectra measurement in acetonitrile was measured using a Labda 900 spectrometer. <sup>1</sup>H NMR

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Table 1.	Crystallographic	data and refinement	t parameters for	complexes I, II
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D	Value			
Parameter	I	П		
Formula weight	634.93	507.15		
Crystal size, mm	$0.17 \times 0.15 \times 0.13$	0.30  imes 0.27  imes 0.27		
Temperature, K	298(2)	298(2)		
Crystal system	Monoclinic	Triclinic		
Space group	$P2_{1}/c$	$P\overline{1}$		
<i>a</i> , Å	8.075(2)	8.0824(6)		
b, Å	13.905(1)	10.5919(8)		
<i>c</i> , Å	16.448(1)	10.7697(8)		
α, deg	90	96.432(2)		
β, deg	91.282(2)	97.438(2)		
γ, deg	90	103.119(2)		
$V, Å^3$	1846.5(4)	880.8(1)		
Ζ	4	2		
$ ho_{calcd}$ , g cm <sup>-3</sup>	2.284	1.912		
$\mu(MoK_{\alpha}), mm^{-1}$	7.231	3.049		
<i>F</i> (000)	1208	500		
Number of measured reflections	12439	7602		
Number of observed reflections with $I > 2\sigma(I)$	2942	3213		
Unique reflections	2349	2770		
Parameters	239	240		
Number of restraints	13	1		
$R_1, wR_2 (I > 2\sigma(I))^*$	0.0859, 0.2066	0.0271, 0.0571		
$R_1$ , $wR_2$ (all data)*	0.1078, 0.2200	0.0361, 0.0608		
Goodness of fit of $F^2$	1.055	1.067		

\*  $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|, wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}.$ 

spectra were measured in DMSO- $d_6$  on Bruker 300 MHz spectrometer.

Synthesis of I. 3,5-Dibromo-2-hydroxybenzaldehyde (0.280 g, 1.0 mmol) and 2-bromobenzohydrazide (0.215 g, 1.0 mmol) were dissolved and mixed in 20 mL methanol. Then,  $MoO_2(Acac)_2$  (0.328 g, 1.0 mmol) dissolved in 20 mL methanol was poured into the above mixture. The final mixture was stirred at room temperature for 30 min to give yellow solution. After leaving the solution for a few days at room temperature, fine orange crystals were formed. The product was filtered and washed with methanol. The yield was 73%. IR (KBr;  $v_{max}$ , cm<sup>-1</sup>): 3451 br.w, v(OH), 1612 m v(C=N), 949 s and 853 s v(Mo=O). Absorption spectrum in acetonitrile ( $\lambda_{max}$ , nm ( $\epsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>)): 300 (11300), 325 (12770), 410 (2123).

For C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> O <sub>5</sub> Br <sub>3</sub> Mo					
anal. calcd., %:	C, 28.38;	Н, 1.75;	N, 4.41.		
Found, %:	C, 28.12;	H, 1.86;	N, 4.53.		

Synthesis of II. 2-Hydroxy-4-methoxybenzaldehyde (0.152 g, 1.0 mmol) and 2-bromobenzohydrazide (0.215 g, 1.0 mmol) were dissolved and mixed in 20 mL methanol. Then,  $MoO_2(Acac)_2$  (0.328 g, 1.0 mmol) dissolved in 20 mL methanol was poured into the above mixture. The final mixture was stirred at room temperature for 30 min, to give yellow solution. After leaving the solution for a few days at room temperature, fine orange crystals were formed. The product was filtered and washed with methanol. The yield was 73%.

IR (KBr;  $v_{max}$ , cm<sup>-1</sup>): 3467 br.w v(OH), 1608 m v(C=N), 950 s and 859 s v(Mo=O). Absorption spectrum in acetonitrile ( $\lambda_{max}$ , nm ( $\epsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>)): 297 (12178), 320 (13040), 400 (2050).

For C<sub>16</sub>H<sub>15</sub>N<sub>2</sub>O<sub>6</sub>BrMo

anal. calcd., %:	C, 37.89;	H, 2.98;	N, 5.52.
Found, %:	C, 37.70;	Н, 3.07;	N, 5.45.

X-ray structure determination. X-ray data for the compounds were collected on a Bruker SMART APEXII diffractometer equipped with graphitemonochromated Mo $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). A preliminary orientation matrix and cell parameters were determined from three sets of  $\omega$  scans at different starting angles. Data frames were obtained at scan intervals of  $0.5^{\circ}$  with an exposure time of 10 s frame<sup>-1</sup>. The reflection data were corrected for Lorentz and polarization factors. Absorption corrections were carried out using SADABS [20]. The structures were solved by direct methods and refined by full-matrix least-squares analysis using anisotropic thermal parameters for non-H atoms with the SHELXTL program [21]. The water H atoms were located from difference Fourier maps and refined isotropically, with O–H distances restrained to 0.85(1) Å. The remaining H atoms were calculated at idealized positions and refined with the riding models. Crystallographic data for the compounds are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1443679 (I) and 1443678 (II); deposit@ccdc.cam.ac.uk or http://www.ccdc. cam.ac.uk).

**Catalytic epoxidation of olefins.** In a typical catalytic experiment, TBHP (1 mmol) was added to a solution of olefin (1 mmol), chlorobenzene (1 mmol) as an internal standard and the complexes  $(2 \times 10^{-4} \text{ mmol})$  in 1,2-dichloroethane (0.5 mL). The mixture was stirred at 80°C under air and the course of the reaction was monitored using gas chromatography (Agilent Technologies Instruments 6890N, equipped with a capillary column (19019J-413 HP-5, 5% Phenyl Methyl Siloxane, Capillary 60.0 m × 250  $\mu$ m × 1.00  $\mu$ m) and a flame ionization detector). Assignments of products were made by comparison with authentic samples. All the reactions were run two times.

## **RESULTS AND DISCUSSION**

The aroylhydrazone ligands were reacted with bis(acetylacetonato)dioxomolybdenum(VI) in methanol solution, generating fine crystalline complexes, as shown in scheme:



Scheme.

Crystals of the complexes are stabilized in air at room temperature, and soluble in methanol, ethanol, and acetonitrile. The molecular structures of the complexes I and II are shown in Fig. 1. Structures of the dioxomolybdenum complex molecules of I and II are very similar to

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Table 2. Selected bond lengths (	Å) and angles (deg)	for complexes I and II
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Bond	d, Å	Bond	d, Å
		I	
Mo(1)–O(1)	1.928(8)	Mo(1)–O(2)	2.033(9)
Mo(1)-O(3)	1.683(10)	Mo(1)–O(4)	1.730(10)
Mo(1)-O(5)	2.299(9)	Mo(1)–N(1)	2.232(10)
	I	II	,
Mo(1)–O(1)	1.929(2)	Mo(1)–O(2)	2.009(2)
Mo(1)-O(4)	2.342(2)	Mo(1)-O(5)	1.698(2)
Mo(1)–O(6)	1.693(2)	Mo(1)-N(1)	2.237(2)
Angle	ω, deg	Angle	ω, deg
		I	
O(3)Mo(1)O(4)	106.1(5)	O(3)Mo(1)O(1)	97.1(5)
O(4)Mo(1)O(1)	103.3(4)	O(3)Mo(1)O(2)	95.5(5)
O(4)Mo(1)O(2)	98.7(4)	O(1)Mo(1)O(2)	150.5(4)
O(3)Mo(1)N(1)	94.6(4)	O(4)Mo(1)N(1)	158.0(4)
O(1)Mo(1)N(1)	80.9(4)	O(2)Mo(1)N(1)	71.5(3)
O(3)Mo(1)O(5)	170.2(4)	O(4)Mo(1)O(5)	82.9(4)
O(1)Mo(1)O(5)	84.3(4)	O(2)Mo(1)O(5) 79.1(4)	
N(1)Mo(1)O(5)	76.0(3)		
	I	II	I.
O(6)Mo(1)O(5)	105.99(11)	O(6)Mo(1)O(1)	98.74(10)
O(5)Mo(1)O(1)	102.31(10)	O(6)Mo(1)O(2)	96.72(10)
O(5)Mo(1)O(2)	98.74(9)	O(1)Mo(1)O(2)	149.24(8)
O(6)Mo(1)N(1)	96.66(10)	O(5)Mo(1)N(1) 156.17(10)	
O(1)Mo(1)N(1)	81.03(8)	O(2)Mo(1)N(1)	70.85(8)
O(6)Mo(1)O(4)	171.63(9)	O(5)Mo(1)O(4)	81.81(9)
O(1)Mo(1)O(4)	82.24(9)	O(2)Mo(1)O(4)	78.81(8)
N(1)Mo(1)O(4)	75.23(8)		

each other, except for the substituent groups of the aroylhydrazone ligands. In each of the complexes, the coordination geometry around the Mo atom can be described as slightly distorted octahedron, with the equatorial plane defined by one phenolic O, one imino N, and one enolic O atoms of the dianionic hydrazone ligand, and one oxo O atom, and with the two axial positions occupied by one O atom of a methanol ligand and the other oxo O atom. The aroylhydrazone ligands coordinate to Mo atoms in meridional fashion forming five- and sixmembered chelate rings with bite angles of  $71.5(3)^{\circ}$  and  $80.9(4)^{\circ}$  for I and  $70.85(8)^{\circ}$  and  $81.03(8)^{\circ}$  for II. The dihedral angles between the two phenyl rings of the aroylhydrazone ligands are  $11.8(3)^{\circ}$  for I and  $7.3(5)^{\circ}$  for II. The displacements of the Mo atoms from the equatorial mean planes toward the axial oxo atoms are 0.302(2) Å for I and 0.335(3) Å for II. The aroylhydrazone ligands are coordinated in their dianionic forms, which are evident from the N–C and O–C bond lengths, indicating the presence of the enolate form of the ligand amide groups. The Mo–O, Mo–N, and Mo=O bonds are



Fig. 1. Molecular structure of I (a) and II (b) with atom labeling scheme and 30% probability thermal ellipsoids for all non-hydrogen atoms.

within normal ranges and are similar to those observed in similar dioxomolybdenum(VI) complexes [22, 23].

In the crystal of I, the complex molecules are linked by methanol ligands through intermolecular  $O-H\cdots N$  hydrogen bonds to form 1D chains along the x axis. The chains are further linked through weak Br $\cdots O$  interactions, to form 2D sheets parallel to the xy plane (Fig. 2a). In the crystal of II, adjacent complex molecules are linked by two methanol molecules through two intermolecular  $O-H\cdots N$  hydrogen bonds to form a dimer (Fig. 2b).

The weak and broad bands in the region  $3400-3500 \text{ cm}^{-1}$  for the complexes are assigned to the v(OH) vibrations. The Mo=O stretching modes occur as a pair of sharp strong bands at about 950 and  $855 \text{ cm}^{-1}$  for the complexes, which are assigned to the anti-symmetric and symmetric stretching modes of

the dioxomolybdenum(VI) moieties. The bands due to the v(C=O) and v(NH) of the hydrazones were absent in the complexes, and new C–O stretches appear at 1155 cm<sup>-1</sup> for the complexes. This suggests occurrence of *keto*-imine tautomerization of the aroylhydrazone ligands during coordination. The strong bands indicative of the C=N–N=C groups in the complexes are shifted to 1612 cm<sup>-1</sup> for I and 1608 cm<sup>-1</sup> for II. The new weak peaks observed in the range 400–800 cm<sup>-1</sup> may be attributed to the Mo–O and Mo–N vibrations in the complexes. The IR spectra of the complexes are similar to each other, indicating the complexes are similar structures, as evidenced by the single crystal X-ray determination.

Considering the structures of two complexes are similar, the present work used complex I as catalyst to explore suitable experimental conditions. The cata-

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**Fig. 2.** Molacular packing diagrams of I viewed along the z axis (a) and II viewed along the x axis (b). Hydrogen bonds are shown as dashed lines.

lytic property of complex I was first studied in the homogeneous epoxidation of cyclohexene, used as a model substrate, and *tert*-butyl hydrogen peroxide (**TBHP**) as the oxygen donor. The influence of several solvents was evaluated (Table 3). It is clear that toluene and 1,2-dichloroethane produce the highest yields and the catalytic activity is the best when 1,2-dichloroethane, a turnover number (TON) of 5210 with the complex can be achieved. So, 1,2-dichloroethane can be used as solvent in the catalyst experiment.

The catalytic epoxidation of some olefins using the complexes as catalyst is summarized in Table 4. In general, both complexes show similar catalytic properties. It is clear that the epoxide yields and selectivity are good for cyclohexene (entries 1 and 2). However, the catalytic property decreased for styrene, *p*-chlorostyrene, *p*-bromostyrene, and *p*-methylstyrene, and substituted styrene. The electronic effects may play key roles in the catalytic process. The catalytic property of *p*-fluorostyrene, *p*-chlorostyrene and *p*-bromostyrene is better than styrene (entries 3–10). The complexes were highly selective for the epoxide for cyclohexene, but lower for various styrenes with benzaldehyde and acetophenone derivatives as side products.

Thus two new structurally similar Mo(VI) aroylhydrazone complexes have been synthesized and characterized by X-ray structure analysis and spectroscopy methods. The aroylhydrazone ligands coordinate to the Mo atoms through the phenolic O, imino N and ethanolic O atoms. The Mo atoms in the complexes are coordinated by aroylhydrazone and methanol ligands, as well as two oxo groups, forming octahedral coordination. The complexes were employed as catalyst for the epoxidation of various olefins with *tert*butylhydroperoxide in dichloroethane. The complexes can catalyze cyclohexene to its epoxide with TBHP as the oxidant, with high yield and selectivity.

Entry	Solvent	Conversion	Time	TON**
1	МеОН	83	1 h	3550
2	EtOH	92	1 h	4130
3	MeCN	93	1 h	4220
4	Cyclohexane	90	1 h	4600
5	Toluene	98	1 h	4870
6	1,2-Dichloroethane	100	30 min	5210

Table 3. The solvent effects on the catalytic epoxidation of cyclohexene with TBHP using complex I as the catalyst\*

\* The molar ratio for the complex : cyclohexene : TBHP is 1 : 5000 : 5000. The reactions were carried out at 80°C.

\*\* TON = (mmol of product)/mmol of catalyst.

Entry	Substrate	Product	Compound	Conversion, %	Selectivity, %	TON
1			Ι	100	100	4600
2		0	II	100	100	3800
3			Ι	58	43	1058
4			Π	55	38	987
5		O O	Ι	67	46	1220
6	F	F	II	71	50	1195
7			Ι	73	61	1107
8	CI	CI	II	77	53	1083
9			Ι	59	44	930
10	Br	Br	II	62	39	915

Table 4. Catalytic oxidation results\*

\* The molar ratio for the catalyst : olefin : TBHP is 1 : 5000 : 5000. The reactions were carried out at 80°C for 1 h.

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