Synthesis, Characterization, and Crystal Structures of Dioxomolybdenum(VI) Complexes Derived from Similar Tridentate Hydrazone Compounds with Catalytic Property¹

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Abstract—Two hydrazone compounds 2-chloro-*N*-(2-hydroxy-4-methoxybenzylidene)benzohydrazide (H₂L¹) and *N*-(2-hydroxy-4-methoxybenzylidene)-3-methylbenzohydrazide (H₂L²) were prepared and characterized by IR, UV-Vis and ¹H NMR spectra. Based on the hydrazone compounds, two new structurally similar dioxomolybdenum(VI) complexes, [MoO₂L¹(CH₃OH)] (I) and [MoO₂L²(CH₃OH)] (II), were prepared and characterized by IR and UV-Vis spectra, and single crystal X-ray diffraction (CIF files nos. 1566491 (I) and 1566492 (II)). Complex I crystallizes as the triclinic space group *P*1 with unit cell dimensions *a* = 8.0750(5), *b* = 10.5223(7), *c* = 10.8110(7) Å, α = 96.975(2)°, β = 97.909(2)°, γ = 104.497(2)°, *V* = 869.2(1) Å³, *Z* = 2, *R*₁ = 0.0323, *wR*₂ = 0.0620, GOOF = 1.089. Complex II crystallizes as the monoclinic space group *P*2₁/*n* with unit cell dimensions *a* = 11.680(1), *b* = 10.496(2), *c* = 14.879(2) Å, β = 98.862(2)°, *V* = 1802.2(4) Å³, *Z* = 4, *R*₁ = 0.0270, *wR*₂ = 0.0675, GOOF = 1.111. X-ray analysis indicates that the complexes are mononuclear dioxomolybdenum(VI) species with the Mo atoms in octahedral coordination. The complexes were studied for their catalytic oxidation property on some olefins with *tert*-butyl hydrogen peroxide as oxidant.

Keywords: hydrazone, molybdenum complex, mononuclear complex, crystal structure, catalytic property

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INTRODUCTION

Study on the oxidation of olefins has received particular interest in recent years. High-valent molybdenum complexes have attracted continuing attention due to their important practical applications as catalysts in the ammoxidation of propene, the sulfoxidation and epoxidation of olefins etc. [1-7]. The ability of molybdenum to form stable complexes with oxygen- and nitrogen-containing ligands led to the development of molybdenum Schiff base complexes which are efficient catalysts both in homogeneous and heterogeneous reactions [8–13]. Recently, we have reported some metal complexes with Schiff bases, and their biological aplications [14–16], as well as catalytic properties [17]. In this paper, as a continuation of the work on the exploration of new catalytic materials based on molybdenum complexes, two new molybdenum(VI) complexes derived from hydrazone compounds 2-chloro-N-(2-hydroxy-4-methoxybenzylidene)benzohydrazide (H₂L¹) and N-(2-hydroxy-4methoxybenzylidene)-3-methylbenzohydrazide (H₂L²) were prepared. They are [MoO₂L¹(CH₃OH)] (I) and [MoO₂L²(CH₃OH)] (II).



MeO OH OH

 (H_2L^2)

¹ The article is published in the original.

EXPERIMENTAL

Materials and methods. $MoO_2(Acac)_2$ and organic materials 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. ¹H NMR spectrum of the complex was recorded on a Bruker FT-NMR 300 MHz spectrometer using (CD₃)₂SO as solvent. GC analyses were performed on a Shimadzu GC-2010 gas chromatograph.

Synthesis of the hydrazones. The hydrazones were synthesized as follows. To the methanolic solution (30 mL) of 2-methoxybenzohydrazide (0.02 mol) was added a methanolic solution (20 mL) of 3-bromosa-licylaldehyde or 3-methylsalicylaldehyde (0.02 mol) with stirring. The mixtures were stirred for 30 min at room temperature, and left to slowly evaporate to give colorless crystalline product, which were recrystallized from methanol and dried in vacuum containing anhydrous CaCl₂.

For $C_{15}H_{13}CIN_2O_3$ (H_2L^1)

Anal. calcd., %	C, 59.1	Н, 4.3	N, 11.6
Found, %	C, 59.3	H, 4.4	N, 11.5

Yield 91%. IR (KBr; v_{max} , cm⁻¹): 3435 w v(OH), 3327 w v(NH), 1653 s v(C=O), 1601 w v(C=N), 1517 m v(Ar–O), 1287 m v(C–O). UV-Vis data (MeOH; λ_{max} , nm): 285, 330. ¹H NMR (300 MHz, *d*⁶-DMSO; δ , ppm): 12.12 (s., 1H, OH), 11.70 (s., 1H, NH), 8.61 (s., 1H, CH=N), 7.72–7.40 (m., 5H, ArH), 6.65 (d., 1H, ArH), 6.45 (s., 1H, ArH), 3.75 (s., 3H, OCH₃).

For $C_{16}H_{16}N_2O_3$ (H_2L^2)					
Anal. calcd., %	C, 67.6	H, 5.7	N, 9.8		
Found, %	C, 67.4	H, 5.6	N, 9.9		

Yield 87%. IR (KBr; v_{max} , cm⁻¹): 3441 w v(OH), 3323 w v(NH), 1653 s v(C=O), 1602 w v(C=N), 1515 m v(Ar–O), 1285 m v(C–O). UV-Vis data (MeOH; λ_{max} , nm): 290, 335. ¹H NMR (300 MHz, d^6 -DMSO; δ , ppm): 12.23 (s., 1H, OH), 11.58 (s., 1H, NH), 8.63 (s., 1H, CH=N), 7.87–7.36 (m., 5H, ArH), 6.65 (d., 1H, ArH), 6.45 (s., 1H, ArH), 3.75 (s., 3H, OCH₃), 2.31 (s., 3H, CH₃).

Synthesis of the complexes. The hydrazone compounds (0.1 mmol each) and $MoO_2(Acac)_2$ (0.1 mmol) were mixed in methanol (10 mL). The mixture was refluxed for 1 h and then cooled to room temperature. Single crystals of the complexes, suitable for X-ray diffraction, were grown from the solution

RUSSIAN JOURNAL OF COORDINATION CHEMISTRY Vol. 44

upon slowly evaporation within a few days. The crystals were isolated by filtration, washed with methanol and dried in vacuum containing anhydrous CaCl₂.

For
$$C_{16}H_{15}N_2O_6ClMo(I)$$

Anal. calcd., %	C, 41.5	Н, 3.3	N, 6.1
Found, %	C, 41.7	H, 3.4	N, 6.2

Yield 63%. IR (KBr; v_{max} , cm⁻¹): 3447 w v(OH), 1613 m v(C=N), 1441 m v(C=C), 1373 m v(Ar–O), 1162 s v(C–O), 952 s, 851 s v(Mo=O). UV-Vis data (MeOH; λ_{max} , nm): 270, 335, 450.

For $C_{17}H_{18}N_2O_6Mo$ (II)

Anal. calcd., %	C, 46.2	H, 4.1	N, 6.3
Found, %	C, 46.3	H, 4.1	N, 6.5

Yield 43%. IR (KBr; v_{max} , cm⁻¹): 3443 w v(OH), 1613 m v(C=N), 1441 m v(C=C), 1372 m v(Ar–O), 1164 s v(C–O), 949 s, 852 s v(Mo=O). UV-Vis data (MeOH; λ_{max} , nm): 270, 330, 445.

X-ray crystallography. X-ray diffraction was carried out at a Bruker APEX II CCD area diffractometer equipped with Mo K_{α} radiation ($\lambda = 0.71073$ Å). The collected data were reduced with SAINT [18], and multi-scan absorption correction was performed using SADABS [19]. The structures of the complexes were solved by direct method, and refined against F^2 by fullmatrix least-squares method using SHELXTL [20]. All of the non-hydrogen atoms were refined anisotropically. The methanol hydrogen atoms were located from electronic density maps and refined isotropically. 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 compounds are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

The supplementary crystallographic data for I and II have been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1566491 and 1566492, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.ac.uk/conts/retrieving.html).

Catalytic oxidation experiment. Catalytic experiment was carried out in a 50 mL glass round-bottom flask fitted with a reflux condenser and placed in an oil bath at prearranged temperature under continuous stirring. The catalytic oxidation experiment was carried out as follows: molybdenum(VI) complex (0.032 mmol) was 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 (retention times in GC).

2018

No 9

Table 1. Crystallographic and refinement data for complexes I and II

Doromotor	Value		
Falameter	I	П	
Formula weight	462.69	442.27	
Crystal shape/color	Block/yellow	Block/yellow	
<i>Т</i> , К	298(2)	298(2)	
Crystal dimensions, mm	$0.26 \times 0.23 \times 0.20$	$0.31\times0.27\times0.23$	
Crystal system	Triclinic	Monoclinic	
Space group	$P\overline{1}$	$P2_1/n$	
<i>a</i> , Å	8.0750(5)	11.680(1)	
b, Å	10.5223(7)	10.496(2)	
c, Å	10.8110(7)	14.879(2)	
α, deg	96.975(2)	90	
β, deg	97.909(2)	98.862(2)	
γ, deg	104.497(2)	90	
V, Å ³	869.2(1)	1802.2(4)	
Ζ	2	4	
ρ_{calcd} , g cm ⁻³	1.768	1.630	
$\mu(MoK_{\alpha}), mm^{-1}$	0.945	0.764	
<i>F</i> (000)	464	896	
Measured reflections	8275	15338	
Unique reflections	3211	3326	
Observed reflections $(I \ge 2\sigma(I))$	2755	3029	
Min. and max. transmission	0.7913 and 0.8335	0.7977 and 0.8439	
Parameters	240	240	
Restraints	1	1	
Goodness of fit on F^2	1.089	1.111	
$R_1, wR_2 \ (I \ge 2\sigma(I)^*$	0.0323, 0.0620	0.0270, 0.0675	
R_1 , wR_2 (all data)*	0.0439, 0.0657	0.0308, 0.0699	

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

RESULTS AND DISCUSSION

The hydrazone compounds H_2L^1 and H_2L^2 were readily prepared by the condensation reaction of a 1 : 1 molar ratio of 2-hydroxy-4-methoxybenzohydrazide with 2-chlorobenzohydrazide and 3-methylbenzohydrazide, respectively, in methanol. Complexes I and II were prepared by the reaction of the hydrazone compounds with MoO₂(Acac)₂ in methanol, followed by recrystallization. Elemental analyses of the complexes are in accordance with the molecular structures proposed by the X-ray analysis.

In the spectra of the hydrazone compounds and the complexes, the weak and broad bands centered at about 3440 cm^{-1} are assigned to the vibration of O–H bonds. The weak and sharp bands located at about 3330 cm^{-1} of the hydrazone compounds are assigned

to the vibration of N–H bonds. The position of the bands demonstrates that the N-H hydrazone protons are engaged in hydrogen bonds. The intense bands at 1653 cm⁻¹ of the hydrazone compounds are generated by v(C=O) vibrations, whereas the bands at about 1600 cm⁻¹ by the v(C=N) ones. The non-observation of the v(C=O) bands, that present in the spectra of the hydrazone compounds, indicates the enolization of the amide functionality upon coordination to the Mocenter. Instead strong bands at 1613 cm⁻¹ for the complexes are observed, which can be attributed to the asymmetric stretching vibration of the conjugated CH=N-N=C-O groups, characteristic for the coordination of the enolate form of the compounds. The medium v(Mo=O) bands at about 950 and 850 cm^{-1} could be clearly identified for both complexes [21].

Bond	d, Å	Bond	<i>d</i> , Å
	·	I	
Mo(1)–O(1)	1.933(2)	Mo(1)-O(2)	2.010(2)
Mo(1)–O(4)	2.348(2)	Mo(1)-O(5)	1.694(2)
Mo(1)-O(6)	1.691(2)	Mo(1)-N(1)	2.234(2)
	1	II	I
Mo(1)-O(1)	1.906(2)	Mo(1)-O(2)	1.975(2)
Mo(1)-O(4)	2.323(2)	Mo(1)-O(5)	1.688(2)
Mo(1)–O(6)	1.714(2)	Mo(1)-N(1)	2.229(2)
Angle	ω, deg	Angle	ω, deg
		Ĭ	
D(6)Mo(1)O(5)	105.84(11)	O(6)Mo(1)O(1)	98.71(10)
D(5)Mo(1)O(1)	102.33(9)	O(6)Mo(1)O(2)	96.94(10)
D(5)Mo(1)O(2)	98.57(9)	O(1)Mo(1)O(2)	149.27(9)
D(6)Mo(1)N(1)	96.67(10)	O(5)Mo(1)N(1)	156.34(10)
D(1)Mo(1)N(1)	80.95(8)	O(2)Mo(1)N(1)	71.07(8)
D(6)Mo(1)O(4)	171.64(9)	O(5)Mo(1)O(4)	82.02(9)
D(1)Mo(1)O(4)	82.08(9)	O(2)Mo(1)O(4)	78.77(8)
N(1)Mo(1)O(4)	75.19(8)		
	1	II	•
D(5)Mo(1)O(6)	105.21(10)	O(5)Mo(1)O(1)	99.64(10)
D(6)Mo(1)O(1)	103.37(8)	O(5)Mo(1)O(2)	98.53(9)
D(6)Mo(1)O(2)	96.44(8)	O(1)Mo(1)O(2)	148.44(7)
D(5)Mo(1)N(1)	94.92(8)	O(6)Mo(1)N(1)	158.15(8)
D(1)Mo(1)N(1)	81.08(7)	O(2)Mo(1)N(1)	71.81(7)
D(5)Mo(1)O(4)	170.95(8)	O(6)Mo(1)O(4)	83.80(8)

O(2)Mo(1)O(4)

No. 9

2018

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In the electronic spectra of the complexes, the lowest energy transition bands are observed at 450 nm for I and 445 nm for II, which are attributed to LMCT transition as charge transfer from *p*-orbital on the lone-pair of ligands' oxygen atoms to the empty d-orbital of the vanadium atoms. The other strong bands in the range of 320-340 nm in the spectra of both complexes are similar to the absorption bands in the spectra of the corresponding hydrazone compounds, so they are attributed to the intra-ligand $\pi \rightarrow$ π^* absorption peak of the ligands. The other mainly LMCT and to some extent $\pi \to \pi^*$ bands appear at 270 nm for both I and II.

O(1)Mo(1)O(4)

N(1)Mo(1)O(4)

Molecular structures of complexes I and II are shown in Fig. 1. The coordination geometry around the Mo atoms can be described as distorted octahedral with the tridentate hydrazone ligand coordinated in a meridional fashion, forming five- and six-membered

RUSSIAN JOURNAL OF COORDINATION CHEMISTRY

chelate rings with bite angles of $71.07(8)^{\circ}$ (I) and $71.81(7)^{\circ}$ (II) (N(1)V(1)O(2)), and $80.95(8)^{\circ}$ (I) and $81.08(7)^{\circ}$ (II) (N(1)V(1)O(1)), respectively, typical for this type of ligand systems [22]. Each chelating hydrazone ligand lies in a plane with one hydroxylato ligand which lies trans to the hydrazone imino N atom. One methanol O atom trans to one of the oxo groups completes the distorted octahedral coordination sphere at a rather elongated distance of about 2.3 Å due to the trans influence of the oxo group. As expected, the hydrazone compounds coordinate in their doubly deprotonated enolate form which is consistent with the observed O(2)-C(8) and N(2)-C(8) bond lengths of 1.308(3) and 1.307(4) Å in I, and 1.323(3) and 1.290(3) Å in II, respectively. This agrees with reported molybdenum or vanadium complexes containing the enolate form of this ligand type [23, 24]. In the crystal packing structure of complex I, hydrazone

79.32(8)

78.68(8)

76.04(7)



Fig. 1. Perspective views of complexes I (a) and II (b) with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

molecules are linked by methanol molecules through intermolecular hydrogen bonds of O–H···N (Table 3), leading to the formation of dimers (Fig. 2a). In the crystal packing structure of complex II, hydrazone molecules are linked together through intermolecular hydrogen bonds of $O-H\cdots O$ (Table 3), leading to the formation of 1D chains along the *b* axis (Fig. 2b).

1-Butene, 1-pentene, 4-chloro-1-butene, phenylene 4-methylphenylene, 3-methylphenylene, 2-methylphenylene, 4-chlorophenylene, 3-chlorophenylene,

Table 3. Geometric parameters of hydrogen bonds for complexes I and II*

	Distance, Å			
D-H…A	D-H	H…A	D···A	$-$ Angle D $-$ H \cdots A, deg
		Ι		
$O(4) - H(4) - N(2)^{i}$	0.85(1)	1.93(1)	2.769(3)	170(4)
		II	1	I
O(4)-H(4)O(6) ⁱⁱ	0.85(1)	1.92(1)	2.748(3)	178(3)
* Symmetry codes: $i_2 - x$	$-v \ 1 - z^{-ii} \ 1/2 - x \ 1/2 + z^{-ii}$	$v_{1} \frac{1}{2} - \tau_{1}$		

RUSSIAN JOURNAL OF COORDINATION CHEMISTRY Vol. 44 No. 9 2018

Substrate	D. 1	Conversion, %**		
Substrate	Product	I	П	
		90.6	85.4	
		93.8	87.1	
Cl		95.2	90.5	
		97.2	95.1	
		98.7	99.2	
		96.3	98.5	
		97.1	99.0	
Cl		100	100	
Cl	CI	100	100	
Cl		100	100	

Table 4. Details of the catalytic oxidation of olefins catalyzed by complexes*

* The molar ratio of catalyst : substrate : TBHP is 1 : 300 : 1000. The reaction was performed in mixture of $CH_3OH-CH_2Cl_2$ (v : v = 3 : 1). ** The GC conversion (%) was measured relative to the starting substrate after 1 h.





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and 2-chlorophenylene were used as the substrates. The catalytic oxidation results are given in Table 4. The selectivities for both aliphatic and aromatic substrates are 100%. High epoxide yields (85-95%) are obtained for aliphatic substrates. While for aromatic substrates, the epoxide yields (96-100%) are higher than aliphatic substrates. In general, the methyl-substituted substrates gave lower epoxide yields when compared to the chloro-substituted ones. And, as for the catalysts, the electronic-withdrawing effect of the Cl group is better than the electronic-donating effect of the Me group for the catalytic property.

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