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Synthesis, Crystal Structures, and Catalytic Property of Dioxomolybdenum(VI) Complexes with Hydrazone Ligands Derived from 3,5-Di-*tert*-Butylsalicylaldehyde[1]

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Abstract—Two new dioxomolybdenum(VI) complexes, $[MoO_2L^1(MeOH)]$ (**I**) and $[MoO_2L^2]$ (**II**), where L^1 and L^2 are the anionic forms of *N'*-(2-hydroxy-3,5-di-*tert*-butylbenzylidene)-4-methoxybenzohydrazide and 2-amino-*N'*-(2-hydroxy-3,5-di-*tert*-butylbenzylidene)benzohydrazide, respectively, have been synthesized and characterized by elemental analysis, FT-IR spectra, and single crystal X-ray determination (CF files CCDC nos. 1448089 (**I**), 1487063 (**II**)). The crystal of **I** is monoclinic: space group $P2_1/n$, $a = 7.353(1)$, $b = 24.758(3)$, $c = 13.891(2)$ Å, $\beta = 101.013(2)°$, $V = 2482.3(6)$ Å^3, $Z = 4$, $R_1 = 0.0848$, $wR_2 = 0.2050$. The crystal of **II** is monoclinic: space group $P2_1/c$, $a = 6.752(1)$, $b = 16.947(1)$, $c = 19.510(1)$ Å, $\beta = 96.891(2)°$, $V = 2216.5(4)$ Å^3, $Z = 4$, $R_1 = 0.0670$, $wR_2 = 0.1638$. The Mo atom in complex **I** is in octahedral coordination, with three donor atoms of the hydrazone ligand, two oxo groups, and one methanol O atom. The Mo atom in complex **II** is in square pyramidal coordination, with three donor atoms of the hydrazone ligand, and two oxo groups. The complexes have interesting catalytic properties for sulfoxidation reactions.

Keywords: dioxomolybdenum, hydrazone, crystal structure, sulfoxidation

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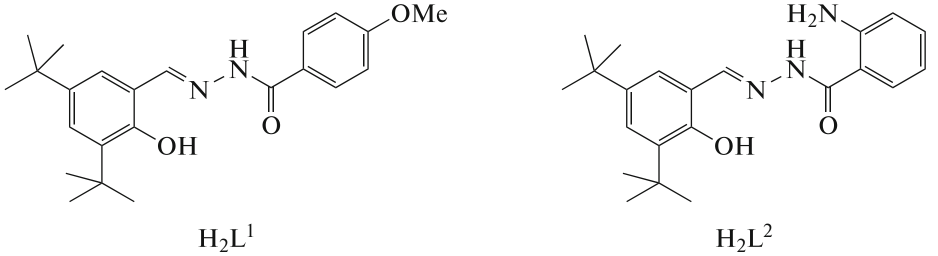
INTRODUCTION

Molybdenum complexes with multi-dentate ligands have received remarkable attention in recent years for their catalytic properties [1–4] and molecular structures [5–7]. Salicylaldehyde and its derivatives have been widely used as ligands for the preparation of metal complexes with various applications [8–10]. A large number of molybdenum complexes with Schiff bases have been reported [11–15]. Some of the dioxomolybdenum complexes have shown oxygen atom transfer properties as they were found to oxidize thiols, hydrazine, polyketones, and tertiary phosphines [16–18]. We report in this paper the synthesis, structures, and catalytic property of two new dioxomolybdenum(VI) complexes, $[MoO_2L^1(MeOH)]$ (**I**) and $[MoO_2L^2]$ (**II**), where L^1 and L^2 are the anionic forms of *N'*-(2-hydroxy-3,5-di-*tert*-butylbenzylidene)-4-methoxybenzohydrazide and 2-amino-*N'*-(2-hydroxy-3,5-di-*tert*-butylbenzylidene)benzohydrazide, respectively (Scheme 1).



Scheme 1.

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EXPERIMENTAL

Materials and methods. 3,5-Di-*tert*-butylsalicylaldehyde, 4-methoxybenzohydrazide, and 2-aminobenzohydrazide were purchased from Fluka. Other reagents and solvents were analytical grade and used without further purification. The hydrazones were prepared according to the literature method [19, 20]. Elemental (C, H, and N) analyses were made on a Perkin-Elmer Model 240B automatic analyzer. IR spectra were recorded on an IR-408 Shimadzu 568 spectrophotometer.

Synthesis of complex I. $MoO_2(Acac)_2$ (0.1 mmol, 33.5 mg) in methanol (10 mL) was added with stirring to H_2L^1 (0.1 mmol, 38.2 mg) in methanol (10 mL). The mixture was stirred at refluxed for 30 min to give a yellow solution. The solution was left still at room temperature in air to give yellow block-shaped single crystals, which were collected by filtration and dried in vacuum containing anhydrous $CaCl_2$. The yield was 33 mg (61%).

For $C_{24}H_{32}N_2O_6Mo$

anal. calcd., %:	C, 53.3;	H, 6.0;	N, 5.2.
Found, %:	C, 53.5;	H, 5.8;	N, 5.1.

Synthesis of complex II. This complex was synthesized from the reaction of $MoO_2(Acac)_2$ and H_2L^2 (0.1 mmol, 36.7 mg) in a procedure analogous to that employed for complex **I**. The yield is 27 mg (55%).

For $C_{24}H_{32}N_2O_6Mo$

anal. calcd., %:	C, 53.6;	H, 5.5;	N, 8.5.
Found, %:	C, 53.4;	H, 5.6;	N, 8.7.

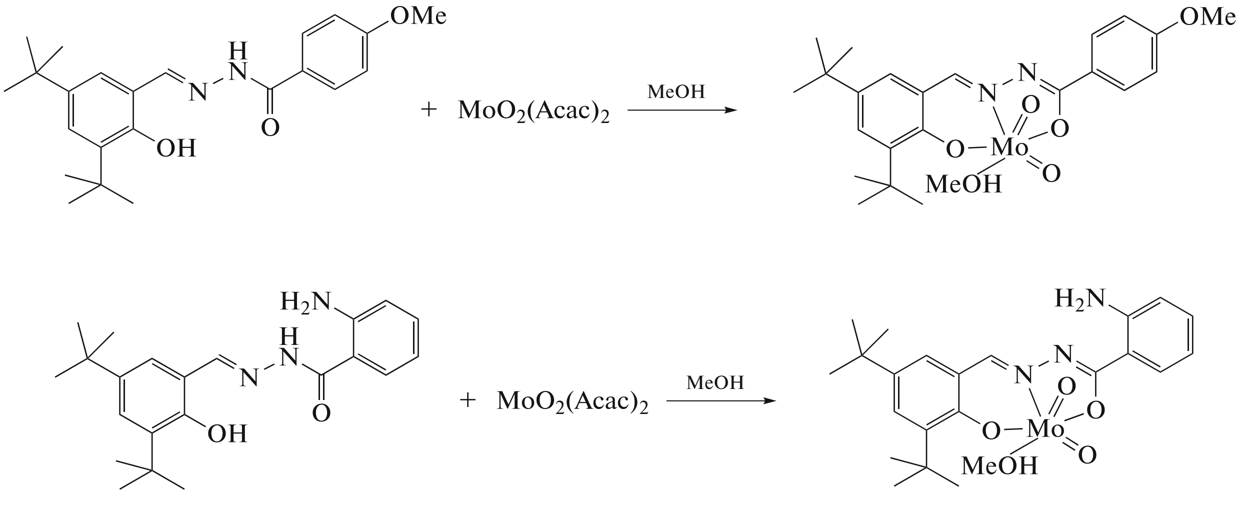
X-ray diffraction. Data were collected from selected crystals mounted on glass fibers. The data for the complexes were processed with SAINT [21] and corrected for absorption using SADABS [22]. Multiscan absorption corrections were applied with ψ scans [23]. The structures of the complexes were solved by direct method using SHELXS-97 program and refined by full-matrix least-squares techniques on F^2 using anisotropic displacement parameters [24]. All non-hydrogen atoms were refined anisotropically. The methanol H atom of complex **I** was located from an electronic map. The remaining hydrogen atoms were placed at the calculated positions. Crystallographic data for the complexes are listed in Table 1. Selected bond lengths and angles are given in Table 2.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1448089 (**I**) and 1487063 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Catalytic oxidation. The dioxomolybdenum complexes (0.001 M) and phenyl methyl sulfide (0.1 M) were dissolved at room temperature in a mixture of CH_2Cl_2 and CH_3OH (6 : 4) together with 1,3,5-trimethoxybenzene (TMB) (0.1 M) as internal standard. The resulting solution was cooled to 283 K and H_2O_2 (35% w/w) added dropwise (0.125 M). An aliquot of the reaction solution (2.0 mL) was quenched with 5 mL of a stock solution of Na_2SO_3 (0.1 M) and extracted with dichloromethane (three times 4 mL). From the collected organic phases the solvent was removed under reduced pressure to complete dryness and the residue redissolved in deuterated chloroform (0.6 mL) and analyzed by ^1H NMR to determine the yield with reference to the internal standard TMB.

RESULTS AND DISCUSSION

Reaction of the hydrazones with $MoO_2(Acac)_2$ afforded complexes **I** and **II** according to Scheme 2:



Scheme 2.

Table 1. Crystallographic data and structure refinement parameters for **I–II**

Parameter	Value	
	I	**II**
Molecular weight	540.5	493.4
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	7.353(1)	6.752(1)
b, Å	24.758(3)	16.947(1)
c, Å	13.891(2)	19.510(1)
β, deg	101.013(2)	96.891(2)
V, Å^3	2482.3(6)	2216.5(4)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.446	1.479
Crystal size, mm	0.20 × 0.18 × 0.18	0.27 × 0.23 × 0.23
μ, mm^{-1}	0.569	0.624
Radiation (λ, Å)	MoK_α (0.71073)	
T_{min}/T_{max}	0.8947/0.9045	0.8496/0.8697
Limiting indices (h, k, l)	$-8 \le h \le 8$, $-29 \le k \le 29$, $-14 \le l \le 16$	$-8 \le h \le 8$, $-19 \le k \le 20$, $-23 \le l \le 18$
θ Range for data collection, deg	2.93–25.50	1.60–25.50
Reflections measured	20337	11193
Unique reflections (R_{int})	4198 (0.0557)	4031 (0.0304)
Observed reflections ($I > 2\sigma(I)$)	3266	3575
Parameters/restraints	309/1	277/0
Goodness of fit on F^2	1.020	1.102
R_1, wR_2 ($I \ge 2\sigma(I)$)*	0.0848, 0.2050	0.0670, 0.1638
R_1, wR_2 (all data)*	0.1056, 0.2231	0.0732, 0.1679

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

The complexes are soluble in DMF, DMSO, methanol, ethanol, and acetonitrile. We have attempted to grow diffraction quality crystals from various solvents. However, well-shaped single crystals suitable for X-ray diffraction were finally obtained from methanol.

The molecular structure of complex **I** is shown in Fig. 1a. The coordination geometry around Mo atom in the complex is octahedrally distorted. The hydrazone ligand L^1 coordinates through phenolic O, imino N, and enolic O atoms to the MoO$_2$ moiety, forming a five- and a sixmembered chelate rings with Mo atom. The sixth coordination is weakly coordinated by a methanol O atom. Atoms O(1), O(2), N(1), and O(4) located at the equatorial plane show a high degree of planarity, with mean deviation from the plane of 0.062(3) Å. The Mo(1) atom deviates from the least-squares plane defined by the four equatorial donor atoms by 0.348(1) Å in the direction of the axial atom O(5). The angular distortion in the octahedral coordination comes from the bites O(2)–Mo(1)–N(1) taken by the hydrazone ligand. The dihedral angle between the benzene rings is 7.1(5)°. In the crystal of the complex, molecules are linked through intermolecular

Table 2. Selected bond lengths (Å) and angles (deg) for the complexes

Bond	*d*, Å	Bond	*d*, Å
		I	
Mo(1)–O(1)	1.922(4)	Mo(1)–O(2)	2.021(4)
Mo(1)–O(4)	1.696(4)	Mo(1)–O(5)	1.705(5)
Mo(1)–N(1)	2.245(5)	Mo(1)–O(3)	2.406(4)
		II	
Mo(1)–O(1)	1.918(4)	Mo(1)–O(2)	2.012(4)
Mo(1)–O(3)	1.747(5)	Mo(1)–O(4)	1.707(5)
Mo(1)–N(1)	2.216(5)		
Angle	ω, deg	Angle	ω, deg
		I	
O(4)Mo(1)O(5)	106.3(2)	O(4)Mo(1)O(1)	103.5(2)
O(5)Mo(1)O(1)	98.5(2)	O(4)Mo(1)O(2)	97.37(18)
O(5)Mo(1)O(2)	97.1(2)	O(1)Mo(1)O(2)	149.21(17)
O(4)Mo(1)N(1)	154.2(2)	O(5)Mo(1)N(1)	98.1(2)
O(1)Mo(1)N(1)	80.27(16)	O(2)Mo(1)N(1)	71.30(17)
O(4)Mo(1)O(3)	81.47(19)	O(5)Mo(1)O(3)	171.5(2)
O(1)Mo(1)O(3)	82.70(18)	O(2)Mo(1)O(3)	78.25(18)
N(1)Mo(1)O(3)	73.68(16)		
		II	
O(4)Mo(1)O(3)	108.9(3)	O(4)Mo(1)O(1)	102.4(2)
O(3)Mo(1)O(1)	99.0(2)	O(4)Mo(1)O(2)	96.2(2)
O(3)Mo(1)O(2)	96.6(2)	O(1)Mo(1)O(2)	150.20(18)
O(4)Mo(1)N(1)	153.1(2)	O(3)Mo(1)N(1)	96.7(2)
O(1)Mo(1)N(1)	81.10(17)	O(2)Mo(1)N(1)	71.99(17)

O(3)–H(3)···N(2)^{i} hydrogen bonds (O(3)–H(3) 0.90(1), H(3)···N(2)^{i} 1.92(2), O(3)···N(2)^{i} 2.821(6) Å, O(3)–H(3)···N(2)^{i} 173(8)°; ^{i} $1 - x, 2 - y, 1 - z$) to form dimers (Fig. 2a).

The molecular structure of complex **II** is shown in Fig. 1b. The coordination geometry around Mo atom in the complex is square pyramidal distorted. The hydrazone ligand L^2 coordinates through phenolic O, imino N, and enolic O atoms to the MoO_2 moiety, forming a five- and a sixmembered chelate rings with Mo atom. Atoms O(1), O(2), N(1), and O(4) located at the basal plane show an approximate degree of planarity, with mean deviation from the plane of 0.064(3) Å. The Mo(1) atom deviates from the least-squares plane defined by the four basal donor atoms by 0.365(1) Å in the direction of the apical atom O(3). The angular distortion in the square pyramidal coordination comes from the bites O(2)–Mo(1)–N(1) taken by the hydrazone ligand. The dihedral angle between the benzene rings is 12.6(6)°. In the crystal of the complex, molecules are linked through intermolecular N(3)–H(3*A*)···O(3)^{ii} hydrogen bonds (N(3)–H(3*A*) 0.86, H(3*A*)···O(3)^{ii} 2.74, N(3)···O(3)^{ii} 3.000(8) Å, N(3)–H(3*A*)···O(3)^{ii} 98.9(6)°; ^{ii} $-x, 2 - y, -z$) to form dimers (Fig. 2b).

In both complexes, the coordinate bond lengths are comparable to each other, and also comparable to those observed in similar complexes [25, 26].

In the infrared spectra of the free hydrazones, there showed stretching bands attributed to C=O, C=N, C–OH and NH at about 1653, 1635, 1185 and 3250–3290 cm^{-1}, respectively. In the spectra of the com-

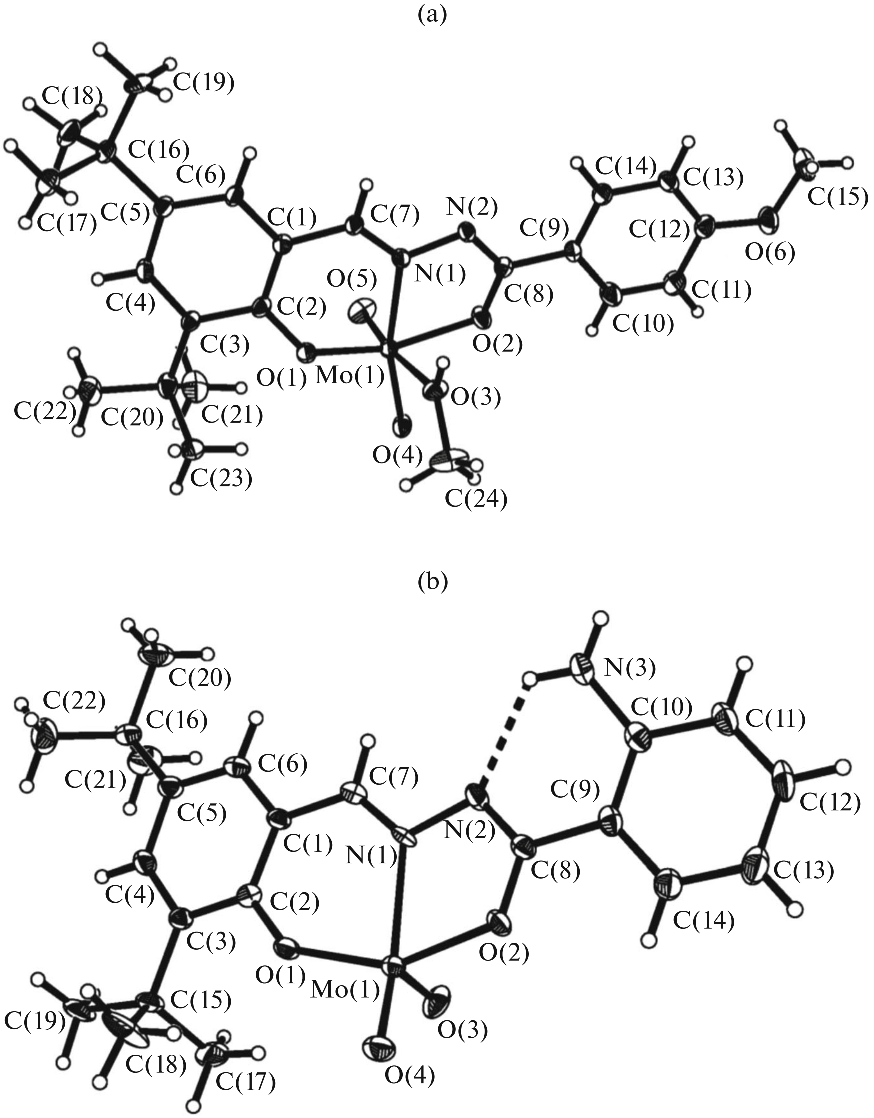
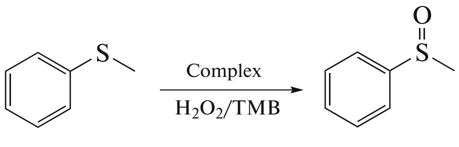


Fig. 1. Molecular structure of complexes **I** (a) and **II** (b) at 30% probability displacement.

plexes, there showed two prominent bands at 955 and 887 cm^{-1} for complex **I**, and 950 and 862 cm^{-1} for complex **II**, which attributed to dioxomolybdenum groups [27]. The bands due to ν(C=O) are absent in both complexes. This suggests occurrence of keto-imino tautomerization of the ligands during complexation. The ν(NH) of complex II is observed at 3336 cm^{-1}. The typical C=N absorptions of complexes **I** and **II** are observed at 1615 cm^{-1} for **I** and 1617 cm^{-1} for **II** [28]. The weak bands in the low wave numbers are assigned to the Mo–O and Mo–N vibrations.

Catalytic oxidation test of the complexes on the oxidation of sulfides under homogeneous conditions in solution using methyl phenyl sulfide (thioanisol) as substrate is shown as Scheme 3:



As oxidant hydrogen peroxide was used in a slight excess of 1.25 equivalents based on the sulfide substrate. Reactions were run with 1 mol % of catalyst based on the substrate at a temperature of 10°C. NMR technique has been used to monitor the formation of the sulfoxides with TMB as internal standard to determine the yields. The reaction was started by the addition of hydrogen peroxide. A control reaction under the same condition without any complex present leads to less than 1% sulfide conversion within 4 h. In the presence of the complexes conversions of 91% for complex **I** and 75% for complex **II** of sulfide to the cor-

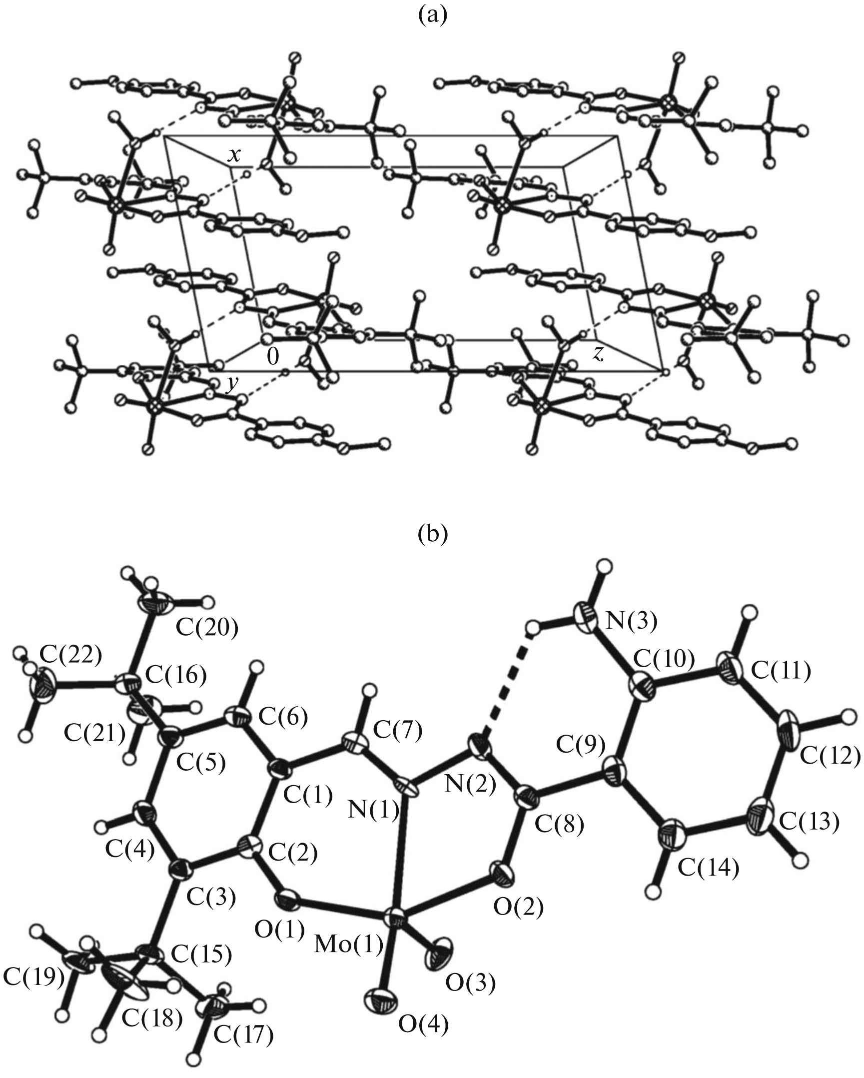


Fig. 2. The hydrogen bonds linked dimeric structure of complexes **I** (a) and **II** (b).

responding sulfoxide within 60 min reaction time were observed. After about 2 h in all cases the conversions of total amount of sulfide were completed. Under the given conditions no over oxidation to the sulfone could be detected. Both complexes show catalytic properties for the sulfoxidation.

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