Two Mononuclear Molybdenum(VI) Oxo Complexes with Tridentate Hydrazone Ligands: Synthesis and Crystal Structures¹

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Abstract—Reaction of $[MoO_2(Acac)_2]$ (Acac = acetylacetonate) with two similar hydrazone ligands in methanol yielded two mononuclear molybdenum(VI) oxocomplexes with general formula $[MoO_2(L)(CH_3OH)]$, where $L = L^1 = (4$ -nitrophenoxy)acetic acid $[1-(3-ethoxy-2-hydroxyphenyl)meth-ylidene]hydrazide (H_2L^1) and <math>L = L^2 = (4$ -nitrophenoxy)acetic acid $[1-(5-bromo-2-hydroxyphenyl)meth-ylidene]hydrazide (H_2L^2)$. Crystal and molecular structures of the complexes were determined by single crystal X-ray diffraction method. All investigated compounds were further characterized by elemental analysis and FT-IR spectra. Single crystal X-ray structural studies indicate that the hydrazone ligands coordinate to the MoO_2 cores through enolate oxygen, phenolate oxygen, and azomethine nitrogen. The Mo atoms in both complexes are in octahedral coordination.

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INTRODUCTION

The coordination chemistry of molybdenum(VI) has attracted considerable attention due to its recently discovered biochemical significance [1-3] as well as for the efficient catalytic properties in several organic synthesis procedures [4-7]. In recent years, a great number of molybdenum(VI) complexes with Schiff bases derived from salicylaldehyde and primary amines have been reported [8-10]. Hydrazones, bearing -C(O)-NH-N=CH- groups, are a kind of special Schiff bases, which are of particular interest in co-

ordination chemistry and biological applications. However, molybdenum(VI) complexes derived from hydrazone ligands have seldom been reported. In the present work, we report synthesis and structures of two dioxomolybdenum(VI) complexes with the general formula [MoO₂L(CH₃OH)], where $L = L^1 = (4$ -nitrophenoxy)acetic acid [1-(3-ethoxy-2-hydroxyphenyl)methylidene]hydrazide (H₂L¹) and $L = L^2 =$ (4-nitrophenoxy)acetic acid [1-(5-bromo-2-hydroxyphenyl)methylidene]hydrazide (H₂L²).



EXPERIMENTAL

Materials and measurements. Commercially available 3-ethoxysalicylaldehyde, 5-bromosalicylaldehyde, and (4-nitrophenoxy)acetic acid hydrazide were purchased from Aldrich and used without further purification. Other solvents and reagents were made in China and used as received. C, H, and N elemental analyses were performed with a PerkinElmer elemental analyser. The infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm⁻¹ region.

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Synthesis of H_2L^1 . 3-Ethoxysalicylaldehyde (1.0 mmol, 0.166 g) and (4-nitrophenoxy)acetic acid hydrazide (1.0 mmol, 0.211 g) were dissolved in methanol (30 mL) with stirring. The mixture was stirred for about 30 min at room temperature to give a yellow solution. The solvent was evaporated to give yellow crystalline product of H_2L^1 . The yield was 91%.

For C₁₇H₁₇N₃O₆

anal. calcd., %:	C, 56.82;	Н, 4.77;	N, 11.69
Found, %:	C, 56.65;	H, 4.68;	N, 11.57

Synthesis of H_2L^2 . 5-Bromosalicylaldehyde (1.0 mmol, 0.201 g) and (4-nitrophenoxy)acetic acid hydrazide (1.0 mmol, 0.211 g) were dissolved in methanol (30 mL) with stirring. The mixture was stirred for about 30 min at room temperature to give a yellow solution. The solvent was evaporated to give yellow crystalline product of H_2L^2 . The yield was 94%.

For C15H12N3O5Br

anal. calcd., %:	C, 45.71;	Н, 3.07;	N, 10.66.
Found, %:	C, 45.59;	Н, 3.16;	N, 10.53.

Synthesis of [MoO₂(L¹)(CH₃OH)] (I). A methanolic solution (10 mL) of [MoO₂(Acac)₂] (0.1 mmol, 32.6 mg) was added to a methanolic solution (10 mL) of H₂L¹ (0.1 mmol, 35.9 mg) with stirring. The mixture was stirred for 20 min to give an orange solution. The resulting solution was allowed to stand in air for a few days. Orange block-shaped crystals suitable for X-ray single crystal analysis were formed at the bottom of the vessel. The isolated product was washed three times with cold methanol and dried in a vacuum over anhydrous CaCl₂. The yield was 62%.

For $C_{18}H_{19}N_3O_9Mo$ anal. calcd., %: C, 41.79; H, 3.70; N, 8.12. Found, %: C, 41.95; H, 3.77; N, 8.20.

Synthesis of [MoO₂(L^2)(CH₃OH)] (II). A methanolic solution (10 mL) of [MoO₂(Acac)₂] (0.1 mmol, 32.6 mg) was added to a methanolic solution (10 mL) of H₂L² (0.1 mmol, 39.4 mg) with stirring. The mixture was stirred for 20 min to give an orange solution. The resulting solution was allowed to stand in air for a few days. Orange block-shaped crystals suitable for X-ray single crystal analysis were formed at the bottom of the vessel. The isolated product was washed three

times with cold methanol and dried in a vacuum over anhydrous $CaCl_2$. The yield was 73%.

For C₁₆H₁₄N₃O₈BrMo

anal. calcd., %:	C, 34.80;	Н, 2.56;	N, 7.61.
Found, %:	C, 34.67;	Н, 2.50;	N, 7.73.

X-ray structure determination. Diffraction intensities for the complexes were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer with Mo K_{α} radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program [11], and multi-scan absorption corrections were performed using the SADABS program [12]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL [13]. All non-hydrogen atoms were refined anisotropically. The methanol H atoms in the complexes were located in difference Fourier maps and refined isotropically with O-H distances restrained to 0.85(1) Å. All other H atoms were placed in idealized positions and constrained to ride on their parent atoms. The crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Supplementary material for structures I and II has deposited with the Cambridge Crystallographic Data Centre (nos. 897243 (I), 897244 (II); deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Replacement of two acetylacetonate ligands in $[MoO_2(Acac)_2]$ by hydrazone ligands resulted in the formation of mononuclear molybdenum(VI) oxocomplexes. In both complexes, the dinegative ligands are coordinated to the *cis*-MoO₂ cores via the phenolate-oxygen, imino-nitrogen, and enolate-oxygen atoms. The sixth coordination site is occupied by the oxygen atom from the methanol solvent. The complexes are soluble in methanol, ethanol, and acetonitrile. The molar conductance of the complexes I and II at the concentrations of 10^{-4} mol/L are 8 and $11 \Omega^{-1}$ cm² mol⁻¹, respectively, indicating they are non-electrolytes.

The molecular structures and the atom numbering schemes of the complexes I and II are shown in Fig. 1. The coordination geometry around each Mo atom is highly distorted octahedral. In each complex, the hydrazone ligand behaves in a tridentate manner in which the phenolate O, imino N, and enolate O atoms occupy a meridonial plane. The coordination geometry around molybdenum can be described as distorted octahedral in the complexes. The dianionic hydrazone ligands act in planar tridentate manner, forming one

	Val	ue	Bond	d, Å	Bond	d, Å
Parameter	I	II			I	
M	517.3	552.2	Mo(1)–O(1)	1.908(3)	Mo(1)-O(6)	2.026(3
Crystal color, habit	Orange, block	Orange, block	Mo(1)–O(7)	1.695(3)	Mo(1)-O(8)	1.697(3
Crystal size mm	$0.17 \times 0.15 \times 0.15$	$0.32 \times 0.30 \times 0.27$	Mo(1)-N(1)	2.242(3)	Mo(1)-O(9)	2.337(3
	T.1.1.	Trialiais	II			
Lrystal system	Iriclinic	Triclinic	Mo(1)–O(1)	1.902(4)	Mo(1)-O(2)	2.021(3
Space group	$P\overline{1}$	$P\overline{1}$	Mo(1)–O(6)	1.676(4)	Mo(1)-O(7)	2.335(4
Unit cell parameters:			Mo(1)-N(1)	2.235(4)	Mo(1)–O(8)	1.699(3
a, Å	7.4919(17)	7.5508(12)	Angle	ω, deg	Angle	ω, deg
b, Å	8.423(2)	8.458(2)			 I	
<i>c</i> , Å	18.343(2)	16.349(3)	O(7)Mo(1)O(8)	105.33(16)	- 0(7)Mo(1)O(1)	100.12(1
x, deg	80.482(2)	91.254(2)	O(8)Mo(1)O(1)	104.60(14)	O(7)Mo(1)O(6)	94.51(1
3, deg	81.975(3)	90.887(2)	O(8)Mo(1)O(6)	95.71(13)	O(1)Mo(1)O(6)	150.67(1
y, deg	72.458(2)	107.660(2)	O(7)Mo(1)N(1)	96.65(14)	O(8)Mo(1)N(1)	155.51(1
<i>V</i> , Å ³	1083.5(4)	994.5(3)	O(1)Mo(1)N(1)	81.56(12)	O(6)Mo(1)N(1)	71.54(1
Ζ	2	2	O(7)Mo(1)O(9)	170.85(13)	O(8)Mo(1)O(9)	82.26(1
$D_{calcd}, g cm^{-3}$	1.586	1.844	O(1)Mo(1)O(9)	82.53(14)	O(6)Mo(1)O(9)	79.46(1
μ , mm ⁻¹	0.659	2.717	N(1)Mo(1)O(9)	74.98(12)		
F(000)	524	544]	I II	
Number of unique data	4576	4232	O(6)Mo(1)O(8)	104.90(17)	O(6)Mo(1)O(1)	100.10(1
Number of observed	3856	2676	O(8)Mo(1)O(1)	105.10(15)	O(6)Mo(1)O(2)	94.32(1
data, $I > 2\sigma(I)$			O(8)Mo(1)O(2)	95.15(15)	O(1)Mo(1)O(2)	151.02(1
Number of parameters	285	266	O(6)Mo(1)N(1)	97.08(16)	O(8)Mo(1)N(1)	155.31(1
$R_1, wR_2(I > 2\sigma(I))$	0.0504, 0.1274	0.0568, 0.0860	O(1)Mo(1)N(1)	81.51(15)	O(2)Mo(1)N(1)	71.80(1
R_1, wR_2 (all data)	0.0615, 0.1348	0.1058, 0.0982	O(6)Mo(1)O(7)	171.27(15)	O(8)Mo(1)O(7)	82.22(1
Goodness of fit on F^2	1.029	0.988	O(1)Mo(1)O(7)	82.56(15)	O(2)Mo(1)O(7)	79.84(1
$\Delta ho_{ m max} / \Delta ho_{ m min}$, $e { m \AA}^{-3}$	1.069/-1.206	0.554/-0.612	N(1)Mo(1)O(7)	75.00(13)		

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

Table 2. Selected bond distances (Å) and angles (deg) for complexes I and II



Fig. 1. ORTEP plot of the crystal structures of I (a) and II (b). Displacement ellipsoids of non-hydrogen atoms are drawn at the 30% probability level.

five- and one six-membered chelate rings involving the MoO_2 core. The hydrazone ligand in each of the complexes is bonded to the MoO_2 core in a planar fashion, coordinating through the phenolate O, imino N, and enolate O atoms and an oxogroup lying *trans* to the nitrogen donor. In each of the complexes, a methanol molecule completes the distorted octahedral coordination sphere which lies *trans* to the other oxogroup. The Mo–O(methanol) bonds are significantly longer than the other Mo–O bonds, indicating that the methanol molecules are weakly bonded to the MoO₂ core, and this position holds the possibility of functioning as a substrate binding site.

The atoms O(1), O(6), O(8), and N(1) in I and O(1), O(2), O(8), and N(1) in II show high degree of planarity from the equatorial planes, the Mo atoms are displaced by 0.324(1) Å (I) and 0.320(1) Å (II) toward the axial oxogroups. The Mo=O bonds in the complexes are almost equal within the standard deviations and are within previously reported ranges [14, 15]. The angular distortion in the octahedral environment around Mo comes from the five- and six-membered chelate rings taken by the hydrazone ligands. For the

same reason, the *trans* angles are significantly deviate from the ideal values of 180° . The hydrazone ligands in the complexes are approximately planar with the corresponding two benzene rings make dihedral angles of $1.3(3)^{\circ}$ for I and $4.8(4)^{\circ}$ for II.

In the crystal structures of both complexes (Fig. 2), adjacent two molecules are linked by methanol molecules through two intermolecular O–H···N hydrogen bonds (for I, O(9)–H(9) 0.85(1), H(9)···N(2) 1.99(2) Å, O(9)–H(9)···N(2) 171(7)°; for II, O(7)–H(7*A*) 0.85(1), H(7*A*)···N(2) 1.99(2) Å, O(7)–H(7*A*)···N(2) 166(6)°) to form dimers.

The hydrazone ligands showed stretching bands attributed to C=O, C=N, C-OH and NH at 1662, 1635, 1154 and 1232, and 3227 cm⁻¹ for H₂L¹ and at 1667, 1636, 1151 and 1235, and 3213 cm⁻¹ for H₂L², respectively. In addition, strong bands observed at 1612 cm⁻¹ for H₂L¹ and at 1615 cm⁻¹ for H₂L² are attributed to -C=N-N=C- groups. Both complexes exhibit two bands at ~903 and 941 cm⁻¹, assigned to symmetric and asymmetric vibrations respectively, of the *cis*-MoO₂ cores. The



Fig. 2. Molecular packing arrangement of I (a) and II (b) displayed in the unit cell. Hydrogen bonds are shown as dashed lines.

bands due to v(C=O) and v(NH) were absent in the complexes, but new C-O stretches appeared at

1257 cm⁻¹ for I and 1263 cm⁻¹ for II. This suggests occurrence of keto-imine tautomerization of the ligands during complexation. The v(C=N) absorption observed at 1635 and 1636 cm⁻¹ in the free hydrazone ligands shifted to 1611 cm⁻¹ for I and II upon coordination to Mo atoms. The weak peaks in the low wave numbers in the region 550– 850 cm⁻¹ may be attributed to Mo–O and Mo–N bonds in the complexes.

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