

TWO WATER-COORDINATED MONONUCLEAR MOLYBDENUM(VI) OXO COMPLEXES WITH SIMILAR TRIDENTATE HYDRAZONE LIGANDS: SYNTHESIS AND CRYSTAL STRUCTURES

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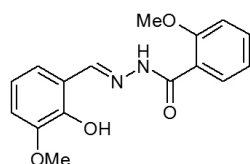
ABSTRACT

Reaction of $[\text{MoO}_2(\text{acac})_2]$ (where acac = acetylacetonate) with two similar hydrazone ligands in methanol yielded two water coordinated mononuclear molybdenum(VI) oxo complexes with general formula $[\text{MoO}_2\text{L}(\text{OH})_2]$, where $\text{L} = \text{L}^1 = N'-(2\text{-hydroxy-3-methoxybenzylidene})\text{-2-methoxybenzohydrazide}$ (H_2L^1), and $\text{L} = \text{L}^2 = N'-(3\text{-ethoxy-2-hydroxybenzylidene})\text{-2-methoxybenzohydrazide}$ (H_2L^2). Crystal and molecular structures of the complexes were determined by single crystal X-ray diffraction method. All of the 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.

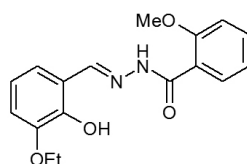
Keywords: molybdenum complex; hydrazone ligand; crystal structure; X-ray diffraction.

INTRODUCTION

The coordination chemistry of molybdenum(VI) has attracted considerable attention due to its recently discovered biochemical significance¹⁻³ 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 $-\text{C}(\text{O})-\text{NH}=\text{CH}-$ groups, are a kind of special Schiff bases, which are of particular interest in coordination chemistry and biological applications. However, molybdenum(VI) complexes derived from hydrazone ligands have seldom been reported. In the present work, we report the synthesis and structures of two dioxomolybdenum(VI) complexes with the general formula $[\text{MoO}_2\text{L}(\text{OH})_2]$, where $\text{L} = \text{L}^1 = N'-(2\text{-hydroxy-3-methoxybenzylidene})\text{-2-methoxybenzohydrazide}$ (H_2L^1), and $\text{L} = \text{L}^2 = N'-(3\text{-ethoxy-2-hydroxybenzylidene})\text{-2-methoxybenzohydrazide}$ (H_2L^2).



H_2L^1



H_2L^2

EXPERIMENTAL

Materials and measurements: Commercially available 3-methoxysalicylaldehyde, 3-ethoxysalicylaldehyde, and 2-methoxybenzohydrazide 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 Perkin-Elmer elemental analyser. The infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm^{-1} region.

Synthesis of H_2L^1 : 3-Methoxysalicylaldehyde (1.0 mmol, 0.152 g) and 2-methoxybenzohydrazide (1.0 mmol, 0.166 g) were dissolved in methanol (30 mL) with stirring. The mixture was stirred for about 30 min at room temperature to give a colorless solution. The solvent was evaporated to give colorless crystalline product of H_2L^1 . Yield, 87%. For $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4$: anal. calcd., %: C, 64.0; H, 5.4; N, 9.3. Found, %: C, 63.7; H, 5.4; N, 9.4.

Synthesis of H_2L^2 : 3-Ethoxysalicylaldehyde (1.0 mmol, 0.166 g) and 2-methoxybenzohydrazide (1.0 mmol, 0.166 g) were dissolved in methanol (30 mL) with stirring. The mixture was stirred for about 30 min at room

temperature to give a colorless solution. The solvent was evaporated to give colorless crystalline product of H_2L^2 . Yield, 92%. For $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_4$: anal. calcd., %: C, 65.0; H, 5.8; N, 8.9. Found, %: C, 64.8; H, 5.7; N, 8.9.

Synthesis of $[\text{MoO}_2\text{L}^1(\text{OH})_2]$ (1): A methanolic solution (10 mL) of $[\text{MoO}_2(\text{acac})_2]$ (0.1 mmol, 32.6 mg) was added to a methanolic solution (10 mL) of H_2L^1 (0.1 mmol, 30.0 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 . Yield, 45%. For $\text{C}_{16}\text{H}_{16}\text{MoN}_2\text{O}_7$: anal. calcd., %: C, 43.3; H, 3.6; N, 6.3. Found, %: C, 43.2; H, 3.7; N, 6.4.

Synthesis of $[\text{MoO}_2\text{L}^2(\text{OH})_2]$ (2): A methanolic solution (10 mL) of $[\text{MoO}_2(\text{acac})_2]$ (0.1 mmol, 32.6 mg) was added to a methanolic solution (10 mL) of H_2L^2 (0.1 mmol, 31.4 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 . Yield, 51%. For $\text{C}_{17}\text{H}_{18}\text{MoN}_2\text{O}_7$: anal. calcd., %: C, 44.6; H, 4.0; N, 6.1. Found, %: C, 44.8; H, 3.9; N, 6.0.

Data collection, structural determination and refinement: Diffraction intensities for the complexes were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer with MoK 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 of the non-hydrogen atoms were refined anisotropically. The water H atoms in the complexes were located in difference Fourier maps and refined isotropically, with O–H and H...H distances restrained to 0.85(1) and 1.37(2) Å, respectively. 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.

Table 1. Crystallographic data and refinement parameters for the complexes.

	1	2
Chemical formula	C ₁₆ H ₁₆ MoN ₂ O ₇	C ₁₇ H ₁₈ MoN ₂ O ₇
<i>Mr</i>	444.2	458.3
Crystal color, habit	Orange, block	Orange, block
Crystal size (mm ³)	0.20 × 0.20 × 0.18	0.20 × 0.20 × 0.18
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell parameters		
<i>a</i> (Å)	8.5723(18)	9.2195(19)
<i>b</i> (Å)	11.724(2)	11.8999(11)
<i>c</i> (Å)	18.222(3)	17.639(3)
β (°)	100.318(2)	102.926(1)
<i>V</i> (Å ³)	1801.7(6)	1886.1(5)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.638	1.614
Temperature (K)	298(2)	298(2)
μ (mm ⁻¹)	0.768	0.737
<i>F</i> (000)	896	928
Number of unique data	3917	4088
Number of observed data [<i>I</i> > 2 σ (<i>I</i>)]	3166	3180
Number of parameters	243	252
Number of restraints	3	3
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0297, 0.0768	0.0357, 0.0823
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0412, 0.0837	0.0514, 0.0888
Goodness of fit on <i>F</i> ²	1.052	1.028
Max and min electron density (e Å ⁻³)	0.374, -0.556	0.996, -0.347

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

1			
Mo1-O1	1.903(2)	Mo1-O3	1.9935(18)
Mo1-O5	1.689(2)	Mo1-O6	2.3380(19)
Mo1-O7	1.7126(19)	Mo1-N1	2.238(2)
O5-Mo1-O7	106.16(10)	O5-Mo1-O1	99.02(11)
O7-Mo1-O1	103.26(9)	O5-Mo1-O3	96.37(10)
O7-Mo1-O3	96.91(9)	O1-Mo1-O3	150.00(8)
O5-Mo1-N1	96.05(9)	O7-Mo1-N1	156.09(9)
O1-Mo1-N1	81.41(8)	O3-Mo1-N1	71.46(7)
O5-Mo1-O6	169.49(9)	O7-Mo1-O6	83.67(8)
O1-Mo1-O6	81.95(9)	O3-Mo1-O6	78.43(8)
N1-Mo1-O6	73.69(7)		
2			
Mo1-O1	1.907(2)	Mo1-O3	1.989(2)
Mo1-O5	1.685(2)	Mo1-O6	1.708(2)
Mo1-N1	2.225(3)	Mo1-O7	2.340(2)
O5-Mo1-O6	106.21(11)	O5-Mo1-O1	99.34(12)

O6-Mo1-O1	103.15(10)	O5-Mo1-O3	95.72(11)
O6-Mo1-O3	96.95(10)	O1-Mo1-O3	150.30(9)
O5-Mo1-N1	95.82(10)	O6-Mo1-N1	156.13(10)
O1-Mo1-N1	81.72(9)	O3-Mo1-N1	71.35(9)
O5-Mo1-O7	169.99(10)	O6-Mo1-O7	82.87(9)
O1-Mo1-O7	82.28(10)	O3-Mo1-O7	78.73(9)
N1-Mo1-O7	74.57(8)		

RESULTS AND DISCUSSION

Replacement of two acetylacetonate ligands in [MoO₂(acac)₂] by hydrazone ligands resulted in the formation of water coordinated mononuclear molybdenum(VI) oxo complexes. In both complexes, the dinegative ligands are coordinated to the *cis*-MoO₂ cores *via* the phenolate-oxygen, imino-nitrogen, and enolate-oxygen. The sixth coordination site is occupied by the oxygen atom from a water solvent. The complexes are soluble in methanol, ethanol, and acetonitrile. The molar conductance of the complexes **1** and **2** at the concentrations of 10⁻⁴ M are 17 and 14 Ω⁻¹ cm² mol⁻¹, respectively, indicating they are non-electrolytes.

Structure Description of the Complexes: The molecular structures and the atom numbering schemes of the complexes **1** and **2** are shown in Figures 1 and 2, respectively. 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 meridional 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 five- and one six-membered chelate rings involving the MoO₂ core. The hydrazone ligand in each of the complexes is bonded to the MoO₂ core in a planar fashion, coordinating through the phenolate O, imino N, and enolate O, and an oxo group lying *trans* to the nitrogen donor. In each of the complexes, a water molecule completes the distorted octahedral coordination sphere which lies *trans* to the other oxo group. The Mo–O(water) bonds are significantly longer than the other Mo–O bonds, indicating that the water 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(3), O(7), and N(1) in **1** and O(1), O(3), O(6), and N(1) in **2** show high degree of planarity from the equatorial planes, the Mo atoms are displaced by 0.332(1) Å (**1**) and 0.328(1) Å (**2**) toward the axial oxo groups. 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 for 2.6(3)° **1** and 2.7(3)° for **2**.

In the crystal structures of both complexes (Figure 3 for **1** and Figure 4 for **2**), adjacent two molecules are linked by water molecules through intermolecular O–H⋯N and O–H⋯O hydrogen bonds (Table 3), to form 1D chains running along the axis.

Table 3. Geometrical Parameters for Hydrogen Bonds

Hydrogen bonds	<i>D</i> –H (Å)	H⋯ <i>A</i> (Å)	<i>D</i> ⋯ <i>A</i> (Å)	<i>D</i> –H⋯ <i>A</i> (°)
1				
O6–H6A⋯O7 ^{#1}	0.85(1)	1.88(2)	2.718(3)	169(8)
O6–H6B⋯N2 ^{#2}	0.85(1)	2.05(3)	2.850(3)	159(8)
O6–H6B⋯O4 ^{#2}	0.85(1)	2.43(7)	2.981(3)	124(7)
2				
O7–H7B⋯N2 ^{#3}	0.85(1)	2.11(2)	2.899(3)	156(4)
O7–H7B⋯O4 ^{#3}	0.85(1)	2.39(3)	2.977(3)	127(3)
O7–H7A⋯O6 ^{#4}	0.85(1)	1.94(2)	2.764(3)	167(4)

^{#1} 1 – *x*, – *y*, – *z*; ^{#2} – *x*, – *y*, – *z*; ^{#3} 1 – *x*, 1 – *y*, – *z*; ^{#4} 2 – *x*, 1 – *y*, – *z*.

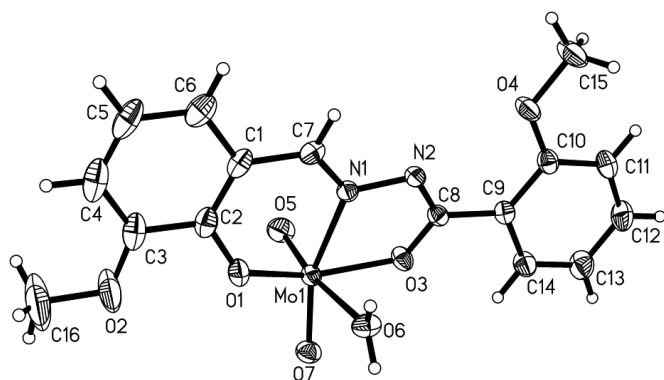


Figure 1. ORTEP plot of the crystal structure of **1**. Displacement ellipsoids of non-hydrogen atoms are drawn at the 30% probability level.

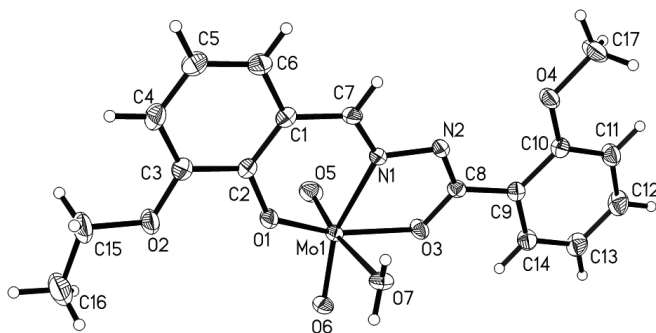


Figure 2. ORTEP plot of the crystal structure of **2**. Displacement ellipsoids of non-hydrogen atoms are drawn at the 30% probability level.

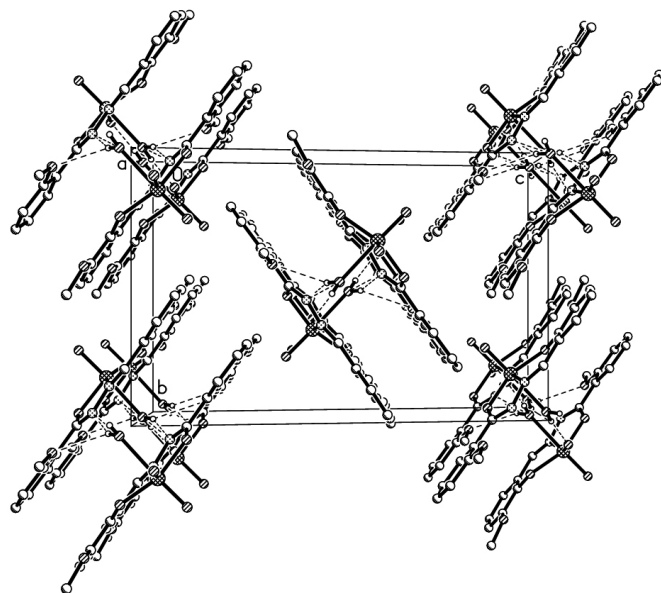


Figure 3. Molecular packing arrangement of **1** displayed in the unit cell. Hydrogen bonds are shown as dashed lines.

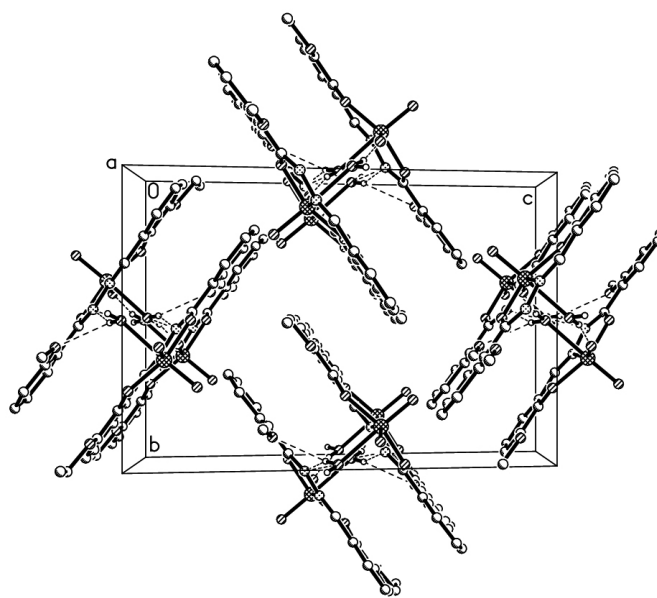


Figure 4. Molecular packing arrangement of **2** displayed in the unit cell. Hydrogen bonds are shown as dashed lines.

IR Spectra: The hydrazone ligands showed stretching bands attributed to C=O, C=N, C-OH and NH at 1656, 1627, 1148 and 1227, and 3246 cm^{-1} for H_2L^1 , and at 1656, 1626, 1148 and 1226, and 3237 cm^{-1} for H_2L^2 , respectively. In addition, strong bands observed at 1607 cm^{-1} for H_2L^1 and H_2L^2 are attributed to $-\text{C}=\text{N}=\text{N}=\text{C}-$ groups. Both complexes exhibit two bands at ca. 891 and 940 cm^{-1} , assigned to symmetric and asymmetric vibrations respectively, of the *cis*- MoO_2 cores. The bands due to $\nu_{\text{C=O}}$ and ν_{NH} were absent in the complexes, but new C-O stretches appeared at 1262 cm^{-1} for **1** and 1263 cm^{-1} for **2**. This suggests occurrence of *keto*-imine tautomerization of the ligands during complexation. The $\nu_{\text{C=N}}$ absorption observed at 1627 and 1626 cm^{-1} in the free hydrazone ligands shifted to 1606 cm^{-1} for **1** and 1607 cm^{-1} for **2** upon coordination to Mo atoms. The weak peaks in the low wave numbers in the region 450–800 cm^{-1} may be attributed to Mo-O and Mo-N bonds in the complexes.

CONCLUSION

Two water coordinated mononuclear molybdenum(VI) oxo complexes with similar hydrazone ligands have been prepared and structurally characterized by single crystal X-ray diffraction method, as well as elemental analysis and FT-IR spectra. The hydrazone ligands coordinate to the MoO_2 cores through the enolate oxygen, the phenolate oxygen and the azomethine nitrogen.

Supplementary material

CCDC-897240 (**1**) and 897241 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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