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TWO MONONUCLEAR MOLYBDENUM(VI) OXO COMPLEXES WITH TRIDENTATE HYDRAZONE LIGANDS: SYNTHESIS, STRUCTURES, AND THERMAL STABILITY**S.-S. Qian¹, H.-H. Li², Y.-N. Li², Z.-L. You², H.-L. Zhu¹**¹*School of Life Sciences, Shandong University of Technology, Zibo 255049, P. R. China*

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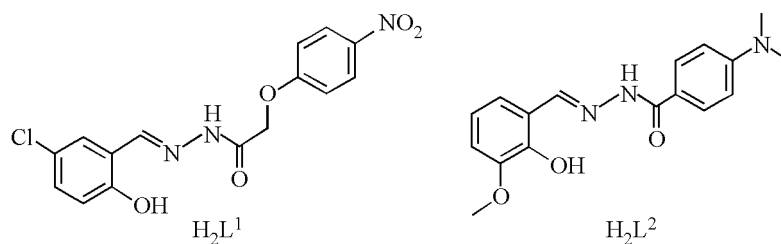
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A reaction of $[\text{MoO}_2(\text{acac})_2]$ (where acac = acetylacetonate) with two hydrazone ligands in methanol yields two mononuclear molybdenum(VI) oxo complexes with the general formula $[\text{MoO}_2\text{L}(\text{CH}_3\text{OH})]$, where $\text{L} = \text{L}^1 = (4\text{-nitrophenoxy})\text{acetic acid [1-(5-chloro-2-hydroxyphenyl)-methylidene]hydrazide (H}_2\text{L}^1)$ and $\text{L} = \text{L}^2 = 4\text{-dimethylaminobenzoic acid [1-(2-hydroxy-3-methoxyphenyl)methylidene]hydrazide (H}_2\text{L}^2)$. The crystal and molecular structures of the complexes are determined by the single crystal X-ray diffraction method. All of the investigated compounds are further characterized by the elemental analysis, FT-IR spectra, and thermogravimetric analyses. Single crystal X-ray structural studies indicate that hydrazone ligands coordinate to MoO_2 cores through enolate oxygen, phenolate oxygen, and azomethine nitrogen atoms. 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 significance [1–3] as well as 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 $-\text{C}(\text{O})-\text{NH}-\text{N}=\text{CH}-$ 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 $[\text{MoO}_2\text{L}(\text{CH}_3\text{OH})]$, where $\text{L} = \text{L}^1 = (4\text{-nitrophenoxy})\text{acetic acid [1-(5-chloro-2-hydroxyphenyl)-methylidene]hydrazide (H}_2\text{L}^1)$ and $\text{L} = \text{L}^2 = 4\text{-dimethylaminobenzoic acid [1-(2-hydroxy-3-methoxyphenyl)methylidene]hydrazide (H}_2\text{L}^2)$. The thermal stability of the complexes is also reported.



EXPERIMENTAL

Materials and physical methods. Commercially available 5-chlorosalicylaldehyde, 3-methoxysalicylaldehyde, (4-nitrophenoxy)acetic acid hydrazide, and 4-dimethylaminobenzohydrazide 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 range 4000—400 cm^{-1} . Thermal stability analysis was performed on a Perkin-Elmer Pyris Diamond TG-DTA thermal analyses system.

Synthesis of H_2L^1 . 5-Chlorosalicylaldehyde (1.0 mmol, 0.157 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 a yellow crystalline product of H_2L^1 . Yield, 93 %. Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{ClN}_3\text{O}_5$ (FW 349.7): C, 51.5; H, 3.5; N, 12.0 %. Found: C, 51.3; H, 3.4; N, 12.1 %.

Synthesis of H_2L^2 . 3-Methoxysalicylaldehyde (1.0 mmol, 0.152 g) and 4-dimethylaminobenzohydrazide (1.0 mmol, 0.179 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 a colorless crystalline product of H_2L^2 . Yield, 91 %. Anal. Calcd. for $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3$ (FW 313.4): C, 65.2; H, 6.1; N, 13.4 %. Found: C, 65.4; H, 6.1; N, 13.3 %.

Synthesis of $[\text{MoO}_2\text{L}^1(\text{CH}_3\text{OH})]$ (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, 35.0 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 the X-ray single crystal analysis 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, 53 %. Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{ClMoN}_3\text{O}_8$ (FW 507.7): C, 37.9; H, 2.8; N, 8.3 %. Found: C, 37.8; H, 2.7; N, 8.2 %.

Synthesis of $[\text{MoO}_2\text{L}^2(\text{CH}_3\text{OH})]$ (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, 31.3 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 the X-ray single crystal analysis 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, 61 %. Anal. Calcd. for $\text{C}_{18}\text{H}_{21}\text{MoN}_3\text{O}_6$ (FW 471.3): C, 45.9; H, 4.5; N, 8.9 %. Found: C, 45.7; H, 4.6; N, 8.9 %.

X-ray crystallography. Diffraction intensities for the complexes were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer with MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). 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 SHELXTL [13]. All of the 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) \AA . 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.

RESULTS AND DISCUSSION

Synthesis. The replacement of two acetylacetonate ligands in $[\text{MoO}_2(\text{acac})_2]$ by hydrazone ligands resulted in the formation of mononuclear molybdenum(VI) oxo complexes. In both complexes, the dinegative ligands are coordinated to the *cis*- MoO_2 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 complexes **1** and **2** at the concentrations of 10^{-4} M are $10 \text{ } \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ and $13 \text{ } \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ respectively, indicating that they are non-electrolytes.

Crystallographic data and refinement parameters for the complexes

Parameters	1	2
Chemical formula	C ₁₆ H ₁₄ ClMoN ₃ O ₈	C ₁₈ H ₂₁ MoN ₃ O ₆
<i>M_r</i>	507.7	471.3
Crystal color, habit	Orange, block	Orange, block
Crystal size, mm ³	0.30×0.27×0.22	0.27×0.25×0.23
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
Unit cell parameters <i>a</i> , <i>b</i> , <i>c</i> , Å	7.5564(10), 8.4323(11), 16.337(2)	7.540(2), 10.045(3), 13.582(3)
α, β, γ, deg.	91.814(2), 90.937(2), 107.585(2)	89.577(2), 74.819(2), 85.216(2)
<i>V</i> , Å ³ ; <i>Z</i>	991.4(2); 2	989.2(5); 2
<i>d</i> _{calc} , g/cm ⁻³	1.701	1.582
Temperature, K	298(2)	298(2)
μ, mm ⁻¹	0.845	0.702
<i>F</i> (000)	508	480
Number of unique / observed data [<i>I</i> > 2σ(<i>I</i>)]	4195 / 3475	4091 / 3183
Number of parameters / restraints	266 / 1	259 / 1
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0417, 0.0885	0.0441, 0.0900
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0531, 0.0946	0.0604, 0.0974
Goodness of fit on <i>F</i> ²	1.042	1.090
Max and min electron density, e/Å ⁻³	0.520 and -0.557	0.339 and -0.636

Structure description of the complexes. The molecular structures and the atom numbering schemes of complexes **1** and **2** are shown in Figs. 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 a planar tridentate manner, forming one five- and one six-membered chelate rings involving the MoO₂ core. The hydrazone ligand in each of the com-

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

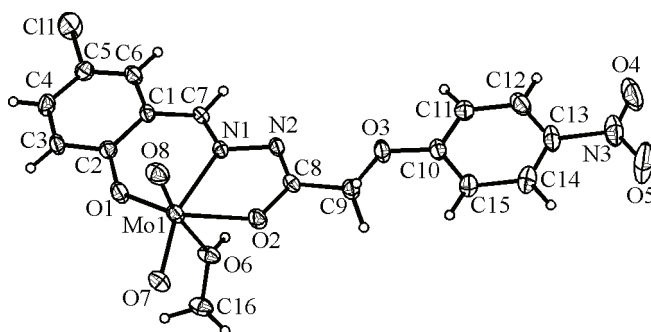
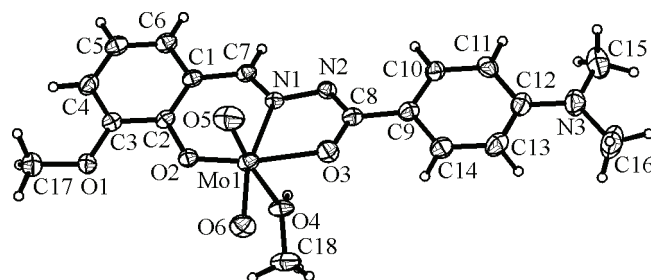


Fig. 2. ORTEP plot of the crystal structure of **2**. Displacement ellipsoids of non-hydrogen atoms are drawn at the 30 % probability level



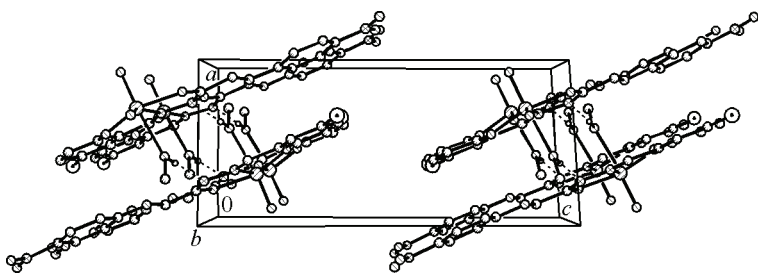


Fig. 3. Molecular packing arrangement of **1** displayed in the unit cell. Hydrogen bonds are shown as dashed lines

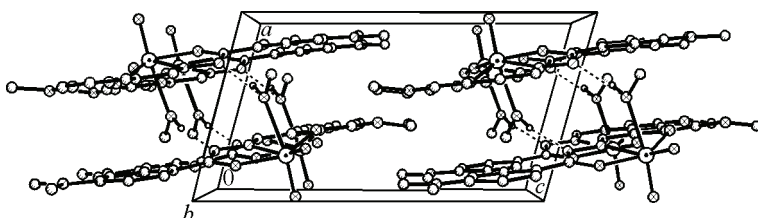


Fig. 4. Molecular packing arrangement of **2** displayed in the unit cell. Hydrogen bonds are shown as dashed lines

plexes is bonded to the MoO₂ core in a planar fashion, coordinating through the phenolate O, imino N, and enolate O atoms, and an oxo group 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 oxo group. 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 O1, O2, O7, and N1 atoms in **1** and O2, O3, O6, and N1 in **2** show a high degree of planarity from the equatorial planes; the Mo atoms are displaced by 0.323(1) Å (**1**) and 0.329(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 the 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 significantly deviate from the ideal values of 180°. The hydrazone ligands in the complexes are approximately planar, with the corresponding two benzene rings making dihedral angles of 5.5(3)° for **1** and 3.0(3)° for **2**.

In the crystal structures of both complexes (Fig. 3 for **1** and Fig. 4 for **2**), the two adjacent molecules are linked by methanol molecules through two intermolecular O—H⋯N hydrogen bonds [For **1**, O6—H6 = 0.85(1) Å, H6⋯N2 = 1.98(2) Å, O6—H6⋯N2 = 168(5)°; For **2**, O4—H4A = 0.85(1) Å, H4A⋯N2 = 1.90(2) Å, O4—H4A⋯N2 = 167(5)°], to form dimers.

IR spectra. The hydrazone ligands showed stretching bands attributed to C=O, C=N, C—OH, and NH at 1665 cm⁻¹, 1638 cm⁻¹, 1155 cm⁻¹ and 1229 cm⁻¹, and 3253 cm⁻¹ for H₂L¹, and at 1663 cm⁻¹, 1635 cm⁻¹, 1153 cm⁻¹ and 1230 cm⁻¹, and 3235 cm⁻¹ for H₂L² respectively. In addition, strong bands observed at 1616 cm⁻¹ for H₂L¹ and at 1614 cm⁻¹ for H₂L² are attributed to —C=N—N=C— groups. Both complexes exhibit two bands at *ca.* 906 cm⁻¹ and 938 cm⁻¹, assigned to symmetric and asymmetric vibrations respectively of the *cis*-MoO₂ cores. The bands due to ν_{C=O} and ν_{NH} were absent in the spectra of the complexes, but new C—O stretches appeared at 1262 cm⁻¹ for **1** and 1256 cm⁻¹ for **2**. This suggests the occurrence of *keto*-imine tautomerization of the ligands during complexation. The ν_{C=N} absorption observed at about 1637 cm⁻¹ in the free hydrazone ligands shifted to 1612 cm⁻¹ for **1** and 1606 cm⁻¹ for **2** upon coordination to Mo atoms. The weak peaks in the low wave numbers in the region 600—850 cm⁻¹ may be attributed to Mo—O and Mo—N bonds in the complexes.

Thermal analysis. Differential thermal (DT) and thermal gravimetric analyses (TGA) were conducted to examine the stability of the complexes. Both complexes show similar thermal behavior. The first weight losses occurred in the range 121—143 °C for **1** and 105—139 °C for **2** in the thermogravimetric curves were related to the loss of the coordinated methanol molecules. The second step, from 263 °C to 498 °C for **1** and from 263 °C to 574 °C for **2**, corresponds to the loss of the hydrazone ligands and the formation of MoO₃. The observed weight loss of 65.5 % for **1** and 64.3 % for **2** are in

accordance with the calculated values. Afterward, MoO₃ is stable up to about 660 °C and then sublimated until 870 °C.

CONCLUSIONS

Two mononuclear molybdenum(VI) oxo complexes with hydrazone ligands have been prepared and characterized by the single crystal X-ray diffraction method, as well as the elemental analysis, FT-IR spectra, and thermogravimetric analyses. The hydrazone ligands coordinate to the MoO₂ cores through the enolate oxygen, phenolate oxygen, and azomethine nitrogen atoms.

Supplementary information. CCDC-897242 (**1**) and 897245 (**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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