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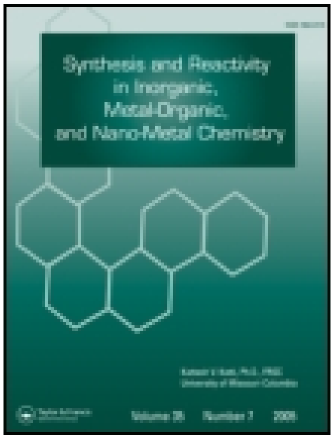

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Synthesis, Characterization, and Crystal Structures of Dioxomolybdenum(VI) Complexes [$MoO_2L^1(CH_3OH)$] and [$MoO_2L^2(CH_3OH)$] Derived from 4-Halo-2-[(2-hydroxypropylimino)methyl]phenol

Hong-Ge Zhang [a]

[a] Department of Chemistry and Chemical Engineering , Baoji University of Arts and Sciences , Baoji , P. R. China

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Synthesis, Characterization, and Crystal Structures of Dioxomolybdenum(VI) Complexes [$MoO_2L^1(CH_3OH)$] and [$MoO_2L^2(CH_3OH)$] Derived from 4-Halo-2-[(2-hydroxypropylimino)methyl]phenol

Hong-Ge Zhang
Department of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji, P. R. China

Two new mononuclear dioxomolybdenum(VI) complexes, [$MoO_2L^1(CH_3OH)$] (1) and [$MoO_2L^2(CH_3OH)$] (2), have been prepared by the reaction of $MoO_2(acac)_2$ with the tridentate Schiff base ligands 4-chloro-2-[(2-hydroxypropylimino)methyl]phenol (H_2L^1) and 4-bromo-2-[(2-hydroxypropylimino)methyl]phenol (H_2L^2), respectively, in methanol. The complexes were characterized by elemental analyses, infrared spectra, and single-crystal X-ray diffraction. Complex 1 crystallizes in triclinic space group $P\overline{1}$ with unit cell dimensions $a = 6.970(2)$, $b = 10.350(2)$, $c = 10.570(2)$ Å, $\alpha = 68.680(3)$, $\beta = 78.813(3)$, $\gamma = 77.321(3)°$, V = 687.5(3) Å^3, Z = 2, $R_1 = 0.0381$, and $wR_2 = 0.0860$. Complex 2 crystallizes in triclinic space group $P\overline{1}$ with unit cell dimensions $a = 7.075(2)$, $b = 10.473(2)$, $c = 10.691(2)$ Å, $\alpha = 68.744(3)$, $\beta = 77.959(3)$, $\gamma = 76.320(3)°$, V = 710.8(3) Å^3, Z = 2, $R_1 = 0.0477$, and $wR_2 = 0.1171$. Both complexes consist of *cis*-MoO_2 core coordinated by a Schiff base ligand through two deprotonated hydroxyl groups and one imino nitrogen atom. The octahedral coordination around the molybdenum atom is completed by the neutral methanol ligand.

Supplemental materials are available for this article. Go to the publisher's online edition of* Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry *to view the supplemental file.

Keywords crystal structure, hydrogen bonding, molybdenum, Schiff bases, X-ray diffraction

INTRODUCTION

Molybdenum has been found to be a very important element in biological systems. Apart from the nitrogenases in where a molybdenum atom can be a component of the multinuclear active sites,[1] there are a number of mononuclear molybdenum enzymes that are often referred to as oxomolybdenum enzymes.[2] Therefore, the mononuclear dioxomolybdenum complexes might be interesting model systems. In recent years, a number of dioxomolybdenum complexes have been synthesized and characterized to mimic the biological systems.[3–5] Schiff bases are a kind of important ligands in coordination chemistry, however, the number of dioxomolybdenum complexes with Schiff bases is small. I report here the synthesis and characterization of two new dioxomolybdenum(VI) complexes, [$MoO_2L^1(CH_3OH)$] (**1**) and [$MoO_2L^2(CH_3OH)$] (**2**), derived from the tridentate Schiff base ligands 4-chloro-2-[(2-hydroxypropylimino)methyl]phenol (H_2L^1) and 4-bromo-2-[(2-hydroxypropylimino)methyl]phenol (H_2L^2).

EXPERIMENTAL

Materials and Physical Measurements

The chemicals 5-chlorosalicylaldehyde, 5-bromosalicyl aldehyde, 1-aminopropan-2-ol (Fluka), and solvents (AR grade) were used without further purification. [$MoO_2(acac)_2$] was prepared as described in literature.[6] Elemental analyses of the Schiff bases and the complexes were carried out using a Vario EL III CHNS analyzer. Infrared spectra were recorded on a JASCO FT/IR-4100 type A spectrometer in the range 4000–400 cm^{-1} using KBr pellets.

Synthesis of the Schiff Bases

H_2L^1: To a stirred methanolic solution (50 mL) of 5-chlorosalicylaldehyde (10 mmol, 1.56 g) was added dropwise a methanolic solution (30 mL) of 1-aminopropan-2-ol (10 mmol, 0.75 g). The mixture was then stirred for 1 h at reflux. Afterwards the mixture was cooled to room temperature, and the yellow products formed were collected by filtration. Yield, 82%. Anal. Calcd. for $C_{10}H_{12}ClNO_2$: C, 56.2; H, 5.7; N, 6.6. Found, C, 56.1; H, 5.6; N, 6.7%.

H_2L^1: This compound was prepared by the similar method as described for H_2L^1, but with 5-chlorosalicylaldehyde replaced by 5-bromosalicylaldehyde (10 mmol, 2.01 g). Yield,

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Address correspondence to Hong-Ge Zhang, Department of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji 721007, P. R. China. E-mail: zhang_hongge@126.com

87%. Anal. Calcd. for $C_{10}H_{12}BrNO_2$: C, 46.5; H, 4.7; N, 5.4. Found: C, 46.7; H, 4.7; N, 5.5%.

Synthesis of 1

To a methanolic solution (10 mL) of H_2L^1 (1.0 mmol, 0.21 g) was added a methanolic solution (10 mL) of $MoO_2(acac)_2$ (1.0 mmol, 0.33 g) at room temperature. The mixture was stirred for 1 h and the solvent was removed under reduced pressure to give a quantitative yield of the product. Analytically pure samples and crystals for X-ray structural determination were re-crystallized from methanol solvent. Anal. Calcd. for $C_{11}H_{14}ClMoNO_5$: C, 35.6; H, 3.8; N, 3.8. Found: C, 35.5; H, 3.8; N, 3.7%.

TABLE 1
Crystallographic and experimental data for the complexes **1** and **2**

Complex	**1**	**2**
Empirical formula	$C_{11}H_{14}ClMoNO_5$	$C_{11}H_{14}BrMoNO_5$
Formula weight	371.6	416.1
Crystal color, shape	Yellow, block	Yellow, block
Crystal size (mm)	0.32 × 0.30 × 0.27	0.27 × 0.23 × 0.23
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	6.970(2)	7.075(2)
b (Å)	10.350(2)	10.473(3)
c (Å)	10.570(2)	10.691(3)
α (°)	68.680(3)	68.744(3)
β (°)	78.813(3)	77.959(3)
γ (°)	77.321(3)	76.320(3)
V (Å^3)	687.5(3)	710.8(3)
Z	2	2
ρ_{calc} (g cm^{-3})	1.795	1.944
$F(000)$	372	408
μ(MoKα) (mm^{-1})	1.162	3.747
θ range (°)	2.4–27.3	2.1–24.3
No. of reflections measured	5544	4169
Unique reflections	2911	2999
Observed reflections [$I > 2\sigma(I)$]	2487	2287
Parameters	177	177
Restraints	1	1
R_{int}	0.0229	0.0246
Goodness-of-fit on F^2	1.081	1.060
Max. and min. Transmission	0.7074, 0.7443	0.4311, 0.4794
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0358$, $wR_2 = 0.0737$	$R_1 = 0.0477$, $wR_2 = 0.1171$
R indices	$R_1 = 0.0459$, $wR_2 = 0.0775$	$R_1 = 0.0676$, $wR_2 = 0.1297$
Largest difference in peak and hole (e Å^{-3})	0.510, −0.494	0.886, –1.058

Synthesis of 2

This complex was prepared by the similar method as described for **1**, but with H_2L^1 replaced by H_2L^2. Anal. Calcd. for $C_{11}H_{14}BrMoNO_5$: C, 35.6; H, 3.5; N, 3.8. Found: C, 35.8; H, 3.6; N, 3.7%.

X-Ray Structure Determination

Intensity data for complexes **1** and **2** were collected on a Bruker APEX II CCD area diffractometer (College of Chemistry and Chemical Engineering, Lanzhou University, China) equipped with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) and ω scan technique. Crystal data, experimental conditions, details of structure determination, and final refinement parameters are summarized in Table 1. Selected bond distances and angles are listed in Table 2. The structures were solved by direct method and Fourier synthesis using SHELXS97[7] and refined by full-matrix least-squares method assuming anisotropic temperature factors for all non-hydrogen atoms using SHELXL97.[8] The final Fourier maps revealed positions of all H atoms, but some with poor geometry. Therefore all hydrogen atoms attached to carbon atoms were generated on geometrical grounds. The hydrogen atoms bound to the oxygen

TABLE 2
Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

1			
Mo1-O1	1.944(3)	Mo1-O2	1.939(2)
Mo1-O3	2.324(3)	Mo1-O4	1.683(3)
Mo1-O5	1.696(2)	Mo1-N1	2.243(3)
O4-Mo1-O5	106.6(1)	O4-Mo1-O2	97.1(1)
O5-Mo1-O2	96.5(1)	O4-Mo1-O1	97.1(1)
O5-Mo1-O1	102.1(1)	O2-Mo1-O1	152.2(1)
O4-Mo1-N1	93.6(1)	O5-Mo1-N1	159.0(1)
O2-Mo1-N1	74.8(1)	O1-Mo1-N1	80.6(1)
O4-Mo1-O3	170.6(1)	O5-Mo1-O3	82.8(1)
O2-Mo1-O3	82.3(1)	O1-Mo1-O3	79.8(1)
N1-Mo1-O3	77.2(1)		
2			
Mo1-O1	1.964(4)	Mo1-O2	1.960(4)
Mo1-O3	2.334(4)	Mo1-O4	1.692(4)
Mo1-O5	1.714(4)	Mo1-N1	2.267(4)
O4-Mo1-O5	106.5(2)	O4-Mo1-O2	97.1(2)
O5-Mo1-O2	96.8(2)	O4-Mo1-O1	97.0(2)
O5-Mo1-O1	102.0(2)	O2-Mo1-O1	152.2(2)
O4-Mo1-N1	93.6(2)	O5-Mo1-N1	159.1(2)
O2-Mo1-N1	74.6(2)	O1-Mo1-N1	80.7(2)
O4-Mo1-O3	170.8(2)	O5-Mo1-O3	82.7(2)
O2-Mo1-O3	82.0(2)	O1-Mo1-O3	80.3(2)
N1-Mo1-O3	77.3(2)		

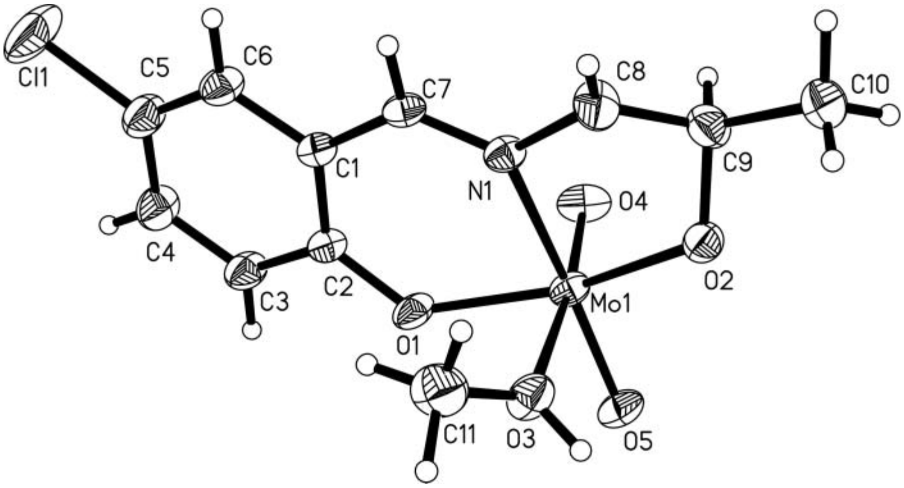

FIG. 1. ORTEP plot of **1** showing the labeling system of non-hydrogen atoms. Displacement ellipsoids are plotted at 30% probability level.

atoms of coordinated methanol molecules were located from difference Fourier maps and refined isotropically, with O−H distances restrained to 0.85(1) Å.

RESULTS AND DISCUSSION

Schiff base ligands H_2L^1 and H_2L^2 were synthesized in-situ from 5-chlorosalicylaldehyde and 5-bromosalicylaldehyde, respectively, with 1-aminopropan-2-ol in methanol. The Schiff bases reacted with bis(acetylacetonato)dioxomolybdenum(VI) in methanol to form the methanol-coordinated dioxomolybdenum(VI) complexes. The complexes are yellow solids and could be crystallized from methanol. The complexes are soluble in chloroform, DMSO, methanol, and acetonitrile.

Infrared Spectra

In the infrared spectra of the complexes the intense bands at 1651 cm^{-1} for **1** and 1650 cm^{-1} for **2** are assigned to the azomethine groups, ν(C=N).[9] The weak and broad bands centered at 3421 cm^{-1} for **1** and 3433 cm^{-1} for **2** are assigned to the O–H vibrations of the methanol ligands. Each spectrum of the complexes exhibits two strong bands in the region 900–930 cm^{-1} characteristic of the *cis*-[MoO_2].[9,10] The middle stretching frequencies at about 1130 cm^{-1} for both complexes were attributed to the coordinated C–O groups.

Structure Description of the Complexes

The crystal structures of complexes **1** and **2** are built up of mononuclear complex molecules with *cis*-MoO_2 core (Figures 1 and 2). In both complexes, the Schiff base ligands act in a dianionic tridentate manner. The coordination geometry around the Mo center in these molybdenum complexes can be best described as a distorted octahedron in which the ONO tridentate ligand occupies meridional position with two anionic oxygens mutually *trans* and are *cis* to the oxygens of *cis*-dioxo group.

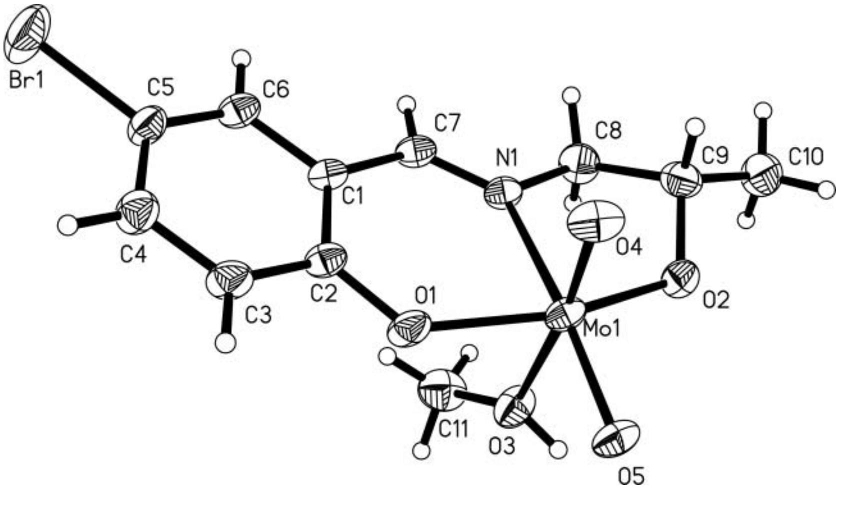

FIG. 2. ORTEP plot of **2** showing the labelling system of non-hydrogen atoms. Displacement ellipsoids are plotted at 30% probability level.

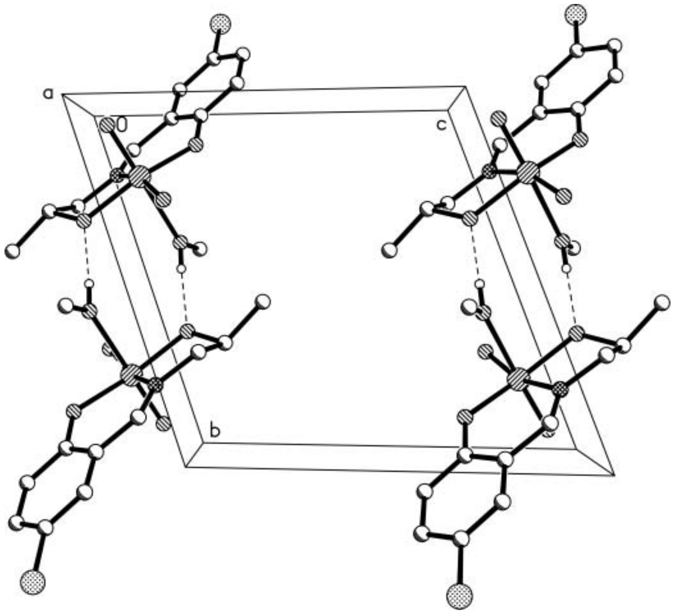

FIG. 3. Molecular packing diagram of the complexes, viewed along the *a*-axis. Intermolecular O−H···O hydrogen bonds are shown as dashed lines.

The octahedral geometry of molybdenum center is additionally completed by coordinated methanol solvent molecule. In **1** and **2**, the Mo atoms deviate from the corresponding least-squares planes defined by the equatorial donor atoms by 0.306(1) and 0.309(1) Å, respectively, toward the O4 axial donor atoms. Both Mo=O distances, ranging from 1.683(2) to 1.714(2) Å, and the O=Mo=O angles, from 106.5(2) to 106.6(1)°, are in the usual range for *cis*-MoO_2 complexes.[11–13] In the structures of both complexes, the tridentate Schiff base ligands form one six- and one five-membered chelate rings, with Mo-O bond lenghts varying from 1.939(2) to 1.964(2) Å, and Mo-N distances varying from 2.243(2) to 2.267(2) Å. The longest Mo-O bonds are Mo-O_{methanol}, ranging from 2.324(2) to 2.334(2) Å, as already observed in the similar structures with coordinated methanol molecules.[11–13]

In the crystal structures of the complexes **1** and **2**, adjacent two molecules are linked through intermolecular O−H···O hydrogen bonds [for **1**, O−H = 0.85(1) Å, H···O = 1.82(2) Å, O···O = 2.645(4) Å, O−H···O = 167(6)°; for **2**, O−H = 0.85(1) Å, H···O = 1.84(3) Å, O···O = 2.657(5) Å, O−H···O = 161(7)°], to form centrosymmetric dimeric structures, as shown in Figure 3.

SUPPLEMENTARY MATERIALs

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 885123 (**1**) and 885124 (**2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

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