Synthesis, Crystal Structures and Catalytic Property of Dioxidomolybdenum(VI) Complexes with Tridentate Hydrazones

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Received: 01-07-2020

Abstract

New dioxidomolybdenum(VI) complexes with the formula [MoO₂L(MeOH)], derived from N'-(5-chloro-2-hydroxybenzylidene)-2-methylbenzohydrazide (H₂L¹) and N'-(3,5-dichloro-2-hydroxybenzylidene)-2-methylbenzohydrazide (H₂L²) were prepared. Crystal and molecular structures of the complexes were determined by single crystal X-ray diffraction method. Both complexes were further characterized by elemental analysis and FT-IR spectra. Single crystal X-ray structural studies indicate that the hydrazones L¹ and L² coordinate to the MoO₂ cores through the enolate oxygen, phenolate oxygen and azomethine nitrogen. The Mo atoms in both complexes are in octahedral coordination. Catalytic properties for epoxidation of styrene by the complexes using PhIO and NaOCl as oxidant have been studied.

Keywords: Molybdenum; hydrazine; crystal structure; hydrogen bonding; catalytic property

1. Introduction

The oxidation of organic compounds is an important chemical process in the chemical industry to synthesize a large variety of organic materials. Due to the slow rate of most oxidation reactions in the absence of catalysts, the catalytic oxidation of organic substrates by metal complexes has received much attention in organic synthesis. Many transition metals have been used as homogenous or heterogeneous catalysts in various oxidation systems. The epoxidation products of olefins have widely applications in various fields. They are intermediates or precursors for the synthesis of pharmaceuticals, agrochemicals, and many other compounds. Among various metal complexes, those with Mo centers have been attracted considerable attention due

to their recently discovered biochemical significance³ as well as their efficient catalytic properties in several organic synthesis procedures.⁴ Schiff bases are widely used as ligands in the construction of metal complexes.⁵ In recent years, a large number of molybdenum complexes with Schiff bases derived from salicylaldehyde and primary amines have been reported.⁶ Hydrazones, bearing –C(O)–NH–N=CH– groups, are a kind of special Schiff bases, which are of particular interest in coordination chemistry and biological applications.⁷ However, due to the search of the Crystallographic Structural Database, the number of molybdenum(VI) complexes with hydrazone ligands are much less than other metal complexes with such type of ligands. In this paper, two new dioxidomolybdenum(VI) complexes with the formula [MoO₂L (MeOH)], derived

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from N'-(5-chloro-2-hydroxybenzylidene)-2-methylbenzohydrazide (H_2L^1) and N'-(3,5-dichloro-2-hydroxybenzylidene)-2-methylbenzohydrazide (H_2L^2) are reported.

2. Experimental

2. 1. Materials and Measurements

5-Chlorosalicylaldehyde, 3,5-dichlorosalicylaldehyde and 2-methylbenzohydrazide were purchased from Aldrich and used without further purification. [$MoO_2(a-cac)_2$] and 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. GC experiments were performed with Agilent 5977A Network GC systems. Infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm⁻¹ region.

2. 2. Synthesis of H₂L¹

5-Chlorosalicylaldehyde (1.0 mmol, 0.156 g) and 2-methylbenzohydrazide (1.0 mmol, 0.150 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, 91%. For $C_{15}H_{13}ClN_2O_2$: anal. calcd., %: C, 62.4; H, 4.5; N, 9.7. Found, %: C, 62.2; H, 4.6; N, 9.8.

2. 3. Synthesis of H₂L²

3,5-Dichlorosalicylaldehyde (1.0 mmol, 0.190 g) and 2-methylbenzohydrazide (1.0 mmol, 0.150 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, 95%. For $C_{15}H_{12}Cl_2N_2O_2$: anal. calcd., %: C, 55.8; H, 3.7; N, 8.7. Found, %: C, 55.7; H, 3.8; N, 8.6.

2. 4. Synthesis of [MoO₂L¹(MeOH)] (1)

A methanolic solution (10 mL) of $[MoO_2(acac)_2]$ (0.1 mmol, 32.6 mg) was added to a methanolic solution (10 mL) of H_2L^1 (0.1 mmol, 28.9 mg) with stirring. The mixture was stirred for 20 min to give a yellow solution. The resulting solution was allowed to stand in air for a few days. Yellow 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, 63%. For $C_{16}H_{15}ClMoN_2O_5$: anal. calcd., %: C, 43.0; H, 3.4; N, 6.3. Found, %: C, 43.2; H, 3.4; N, 6.2.

2. 5. Synthesis of $[MoO_2L^2(MeOH)]$ (2)

A methanolic solution (10 mL) of $[MoO_2(acac)_2]$ (0.1 mmol, 32.6 mg) was added to a methanolic solution

Tabl	e 1.	Crystal	lographic	data and	l refinement	parameters f	tor the	compl	exes
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	1	2	
Chemical formula	C ₁₆ H ₁₅ ClMoN ₂ O ₅	$C_{16}H_{14}Cl_2MoN_2O_5$	
Mr	446.7	481.1	
Crystal color, habit	Yellow, block	Yellow, block	
Crystal size (mm ³)	$0.32 \times 0.30 \times 0.27$	$0.20 \times 0.20 \times 0.17$	
Crystal system	Monoclinic	Monoclinic	
Space group	$P2_1/c$	$P2_1/c$	
Unit cell parameters			
a (Å)	7.957(1)	7.961(2)	
b (Å)	14.073(1)	14.123(2)	
c (Å)	15.172(1)	15.981(2)	
β (°)	92.767(2)	92.277(2)	
V (Å ³)	1697.0(3)	1795.4(6)	
Z	4	4	
$D_{\rm calc}$ (g cm ⁻³)	1.748	1.780	
Temperature (K)	298(2)	298(2)	
$\mu (\text{mm}^{-1})$	0.960	1.058	
F(000)	896	960	
Number of unique data	3702	3919	
Number of observed data $[I > 2\sigma(I)]$	2963	3151	
Number of parameters	231	240	
Number of restraints	1	1	
R_1 , $wR_2[I > 2\sigma(I)]$	0.0261, 0.0595	0.0313, 0.0688	
R_1 , wR_2 (all data)	0.0388, 0.0668	0.0466, 0.0764	
Goodness of fit on F^2	1.080	1.043	
Max and min electron density (e Å ⁻³)	0.699, -0.436	0.881, -0.710	

(10 mL) of $\rm H_2L^2$ (0.1 mmol, 32.2 mg) with stirring. The mixture was stirred for 20 min to give a yellow solution. The resulting solution was allowed to stand in air for a few days. Yellow 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. Yield, 45%. For $\rm C_{16}H_{14}Cl_2MoN_2O_5$: anal. calcd., %: C, 39.9; H, 2.9; N, 5.8. Found, %: C, 40.0; H, 3.0; N, 5.6.

2. 6. Data Collection, Structural Determination and Refinement

Diffraction intensities for the complexes were collected at 298(2) K using a Bruker Smart 1000 CCD area diffractometer with Mo*Ka* radiation (l = 0.71073 Å). The collected data were reduced using SAINT,⁸ and multi-scan absorption corrections were performed using SADABS.⁹ Structures of the complexes were solved by direct methods and refined against *F*² by full-matrix least-squares methods using SHELXTL.¹⁰ 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) 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.

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

		1	
Mo1-O1	1.918(2)	Mo1-O2 2.012	(2)
Mo1-O3	2.360(2)	Mo1-O4 1.695	(2)
Mo1-O5	1.692(2)	Mo1-N1 2.234	(2)
O1-Mo1-O2	149.57(7)	O1-Mo1-N1	81.23(7)
O4-Mo1-O1	103.03(8)	O4-Mo1-O2	97.65(7)
O4-Mo1-N1	156.30(8)	O2-Mo1-N1	71.12(6)
O5-Mo1-O1	99.90(9)	O5-Mo1-O2	95.61(9)
O5-Mo1-O4	105.77(9)	O5-Mo1-N1	96.26(8)
O5-Mo1-O3	170.96(8)	O4-Mo1-O3	81.89(7)
O1-Mo1-O3	82.69(8)	O2-Mo1-O3	78.37(7)
N1-Mo1-O3	75.49(6)		
		2	
Mo1-O1	1.941(2)	Mo1-O2 2.022	(2)
Mo1-O3	2.326(2)	Mo1-O4 1.686	(2)
Mo1-O5	1.697(2)	Mo1-N1 2.246	(2)
O1-Mo1-O2	149.21(8)	O1-Mo1-N1	80.87(8)
O2-Mo1-N1	70.86(8)	O1-Mo1-O3	82.57(8)
O4-Mo1-O1	98.35(10)	O4-Mo1-O2	96.19(10)
O4-Mo1-O5	105.94(11)	O4-Mo1-N1	95.25(9)
O4-Mo1-O3	170.55(9)	O2-Mo1-O3	78.86(8)
O5-Mo1-O1	103.64(9)	O5-Mo1-O2	98.19(9)
O5-Mo1-N1	157.24(9)	O5-Mo1-O3	82.86(9)
N1-Mo1-O3	75.56(7)		

2. 7. General Method for Styrene Oxidation

The oxidation reactions were carried out according to the literature method. ¹¹ The composition of the reaction mixture was 2.00 mmol of styrene, 2.00 mmol of chlorobenzene (internal standard), 0.10 mmol of the complex (catalyst) and 2.00 mmol iodosylbenzene (PhIO) or sodium hypochlorite (NaClO) as the oxidant in 5.00 mL freshly distilled acetonitrile. When the oxidant was sodium hypochlorite, the solution was buffered to pH 11.2. The composition of reaction medium was determined by GC with styrene and styrene epoxide quantified by the internal standard method (chlorobenzene).

3. Results and Discussion

3. 1. Chemistry

The complexes were prepared by mixing [MoO₂(a-cac)₂] with the hydrazones H_2L^1 and H_2L^2 in methanol. Single crystal structures were obtained by slow evaporation of the complexes in methanol. The difference of the molecular packing modes of the complexes may be caused by the hindrance effects of the chloro-substituent groups. There is only one chloro-substituent group in complex 1, while two in complex 2. 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 25 and $20~\Omega^{-1}$ cm² mol⁻¹, respectively, indicating they are non-electrolytes.¹²

3. 2. Structure Description of the Complexes

The molecular structures and atom numbering schemes of complexes 1 and 2 are shown in Figures 1 and 2, respectively. The coordination geometry around the Mo atoms in both complexes is highly distorted octahedral. The dianionic hydrazones L¹ and L² adopt planar tridentate manner, forming five- and one six-membered chelate rings involving the MoO₂ cores. The hydrazones L^1 and L^2 in the complexes are bonded to the MoO₂ cores in planar fashion, coordinating through the phenolate O, imino N, and enolate O, and an oxo group lying trans to the nitrogen donor. In each complex, a methanol molecule completes the distorted octahedral coordination sphere which lying 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 cores and this position holds the possibility of functioning as a substrate binding site. The atoms O1, O2, O4, and N1 show high degree of planarity from the equatorial plane, the Mo atoms displaced by 0.332(1) Å for complex 1 and 0.320(1) Å for complex 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, 4f,13 The angular distortion in the octahedral environment around Mo atoms come from the five- and six-membered chelate rings taken by the hydrazones L¹ and L². For the same reason, the *trans* angles are significantly deviate from the ideal values of 180°. The hydrazones L¹ and L² in the complexes are distorted, with the two benzene rings make dihedral angles of 12.6(3)° for complex 1 and 9.2(3)° for complex 2. The bond lengths of C6–C7, C7–N1, N1–N2, N2–C8 and C8–O2 are comparable to those observed in similar hydrazone complexes.¹⁴

In the crystal structure of complex 1 (Figure 3), two symmetry related adjacent molecules are linked by the methanol molecules of each other through two intermolecular O3–H3A···N2 hydrogen bonds (Table 3), to form a dimeric moiety. The dimeric moieties are further linked *via* C–H···O interactions (Table 3), to form 3D network. In the crystal structure of complex 2 (Figure 4), two symme-

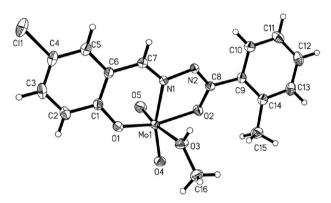


Figure 1. ORTEP plot of the crystal structure of **1.** Displacement ellipsoids of non-hydrogen atoms are drawn at the 30% probability level

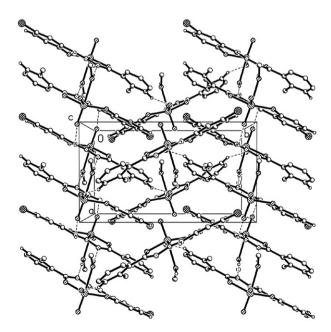


Figure 2. ORTEP plot of the crystal structure of **2.** Displacement ellipsoids of non-hydrogen atoms are drawn at the 30% probability level.

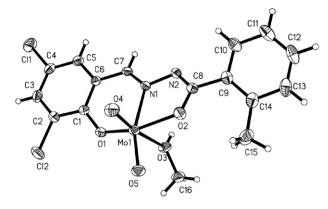


Figure 3. Molecular packing arrangement of **1** displayed in the unit cell. Hydrogen bonds are shown as dashed lines.

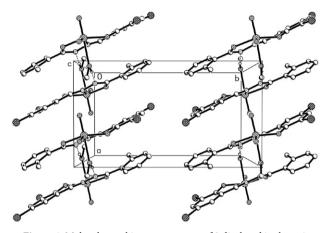


Figure 4. Molecular packing arrangement of **2** displayed in the unit cell. Hydrogen bonds are shown as dashed lines.

Table 3. Geometrical Parameters for Hydrogen Bonds

Hydrogen bonds	D-H (Å)	HA (Å)	DA (Å)	D-HA (°)	
		1			
O3-H3A···N2 ^{#1}	0.85(1)	1.97(1)	2.811(2)	173(4)	
C3-H3···O4 ^{#2}	0.93	2.59(1)	3.419(2)	148(4)	
C7-H7···O5 ^{#3}	0.93	2.55(1)	3.243(2)	131(4)	
C13-H13···O4 ^{#4}	0.93	2.53(1)	3.408(2)	157(4)	
2					
O3-H3A···N2 ^{#5}	0.90(1)	1.89(1)	2.788(3)	175(5)	

try related adjacent molecules are linked by the methanol molecules of each other through two intermolecular O3–H3A···N2 hydrogen bonds (Table 3), to form a dimeric moiety. In addition, there are π ··· π interactions among the rings Mo1-O2-C8-N2-N1, C1-C2-C3-C4-C5-C6 and C9-C10-C11-C12-C13-C14, with centroid to centroid distances of 3.67-4.58 Å for complex 1 and 3.69–4.41 Å for

complex **2**. The C4-Cl1··· π interactions between Cl1 atom with the ring C9-Cl0-Cl1-Cl2-Cl3-Cl4 also contribute to the crystal packing of both complexes, with distances of 3.705(3) Å for complex **1** and 3.944(3) Å for complex **2**.

3. 3. Infrared and Electronic Spectra

The hydrazones showed stretching bands attributed to C=O, C=N, C-OH and NH at about 1654, 1629, 1150 and 1225, and 3253 cm⁻¹. In addition, strong bands observed at 1612 cm⁻¹ for H₂L¹ and H₂L² are attributed to CH=N groups. 15 Both complexes exhibit intense bands at ca. 920 cm⁻¹, assigned to the vibrations of the MoO₂ cores. 16 The bands due to $v_{C=O}$ and v_{NH} are absent in the complexes, but new C-O stretches appeared at 1261 cm⁻¹ for both complexes. Keto-imine tautomerism is present in molecules H_2L^1 and H_2L^2 . Upon coordination to Mo atom, enol-imine tautomerism is present in ligands L^1 and L^2 . The $v_{C=N}$ absorption observed at 1629 cm⁻¹ in the free hydrazones shifted to 1603 cm⁻¹ for the complexes upon coordination to Mo atoms. 16 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 of the complexes.¹⁷

In the electronic spectra of the two complexes, the bands ranging from 250 to 340 nm are assigned to $n \to \pi^*$ transitions, and those at 210-230 nm assigned to $\pi \to \pi^*$ transitions. The bands with the maximum absorption at 400-410 nm are due to the ligand to metal charge transfer transition. The bands with the maximum absorption at 400-410 nm are due to the ligand to metal charge transfer transition.

3. 4. Catalytic Property

Oxidation of styrene was carried out at room temperature with the complexes as the catalysts and PhIO and NaOCl as oxidants. The orange color of the solutions containing the complexes and the substrate was intensified after the addition of oxidant indicating the formation of oxo-metallic intermediates of the catalysts. After completion of oxidation reaction of the alkene, the solution regains its initial color which suggests that the regeneration of the catalysts takes place.

The two complexes as catalysts convert styrene most efficiently in the presence of PhIO or NaOCl. There is no obvious difference for the catalytic properties between the two complexes, as a result of similar structures. The complexes are selective towards the formation of styrene epoxide. When the reactions were carried out with PhIO, styrene conversions are 83% and 85% for 1 and 2, respectively. When the reactions were carried out with NaOCl, styrene conversions are 71% and 74% for 1 and 2, respectively. It is evident that between the oxidants PhIO and NaOCl, the former acts as a better oxidant with respect to the styrene conversion. The two complexes have similar catalytic properties on the oxidation of styrene when compared to the manganese(III) complexes with the ligand *N,N'-o* -phenylenebis(3-ethoxysalicylaldimine). 11

Reaction of the oxidants with the complexes would likely generate a Mo-Cl or Mo-I entity, which further exchange Cl or I for ClO or IO, and homolytic cleavage of Mo-OCl or Mo-OI bond, generate effective epoxidising agent ClO or IO. Then, ClO or IO reacts with styrene to give the styrene epoxide.

4. Conclusion

New dioxidomolybdenum(VI) complexes with similar hydrazones have been prepared and structurally characterized by single crystal X-ray diffraction method, as well as elemental analysis and FT-IR spectra. The hydrazones coordinate to the ${\rm MoO}_2$ cores through the enolate oxygen, phenolate oxygen and azomethine nitrogen. Methanol is a suitable solvent for the preparation of such complexes, which readily coordinates to the Mo atom as a co-ligand. Different substituent groups in the benzene rings of the ligands can result in different molecular packing modes of the final molybdenum(VI) complexes. Both complexes have similar and effective catalytic oxidation property on styrene.

Supplementary Material

CCDC-943080 (1) and 943081 (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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Povzetek

Sintetizirali smo nove dioksidomolibdenove(VI) komplekse s formulo $[MoO_2L(MeOH)]$ z uporabo ligandov N'-(5-kloro-2-hidroksibenziiden)-2-metilbenzohidrazid (H_2L^1) in N'-(3,5-dikloro-2-hidroksibenziliden)-2-metilbenzohidrazid (H_2L^2) . Z rentgensko analizo na monokristalu smo določili kristalno in molekulsko strukturo obeh kompleksov. Obe spojini smo karakterizirali tudi z elementno analizo in FT-IR spektroskopijo. Strukturna analiza je pokazala, da se hidrazona L^1 in L^2 koordinirata na MoO_2 orko enolatnega kisika, fenolatnega kisika in azometinskega dušika. Atomi Mo so v obeh spojinah oktaedrično koordinirani. Preučevali smo katalitske lastnosti obeh spojin pri epoksidaciji stirena z uporabo oksidantov PhIO in NaOCl.



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