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Synthesis and Crystal Structures of Dioxomolybdenum(VI) Complexes With Catalytic Property

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Two new dioxomolybdenum(VI) complexes, $[MoO_2L^1(CH_3 OH)]$ (1) and $[MoO_2L^2(CH_3OH)]$ (2), where L^1 and L^2 are the dianionic form of isonicotinic acid (1-methyl-3-oxobutylidene) hydrazide and nicotinic acid (1-methyl-3-oxobutylidene)hydrazide, respectively, were prepared and structurally characterized by physicochemical and spectroscopic methods and single crystal X-ray determination. The complexes are mononuclear molybde-num compounds. The Mo atom in each complex is in octahedral coordination. The catalytic property of the complexes indicates that they are effective catalyst for sulfoxidation.

Keywords catalytic property, crystal structure, hydrazone, molybdenum complex, synthesis

INTRODUCTION

The mechanism of molybdenum oxotransferase has been received considerable interest for a long time. The synthesis, characterization, and reactivity studies of a number of dioxomolybdenum complexes with Schiff bases have been reported.^[1-4] Some of the complexes have been shown to possess oxygen atom transfer properties as they were found to oxidize thiols, hydrazine, polyketones, and tertiary phosphines.^[5,6] Sulfoxidation activity has been reported for molybdenum salts, composite metal oxides, molybdate doped porous carbons, and molybdenum-containing molecular sieves.^[7-10] The catalytic ability of dioxomolybdenum(VI) complexes with hydrazone ligands toward the oxidation of sulfides has received satisfactory results.^[11,12] However, the number of documented dioxomolybdenum(VI) complexes catalyzing the peroxidic oxidation of sulfides is still very limited. The search in the Cambridge Crystallographic Database (version 5.31 with addenda up to August, 2010)^[13] revealed that there were only 36 mono- and dinuclear molybdenum(VI) complexes with hydrazone ligands have been reported. In the present article, two new dioxomolybdenum(VI) complexes, $[MoO_2L^1(CH_3OH)]$ (1) and $[MoO_2L^2(CH_3OH)]$ (2), where L^1 and L^2 are the dianionic form of isonicotinic acid (1-methyl-3-oxobutylidene)hydrazide (H₂L¹; Scheme 1) and nicotinic acid (1-methyl-3-oxobutylidene)hydrazide (H₂L²; Scheme 1), respectively, are reported. The catalytic property of the complexes indicates that they are effective catalysts for sulfoxidation.

EXPERIMENTAL

All chemicals and solvents were of analytical reagent grade, and were purchased from Beijing Chemical Reagent Company (China). Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 elemental analyzer (Shanghai, China). Infrared spectra were carried out using the JASCO FT-IR model 420 spectrophotometer (Japan) with KBr disk in the region 4000–200 cm⁻¹. Electronic spectra were recorded on a Shimadzu UV 3101 spectrophotometer (Japan).

Syntheses of $[MoO_2L^1(CH_3OH)]$ (1)

A hot methanol solution (15 mL) of $MoO_2(acac)_2$ (0.33 g, 1 mmol) was added to a hot methanol solution (15 mL) of isonicotinohydrazide (0.14 g, 1 mmol). The mixture was stirred for 30 min at reflux, and then cooled to room temperature to give yellow solution. Single crystals suitable for X-ray diffraction were formed by slow evaporation of the methanol solution of the complex in air for a few days. Yield: 45%. Anal. Calcd. for $C_{12}H_{15}MoN_3O_5$: C, 38.2; H, 4.0; N, 11.1. Found: C, 38.0; H, 4.1; N, 11.2%.

Syntheses of $[MoO_2L^2(CH_3OH)]$ (2)

A hot methanol solution (15 mL) of $MoO_2(acac)_2$ (0.33 g, 1 mmol) was added to a hot methanol solution (15 mL) of nicotinohydrazide (0.14 g, 1 mmol). The mixture was stirred for 30 min at reflux, and then cooled to room temperature to give yellow solution. Single crystals suitable for X-ray diffraction were formed by slow evaporation of the methanol solution of the complex in air for a few days. Yield: 61%. Anal. Calcd. for $C_{12}H_{15}MoN_3O_5$: C, 38.2; H, 4.0; N, 11.1. Found: C, 38.1; H, 4.1; N, 11.2%.

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SCH. 1. The hydrazone ligands H_2L^1 (left) and H_2L^2 (right)

X-Ray Structure Determination

X-ray measurements were performed using a Bruker Smart 1000 CCD diffractometer (Germany) with graphite monochromated Mo Ka radiation ($\lambda = 0.71073$ Å) using the ω -scan technique. Determination of the Laue class, orientation matrix, and cell dimensions was performed according to the established procedures where Lorentz polarization and absorption corrections were applied. Absorption corrections were applied by fitting a pseudoellipsoid to the ψ -scan data of selected strong reflections over a wide range of 2θ angles. The positions of non-hydrogen atoms were located with direct methods. Subsequent Fourier syntheses were used to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. The methanol H atoms in both complexes were located from difference Fourier maps and refined isotropically, with O-H distances restrained to 0.85(1) Å. The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The analyses were performed with the aid of the SHELXS-97 and SHELXL-97 suite of codes (Germany).^[14,15] The crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bonds are listed in Table 3.

RESULTS AND DISCUSSION

The dioxomolybdenum(VI) complexes were synthesized by the reaction of the $MoO_2(acac)_2$ with isonicotinohydrazide and nicotinohydrazide, respectively, in methanol in a 1:1 mole proportion at reflux. The ligands H_2L^1 and H_2L^2 were formed by the condensation reaction of isonicotinohydrazide and nicotinohydrazide with acetylacetone come from $MoO_2(acac)_2$, respectively. The reaction progress (Scheme 2) is accompanied by a color change of the solution from colorless to yellow. We attempted to prepare and grow diffraction quality crystals from various solvents; however, good quality crystals were finally obtained from methanol. The chemical formulae of the com-

TABLE 1Crystal data for the complexes

	1	2
Chemical formula	C ₁₂ H ₁₅ MoN ₃ O ₅	C ₁₂ H ₁₅ MoN ₃ O ₅
Fw	377.2	377.2
Crystal shape/color	Block/yellow	Block/yellow
Crystal size (mm)	0.32×0.30	0.32×0.30
	$\times 0.30$	$\times 0.30$
T (K)	298(2)	298(2)
λ (MoK α) (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	Cc	$P2_1/n$
<i>a</i> (Å)	14.279(2)	7.847(1)
<i>b</i> (Å)	7.676(1)	8.012(1)
<i>c</i> (Å)	14.087(2)	23.477(2)
β (°)	112.216(1)	96.597(2)
V (Å ³)	1429.4(3)	1466.2(3)
Ζ	4	4
μ (MoK α) (cm ⁻¹)	0.943	0.919
T (min)	0.752	0.852
T (max)	0.765	0.859
$D_c ({\rm g}{\rm cm}^{-3})$	1.753	1.709
Reflections/parameters	2532/196	3161/196
Restraints	3	1
Unique reflections	2161	2674
Goodness of fit on F^2	1.034	1.108
R _{int}	0.0163	0.0218
$R_1 \left[I \ge 2\sigma(I) \right]$	0.0232	0.0325
$wR_2 [I \ge 2\sigma(I)]$	0.0547	0.0723
R_1 (all data)	0.0290	0.0419
wR_2 (all data)	0.0585	0.0765

plexes have been confirmed by elemental analyses, IR spectra, and X-ray single-crystal structure determination.

Structure Description of the Complexes

The molecular structures of the complexes are shown in Figures 1 and 2, respectively. The structures of the complexes are very similar to each other. In each of the complexes, the coordination geometry around the Mo atom can be described as slightly distorted octahedral, with one imino N and two enolic



SCH. 2. The preparation of the complexes. For 1, X = N, Y = C; for 2, X = C, Y = N.

Selected bond lengths (Å) and angles (°) for the complexes						
1						
Bond lengths						
Mo1-O1	2.008(2)	Mo1-O2	1.958(3)			
Mo1-O3	2.351(3)	Mo1-O4	1.681(3)			
Mo1-O5	1.698(3)	Mo1-N3	2.214(3)			
Bond angles						
O4-Mo1-O5	105.3(2)	O4-Mo1-O2	98.0(1)			
O5-Mo1-O2	101.4(1)	O4-Mo1-O1	97.6(1)			
O5-Mo1-O1	96.4(1)	O2-Mo1-O1	152.2(1)			
O4-Mo1-N3	97.8(1)	O5-Mo1-N3	155.7(1)			
O2-Mo1-N3	82.1(1)	O1-Mo1-N3	73.1(1)			
O4-Mo1-O3	173.0(1)	O5-Mo1-O3	81.6(1)			
O2-Mo1-O3	81.2(1)	O1-Mo1-O3	80.6(1)			
N3-Mo1-O3	75.2(1)					
2						
Bond lengths						
Mo1-O1	2.000(2)	Mo1-O2	1.946(2)			
Mo1-O3	2.376(2)	Mo1-O4	1.694(3)			
Mo1-O5	1.704(2)	Mo1-N3	2.226(2)			
Bond angles						
O4-Mo1-O5	105.7(1)	O4-Mo1-O2	97.9(1)			
O5-Mo1-O2	101.7(1)	O4-Mo1-O1	98.0(1)			
O5-Mo1-O1	96.6(1)	O2-Mo1-O1	151.5(1)			
O4-Mo1-N3	97.9(1)	O5-Mo1-N3	155.3(1)			
O2-Mo1-N3	81.9(1)	O1-Mo1-N3	72.6(1)			
O4-Mo1-O3	173.2(1)	O5-Mo1-O3	81.1(1)			
O2-Mo1-O3	80.2(1)	O1-Mo1-O3 81.3(1)				
N3-Mo1-O3	75.4(1)					

TABLE 2

 TABLE 3

 Distances (Å) and angles (°) involving hydrogen bonding of the complexes

<i>D</i> -H···A	<i>d</i> (<i>D</i> -H)	$d(\mathbf{H} \cdots A)$	$d(D \cdots A)$	Angle $(D-H\cdots A)$
$ \frac{1}{03-H3\cdots N1^{i}} $	0.85(1)	1.84(1)	2.676(4)	171(5)
$O3-H3\cdots N1^{ii}$	0.85(1)	1.88(1)	2.724(3)	178(4)
Symmetry coo	des: i) $1/2 + x$	x, -1/2 - y, 1/2	(2 + z; ii) 1 -	x, 1-y, 1-z.

O atoms of the dianionic hydrazone ligand, and with one oxo O atom defining the equatorial plane, and with one O atom of a methanol ligand and the other oxo O atom occupying the axial positions. The hydrazone ligands coordinate to the Mo atoms in meridional fashion forming five- and six-membered chelate rings with bite angles of 73.1(1) and $82.1(1)^{\circ}$ for **1**, and 72.6(1) and $81.9(1)^{\circ}$ for **2**. The displacement of the Mo atoms



FIG. 1. Molecular structure of 1 with 30% probability thermal ellipsoids.

from the equatorial mean planes toward the apical oxo atoms O4 are 0.335(2) Å for **1** and 0.342(2) Å for **2**. The hydrazone ligands are coordinated in their dianionic enolic forms, which are evident from the C6–O1, C6–N2, C8–C9, and C9–O2 bond lengths (Table 2). The Mo–O, Mo–N, and Mo = O bonds are within normal ranges and are similar to those observed in similar dioxomolybdenum(VI) complexes.^[16–20]

In the crystal structure of 1, the complex molecules are linked through intermolecular O—H···N hydrogen bonds to form 1D chains, as shown in Figure 3. In the crystal structure of 2, adjacent two complex molecules are linked through intermolecular O—H···N hydrogen bonds to form a dimer, as shown in Figure 4.

IR Spectra

The weak bands centered at about 3435 cm^{-1} in the IR spectra of the complexes can be assigned to the ν_{OH} vibrations of the methanol ligands. For both complexes, the Mo=O stretching



FIG. 2. Molecular structure of 2 with 30% probability thermal ellipsoids.



FIG. 3. Molecular packing of 1, viewed along the *b* axis. Hydrogen bonds are drawn as thin dashed lines.

modes occur as a pair of sharp strong bands at about 940 and 910 cm⁻¹, assigned to the antisymmetric and symmetric stretching modes of the dioxomolybdenum(VI) moieties. The bands due to the $v_{C=O}$ and v_{NH} were absent in the complexes, and new C–O stretches appear at 1252–1260 cm⁻¹. This suggests occurrence of ketoimine tautomerization of the hydrazone ligands during the coordination. The strong bands indicative of the C=N–N=C groups in the complexes are shifted to 1612 cm⁻¹ for the complexes. The new weak peaks observed in the range 350–800 cm⁻¹ may be attributed to the Mo–O and Mo–N vibrations in the complexes. The IR spectra of the two complexes are similar to each other, indicating the complexes are of the similar structures, as evidenced by the single crystal X-ray determination.



FIG. 4. Molecular packing of 2, viewed along the *b* axis. Hydrogen bonds are drawn as thin dashed lines.

Catalytic Property

The catalytic oxidation tests of the complexes on the oxidation of sulfides under homogeneous conditions in solution using methyl phenyl sulfide (thioanisol) as substrate were carried out according to the literature method.^[12] As oxidant hydrogen peroxide was used in a slight excess of 1.25 equivalents based on the sulfide substrate. Reactions were run with 1 mol% of catalyst based on the substrate at a temperature of 10°C. The reaction was started by the addition of hydrogen peroxide. A control reaction under the same condition without any complex present leads to less than 1% sulfide conversion within 4 h. In the presence of the complexes conversions of about 76% for 1 and 73% for 2 of sulfide to the corresponding sulfoxide within 30 min reaction time were observed. After about 2 h in all cases the conversions of total amount of sulfide were complete. Under the given conditions no over oxidation to the sulfone could be detected.

CONCLUSION

In summary, two new dioxomolydenum(VI) complexes with similar hydrozone ligands isonicotinic acid (1-methyl-3-oxobutylidene)hydrazide and nicotinic acid (1-methyl-3oxobutylidene)hydrazide, respectively, have been prepared and structurally characterized. The hydrazone ligands coordinate to the Mo atoms through the imino N and ethanolic O atoms. The Mo atoms in the complexes are in octahedral coordination. The complexes have effective catalytic property to the oxidation of sulfides. The position of the N atom in the pyridine ring plays no obvious role for the catalytic procedure.

SUPPLEMENTARY MATERIALS

CCDC 854396 (1) and 854397 (2) contain the supplementary crystallographic data for the complexes. These data can be obtained free of charge *via* http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223–336-033; or email: deposit@ccdc.cam.ac.uk.

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