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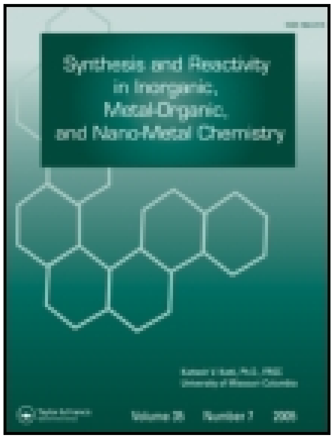

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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Synthesis, Crystal Structure and Catalytic Property of a Dioxomolybdenum(VI) Complex Derived From N′-[1-(2-Hydroxynaphthyl)ethylidene]-3-methylbenzohydrazide

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A new dioxomolybdenum(VI) complex, $[MoO_2L(CH_3OH)]\cdot CH_3OH$, where L is the dianionic form of *N'*-[1-(2-hydroxynaphthyl)ethylidene]-3-methylbenzohydrazide, was prepared and structurally characterized by physicochemical and spectroscopic methods and single crystal X-ray determination. The complex is a mononuclear molybdenum compound. The Mo atom is in octahedral coordination. The catalytic property of the complex indicates that it is an effective catalyst for sulfoxidation.

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

INTRODUCTION

The mechanism of molybdenum oxotransferase has been extensively investigated 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] Even though, 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] has revealed that there were only 36 mono- and dinuclear molybdenum(VI) complexes with hydrazone ligands reported. In the present article, a new dioxomolybdenum(VI) complex, $[MoO_2L(CH_3OH)]\cdot CH_3OH$, with the hydrazone ligand *N'*-[1-(2-hydroxynaphthyl)ethylidene]-3-methylbenzohydrazide (H_2L; Scheme 1), has been reported. The catalytic property of the complex indicates that it is an effective catalyst for sulfoxidation.

EXPERIMENTAL

All chemicals and solvents were of analytical reagent grade, and were purchased from Beijing Chemical Reagent Company. Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 elemental analyzer. Infrared spectra were carried out using the JASCO FT-IR model 420 spectrophotometer with KBr disk in the region 4000–200 cm^{-1}. Electronic spectra were recorded on a Shimadzu UV 3101 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 300 and 500 MHz spectrometers.

Synthesis of H_2L

2-acetylnaphthol (1.86 g, 0.01 mol) dissolved in methanol (30 ml) was added to a stirred methanol solution (20 ml) of 3-methylbenzohydrazide (1.50 g, 0.01 mol). The mixture was refluxed for 2 h on a water bath, and the solvent was evaporated to give colorless solid product. The product was recrystallized from methanol and dried in air. Yield: 91%. Anal. Calcd. for $C_{20}H_{18}N_2O_2$: C, 75.4; H, 5.7; N, 8.8. Found: C, 75.2; H, 5.7; N, 8.9%. ^1H NMR ($CDCl_3$): δ (ppm) 2.32 (s, 3H), 3.56 (s, 3H), 7.37 (q, 1H), 7.48 (d, 1H), 7.67–7.75 (m, 4H), 7.87 (m, 2H), 8.10 (d, 1H), 8.23 (d, 1H). 10.12 (b, 1H).

Syntheses of $[MoO_2L(CH_3OH)]\cdot CH_3OH$

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 H_2L (0.32 g, 1 mmol). The mixture was stirred for 30 min at reflux, and then cooled to room temperature, to give red 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 $C_{22}H_{24}MoN_2O_6$: C, 52.0; H, 4.8; N, 5.5. Found: C, 51.8; H, 4.9; N, 5.6%.

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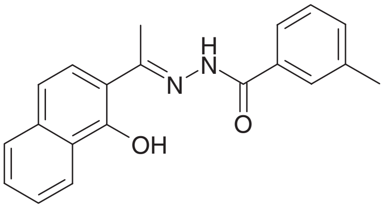


SCH. 1. The hydrazone ligand H_2L.

X-Ray Structure Determination

X-ray measurement was performed using a Bruker Smart 1000 CCD diffractometer 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 were 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. Hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The analysis was performed with the aid of the SHELXS-97 and SHELXL-97 suite of codes.[14,15] The crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

TABLE 1
Crystal data for the complex

Chemical formula	$C_{22}H_{24}MoN_2O_6$
Fw	508.4
Crystal shape/color	Block/red
Crystal size (mm)	0.12 × 0.10 × 0.09
T (K)	298(2)
λ (MoKα) (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.910(3)
b (Å)	21.146(3)
c (Å)	10.415(3)
β (°)	93.650(3)
V (Å^3)	2178.1(9)
Z	4
μ (MoKα) (cm^{-1})	0.643
T (min)	0.9268
T (max)	0.9444
D_c (g cm^{-3})	1.550
Reflections/parameters	3753/285
Unique reflections	2173
Goodness of fit on F^2	1.065
R_{int}	0.0651
R_1 [$I \geq 2\sigma(I)$]	0.0613
wR_2 [$I \geq 2\sigma(I)$]	0.1621
R_1 (all data)	0.1102
wR_2 (all data)	0.2152

RESULTS AND DISCUSSION

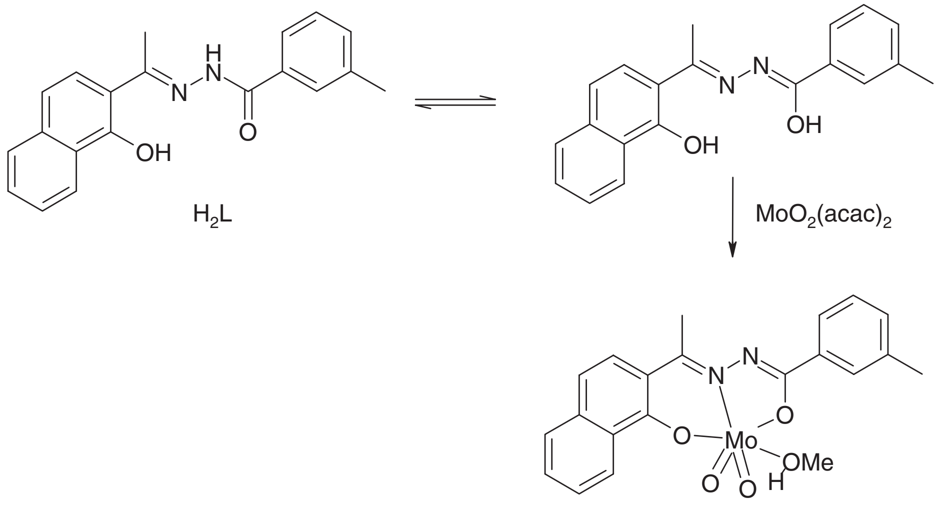
The hydrazone ligand was readily prepared by the condensation reaction of 2-acetylnaphthol with 3-methylbenzohydrazide in methanol, with high yield and purity. The dioxomolybdenum(VI) complex was synthesized by the reaction of the hydrazone ligand and $MoO_2(acac)_2$ in methanol in a 1:1 mole proportion at reflux. The reaction progress (Scheme 2) is accompanied by a color change of the solution from colorless to red. We have attempted to prepare and grow diffraction quality crystals from various solvents; however, good quality crystals were finally obtained from methanol. The chemical formula of the complex has been confirmed by elemental analyses, IR spectra, and X-ray single crystal structure determination.

Structure Description of the Complex

The molecular structure of the complex is shown in Figure 1. The compound consists of a mononuclear $[MoO_2L(CH_3OH)]$ complex and a methanol molecule of crystallization. The coordination geometry around the Mo atom can be described as a slightly distorted octahedral geometry, with the phenolic O, imino N, and enolic 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 ligand coordinates to the Mo atom in a meridional fashion forming five- and six-membered chelate rings with bite angles of 73.2(2)° and 81.2(2)°, respectively. The dihedral angle between the benzene ring and the naphthyl ring of the hydrazone ligand is 2.8(3)°. The displacement of the Mo atom from

TABLE 2
Selected bond lengths (Å) and angles (°) for the complex

(**1**)			
Bond lengths			
Mo1-O1	1.905(5)	Mo1-O2	1.978(5)
Mo1-O3	2.405(6)	Mo1-O4	1.696(5)
Mo1-O5	1.620(7)	Mo1-N1	2.227(5)
Bond angles			
O5-Mo1-O4	104.3(3)	O5-Mo1-O1	100.0(3)
O4-Mo1-O1	102.3(2)	O5-Mo1-O2	98.0(2)
O4-Mo1-O2	95.8(2)	O1-Mo1-O2	150.3(2)
O5-Mo1-N1	97.6(3)	O4-Mo1-N1	156.8(2)
O1-Mo1-N1	81.16(19)	O2-Mo1-N1	73.25(19)
O5-Mo1-O3	173.4(3)	O4-Mo1-O3	82.1(2)
O1-Mo1-O3	79.6(2)	O2-Mo1-O3	79.8(2)
N1-Mo1-O3	75.8(2)		



SCH. 2. The preparation of the complex.

the equatorial mean plane toward the apical oxo atom O5 is 0.343(2) Å. The hydrazone ligand is coordinated in its dianionic form, which is evident from the N2–C13 and O2–C13 bond lengths with values of 1.275(9) and 1.339(9) Å, respectively, indicating the presence of the enolate form of the ligand amide group. 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 the complex, the [MoO$_2$L(CH$_3$OH)] units are linked by methanol molecules through intermolecular O—H···O hydrogen bonds to form chains running along the *c* axis, as shown in Figure 2.

IR Spectra

The weak band centered at 3378 cm^{-1} in the IR spectrum of the complex can be assigned to the ν_{OH} vibration of the methanol molecule. The hydrazone ligand shows stretching bands attributed to C = O, C = N, C-OH, and NH at about 1665, 1643, 1182, and 3213 cm^{-1}, respectively. The Mo = O stretching modes occur as a pair of sharp strong bands at 937 and 872 cm^{-1}, assigned to the antisymmetric and symmetric stretching mode of the dioxomolybdenum(VI) moiety. The bands due to the $\nu_{C=O}$ and ν_{NH} were absent in the complex, and new C–O stretch appears at 1257 cm^{-1}. This suggests occurrence of keto-imine tautomerization of the hydrazone ligand during the

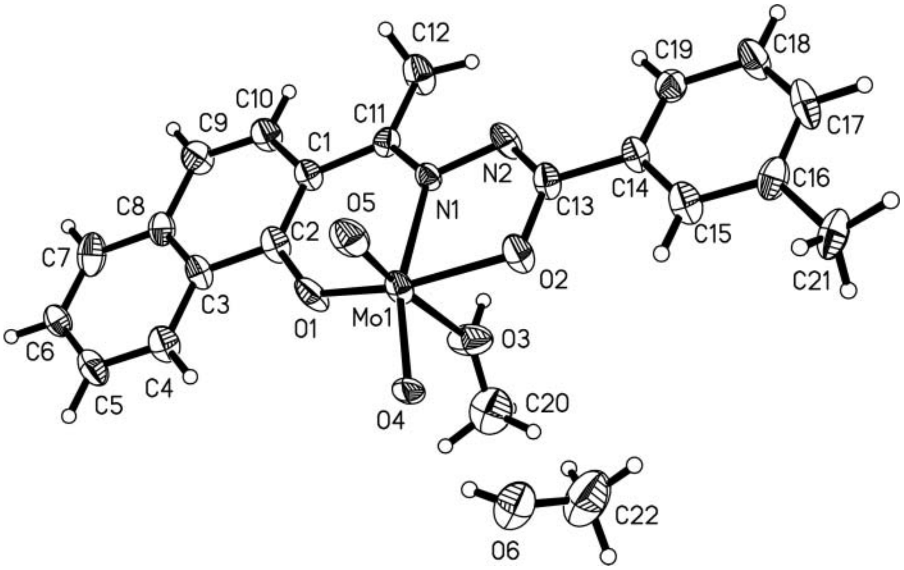


FIG. 1. Molecular structure of (**1**) with 30% probability thermal ellipsoids.

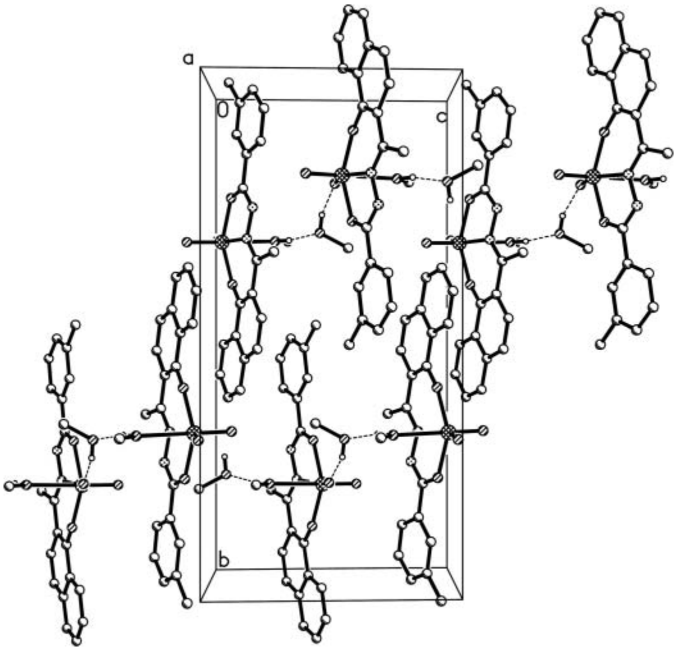


FIG. 2. Molecular packing of (**1**), viewed along the *a* axis.

coordination. The strong band indicative of the C = N–N = C group in the complex is shifted to 1606 cm^{-1} for the complex. The $\nu_{C=N}$ appear at 1620 cm^{-1} in the complex. The new weak peaks observed in the range 400–800 cm^{-1} may be attributed to the Mo–O and Mo–N bonds in the complex. The comparison of the IR spectra of the free hydrazone ligand and the dioxomolybdenum(VI) complex confirms the enolate coordination mode of the ligand.

Catalytic Property

The catalytic oxidation test of the complex on the oxidation of sulfides under homogeneous conditions in solution using methyl phenyl sulfide (thioanisol) as substrate was 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 are 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 both complexes a conversion of about 70% of sulfide to the corresponding sulfoxide within 30 min reaction time was observed. After about 2 h in all cases the conversion of total amount of sulfide was complete. Under the given conditions no over oxidation to the sulfone could be detected.

CONCLUSION

In summary, a new dioxomolydenum(VI) complex with the hydrozone ligand *N'*-[1-(2-hydroxynaphthyl)ethylidene]-3-methylbenzohydrazide has been prepared and structurally characterized. The hydrazone ligand coordinates to the Mo atoms through the phenolic O, imino N, and ethanolic O atoms. The Mo atom is in an octahedral coordination. The complex has effective catalytic property to the oxidation of sulfides.

SUPPLEMENTARY MATERIALS

CCDC 813898 contains the supplementary crystallographic data for the complex. 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 e-mail: deposit@ccdc.cam.ac.uk.

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