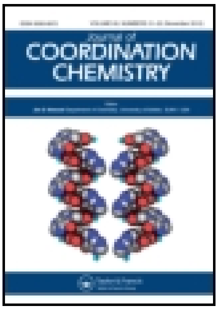
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:42
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Syntheses, crystal structures, and catalytic properties of dioxomolybdenum(VI) complexes with hydrazone ligands

Nan-Yan Jin [a]

[a] College of Chemical Engineering and Pharmacy, Jingchu University of Technology , Jingmen , Hubei 448000 , P.R. China

Accepted author version posted online: 18 Sep 2012.Published online: 01 Oct 2012.

To cite this article: Nan-Yan Jin (2012) Syntheses, crystal structures, and catalytic properties of dioxomolybdenum(VI) complexes with hydrazone ligands, Journal of Coordination Chemistry, 65:22, 4013-4022, DOI: 10.1080/00958972.2012.731049

To link to this article: http://dx.doi.org/10.1080/00958972.2012.731049

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Journal of Coordination Chemistry
Vol. 65, No. 22, 20 November 2012, 4013–4022

Taylor & Francis
Taylor & Francis Group

Syntheses, crystal structures, and catalytic properties of dioxomolybdenum(VI) complexes with hydrazone ligands

NAN-YAN JIN*

College of Chemical Engineering and Pharmacy, Jingchu University of Technology,
Jingmen, Hubei 448000, P.R. China

(*Received 20 May 2012; in final form 13 August 2012*)

Two new dioxomolybdenum(VI) complexes, $[MoO_2L^1(CH_3OH)]$ (**1**) and $[MoO_2L^2(H_2O)]$ (**2**), where L^1 and L^2 are dianionic form of *N′*-(2-hydroxy-3-methoxybenzylidene)-4methoxybenzohydrazide and *N′*-(2-hydroxy-3methoxybenzylidene)-2-hydroxybenzohydrazide, respectively, have been synthesized and structurally characterized by spectroscopic methods and single-crystal X-ray determination. The complexes are mononuclear molybdenum(VI) compounds. Mo in each complex is octahedral. The difference in the substituent groups in the benzohydrazides leads to coordination of different solvent molecules. Crystals of the complexes are stabilized by hydrogen bonds. The complexes are effective catalysts for sulfoxidation.

Keywords: Hydrazone; Molybdenum complex; Crystal structure; Hydrogen-bonding; Sulfoxidation

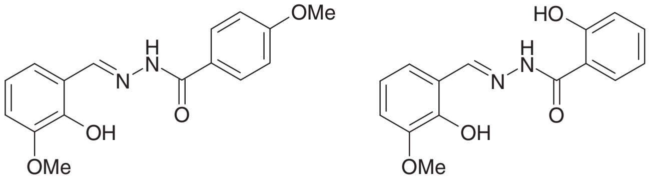
1. Introduction

The mechanism of molybdenum oxotransferase has received considerable interest. The synthesis, characterization, and reactivity of a number of dioxomolybdenum complexes with Schiff bases have been reported [1–4]. Some of the complexes possess oxygen atom transfer properties as they oxidize thiols, hydrazone, polyketones, and tertiary phosphines [5, 6]. Sulfoxidation activity has been reported for molybdenum salts, composite metal oxides, molybdate doped porous carbon atoms, and molybdenum containing molecular sieves [7–10]. The catalytic ability of dioxomolybdenum(VI) complexes with hydrazone ligands toward 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. In this article, two new dioxomolybdenum(VI) complexes, $[MoO_2L^1(CH_3OH)]$ (**1**) and $[MoO_2L^2(H_2O)]$ (**2**), where L^1 and L^2 are the dianions of *N′*-(2-hydroxy-3methoxybenzylidene)-4-methoxybenzohydrazide (H_2L^1; scheme 1) and *N′*-(2-hydroxy-3-methoxybenzylidene)-2-hydroxybenzohydrazide (H_2L^2; scheme 1), respectively, have been prepared, structurally characterized, and investigated for peroxidic oxidation of sulfides.

---

*Email: nanyanjin@163.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.731049



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

2. Experimental

2.1. *Materials and methods*

All chemicals and solvents of analytical reagent grade were used as received. Microanalyses (C, H, and N) were performed using a Perkin-Elmer 2400 elemental analyzer. ^{1}H NMR spectra were recorded on a Bruker Avance 200 spectrometer. Infrared (IR) spectra were carried out using the JASCO FT-IR model 420 spectrophotometer with KBr discs from 4000 to 200 cm^{-1}.

2.2. *Syntheses of H_2L^1 and H_2L^2*

H_2L^1 and H_2L^2 were prepared by similar procedure. 3-Methoxysalicylaldehyde (0.152 g, 1 mmol) dissolved in methanol (50 mL) was added to a stirred methanol solution (30 mL) of substituted benzohydrazide, namely 4-methoxybenzohydrazide (0.166 g, 1 mmol) for H_2L^1 and 2-hydroxybenzohydrazide (0.152 g, 1 mmol) for H_2L^2. Then the reaction mixtures were refluxed for 2 h on a water bath, and the solvent was evaporated to give colorless solid products. Yields: 92% for H_2L^1 and 95% for H_2L^2. Anal. Calcd for $C_{16}H_{16}N_2O_4$ (H_2L^1; %): C, 64.0; H, 5.4; N, 9.3. Found (%): C, 63.8; H, 5.4; N, 9.4. Anal. Calcd for $C_{15}H_{14}N_2O_4$ (H_2L^2; %): C, 62.9; H, 4.9; N, 9.8. Found (%): C, 62.8; H, 5.0; N, 9.9.

2.3. *Synthesis of $[MoO_2L^1(CH_3OH)]$ (1)*

A hot methanol solution (10 mL) of $MoO_2(acac)_2$ (0.033 g, 0.1 mmol) was added to a hot methanol solution (10 mL) of H_2L^1 (0.030 g, 0.1 mmol). The resulting brown solution was stirred for 10 min at reflux, and then cooled to room temperature, to give brown 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: 51%. Anal. Calcd for $C_{17}H_{18}MoN_2O_7$ (%): C, 44.6; H, 4.0; N, 6.1. Found (%): C, 44.4; H, 3.9; N, 6.2.

2.4. *Synthesis of $[MoO_2L^2(H_2O)]$ (2)*

A hot methanol solution (10 mL) of $MoO_2(acac)_2$ (0.033 g, 0.1 mmol) was added to a hot methanol solution (10 mL) of H_2L^2 (0.029 g, 0.1 mmol). The resulting brown solution was stirred for 10 min at reflux, and then cooled to room temperature, to give brown 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: 63%. Anal. Calcd for $C_{15}H_{14}MoN_2O_7$ (%): C, 41.9; H, 3.3; N, 6.5. Found (%): C, 41.8; H, 3.4; N, 6.5.

2.5. *X-ray structure determination*

X-ray measurements were performed using a Bruker Smart 1000 CCD diffractometer with graphite monochromated Mo-Kα 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 almost all 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 hydrogen atoms in **1** and the water hydrogen atoms in **2** were located from difference Fourier maps and refined isotropically, with O–H, N–H, and H···H distances restrained to 0.85(1), 0.90(1), and 1.37(2) Å, respectively. Other hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The analysis was performed with SHELXS-97 and SHELXL-97 suite [13, 14]. 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.

2.6. *Catalytic oxidation*

The molybdenum complex ($0.001\ \mathrm{mol\,L^{-1}}$) and phenyl methyl sulfide ($0.1\ \mathrm{mol\,L^{-1}}$) were dissolved at room temperature in a mixture of CH_2Cl_2 and CH_3OH (6:4) together with 1,3,5-trimethoxybenzene ($0.1\ \mathrm{mol\,L^{-1}}$) as an internal standard. The resulting solution was cooled to 283 K and H_2O_2 (35% w/w) added dropwise ($0.125\ \mathrm{mol\,L^{-1}}$). An aliquot of the reaction solution (2.0 mL) was quenched with 5 mL of a stock solution of Na_2SO_3 ($0.1\ \mathrm{mol\,L^{-1}}$) at 60 min and 2 h, and extracted with dichloromethane (three times 4 mL). From the collected organic phases the solvent was removed under reduced pressure to dryness and the residue was redissolved in deuterated chloroform (0.6 mL) and analyzed by ^{1}H NMR to determine the yield with reference to the internal standard 1,3,5-trimethoxybenzene.

3. Results and discussion

3.1. *Syntheses*

The hydrazones were readily prepared by condensation of 4-methoxysalicylaldehyde with 4-methoxybenzohydrazide and 2-hydroxybenzohydrazide, respectively, in methanol, with no side-products. The dioxomolybdenum(VI) complexes were synthesized by reaction of $MoO_2(acac)_2$ with the hydrazones in methanol in a 1 : 1 mole proportion

Table 1. Crystal data for **1** and **2**.

Complex	**1**	**2**
Chemical formula	$C_{17}H_{18}MoN_2O_7$	$C_{15}H_{14}MoN_2O_7$
Formula weight	458.27	430.22
Crystal shape/color	Block/brown	Block/brown
Crystal size (mm^3)	$0.15 \times 0.13 \times 0.12$	$0.27 \times 0.27 \times 0.26$
Temperature (K)	298(2)	298(2)
Wavelength (Mo-Kα) (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
Unit cell dimensions (Å, °)		
a	13.104(1)	8.343(2)
b	9.939(1)	10.570(3)
c	14.970(2)	10.602(3)
α	90	75.193(2)
β	112.509(1)	72.384(2)
γ	90	67.541(2)
Volume ($Å^3$), Z	1801.2(4), 4	813.1(4), 2
Absorption coefficient (Mo-Kα) (cm^{-1})	0.771	0.848
Temperature (min)	0.8931	0.8033
Temperature (max)	0.9131	0.8096
Calculated density ($g\,cm^{-3}$)	1.690	1.757
Reflections/parameters	3922/250	3419/234
Unique reflections	3356	2559
Restraints	1	3
Goodness of fit on F^2	1.083	1.037
R_{int}	0.0203	0.0421
R_1 [$I \geq 2\sigma(I)$]	0.0257	0.0478
wR_2 [$I \geq 2\sigma(I)$]	0.0610	0.1081
R_1 (all data)	0.0331	0.0702
wR_2 (all data)	0.0646	0.1214

at reflux. The reaction (scheme 2) is accompanied by a color change of the solution from colorless to yellow. The chemical formulae of the complexes have been confirmed by elemental analyses, IR spectra, and single-crystal X-ray structure determinations. Methanol, ethanol, and water readily coordinate to Mo, generating six-coordinate octahedral geometry. The only difference between the two hydrazones is the substituent of the benzohydrazides, which leads to coordination of different solvents.

3.2. *Crystal structure description*

The molecular structures of the complexes are shown in figures 1 and 2. The structures of the complexes are very similar, except for the small difference in the hydrazone ligands and the solvent. The coordination geometry around Mo can be described as slightly distorted octahedral. In **1**, the equatorial plane is defined by phenolic O, imino N, and enolic O of the dianionic hydrazone ligand L^1, and by one oxo, and the two axial positions are occupied by methanol and the other oxo. In **2**, the equatorial plane is defined by the phenolic O, imino N, and enolic O of L^2, and by one oxo, and the two axial positions are occupied by water and the other oxo. The hydrazone ligands coordinate to Mo meridional forming five- and six-membered chelate rings with bite angles of 71.3(1)° and 81.1(1)° for **1** and 71.8(1)° and 81.2(1)° for **2**. Dihedral angles

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

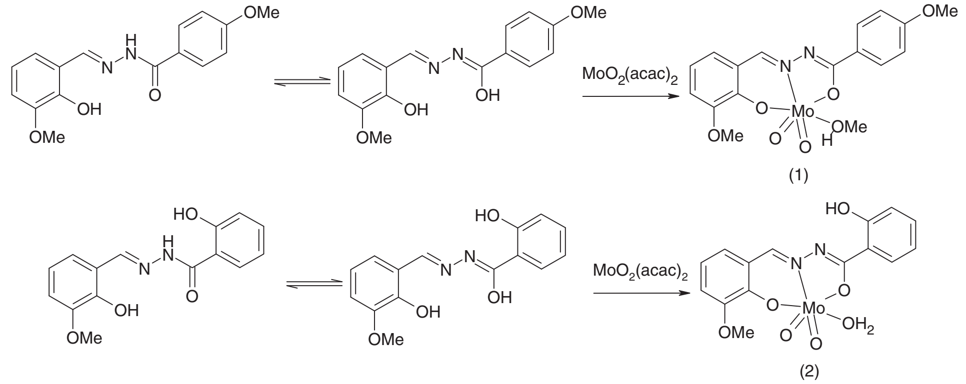
1			
Bond lengths			
Mo1–O1	1.9156(15)	Mo1–O3	2.0092(14)
Mo1–O5	1.6972(15)	Mo1–O6	2.3861(16)
Mo1–O7	1.6897(17)	Mo1–N1	2.2347(16)
Bond angles			
O7–Mo1–O5	106.06(8)	O7–Mo1–O1	100.46(8)
O5–Mo1–O1	102.35(7)	O7–Mo1–O3	96.77(7)
O5–Mo1–O3	97.70(7)	O1–Mo1–O3	148.66(6)
O7–Mo1–N1	95.52(7)	O5–Mo1–N1	156.97(7)
O1–Mo1–N1	81.07(6)	O3–Mo1–N1	71.33(6)
O7–Mo1–O6	171.51(7)	O5–Mo1–O6	81.20(7)
O1–Mo1–O6	81.91(6)	O3–Mo1–O6	77.62(6)
N1–Mo1–O6	76.72(6)		
2			
Bond lengths			
Mo1–O1	1.920(3)	Mo1–O3	2.017(3)
Mo1–O5	1.688(3)	Mo1–O6	2.292(3)
Mo1–O7	1.683(4)	Mo1–N1	2.248(3)
Bond angles			
O7–Mo1–O5	105.9(2)	O7–Mo1–O1	98.6(2)
O5–Mo1–O1	102.9(2)	O7–Mo1–O3	96.0(2)
O5–Mo1–O3	98.1(2)	O1–Mo1–O3	149.9(1)
O7–Mo1–N1	93.6(1)	O5–Mo1–N1	159.1(2)
O1–Mo1–N1	81.2(1)	O3–Mo1–N1	71.8(1)
O7–Mo1–O6	170.0(1)	O5–Mo1–O6	83.8(2)
O1–Mo1–O6	81.3(1)	O3–Mo1–O6	79.8(1)
N1–Mo1–O6	76.5(1)		

Table 3. Distances (Å) and angles (°) involving hydrogen-bonding of the complexes.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠ (D–H···A)
1				
O6–H6A···N2^{i}	0.85(1)	1.98(1)	2.808(2)	171(3)
2				
O4–H4···N2	0.82	1.85	2.573(4)	146
O6–H6A···O4^{i}	0.85(1)	1.90(5)	2.748(4)	178(8)
O6–H6B···O2^{ii}	0.85(1)	2.10(5)	2.811(5)	141(7)
O6–H6B···O1^{ii}	0.85(1)	2.24(4)	2.983(4)	146(7)

Symmetry codes: ^{i} $-x$, $1-y$, $1-z$; ^{ii} $1-x$, $1-y$, $-z$.

between the two substituted benzene rings of the hydrazone ligands are 0.4(3)° for **1** and 3.8(3)° for **2**, indicating the ligands are nearly coplanar. Displacements of Mo from the equatorial mean planes toward the apical oxo O7 are 0.344(2) Å for **1** and 0.308(2) Å for **2**. The hydrazone ligands are coordinated as dianions, evident from the N2–C8 and O3–C8 bond lengths with values of 1.308(3) and 1.313(2) Å for **1** and 1.306(5) and 1.309(5) Å for **2**, indicating the presence of the enolate form of the amide. The Mo–O, Mo–N, and Mo=O bonds are within normal ranges and similar to those observed in similar dioxomolybdenum(VI) complexes [15–19].



Scheme 2. Preparation of the complexes.

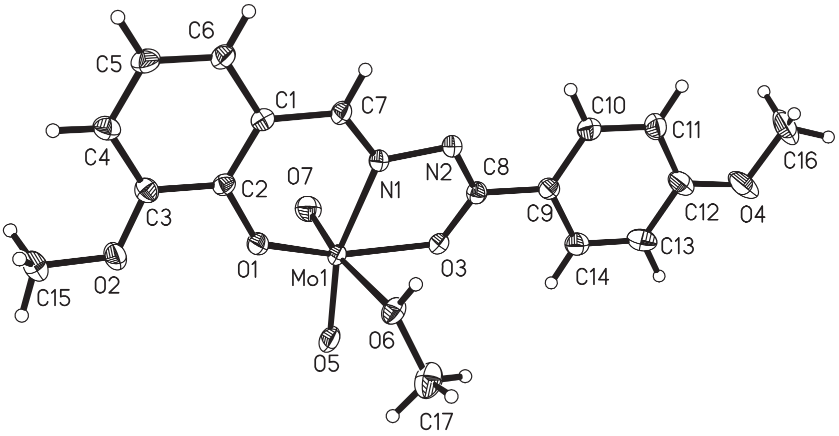


Figure 1. Molecular structure of **1** with 30% probability thermal ellipsoids.

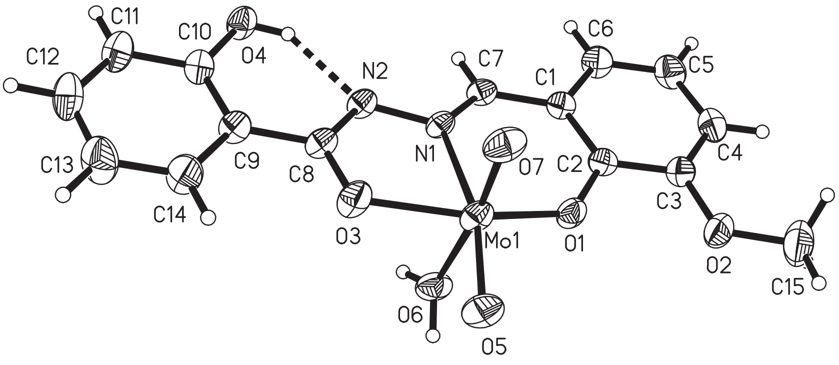


Figure 2. Molecular structure of **2** with 30% probability thermal ellipsoids. Hydrogen bond is shown as a dashed line.

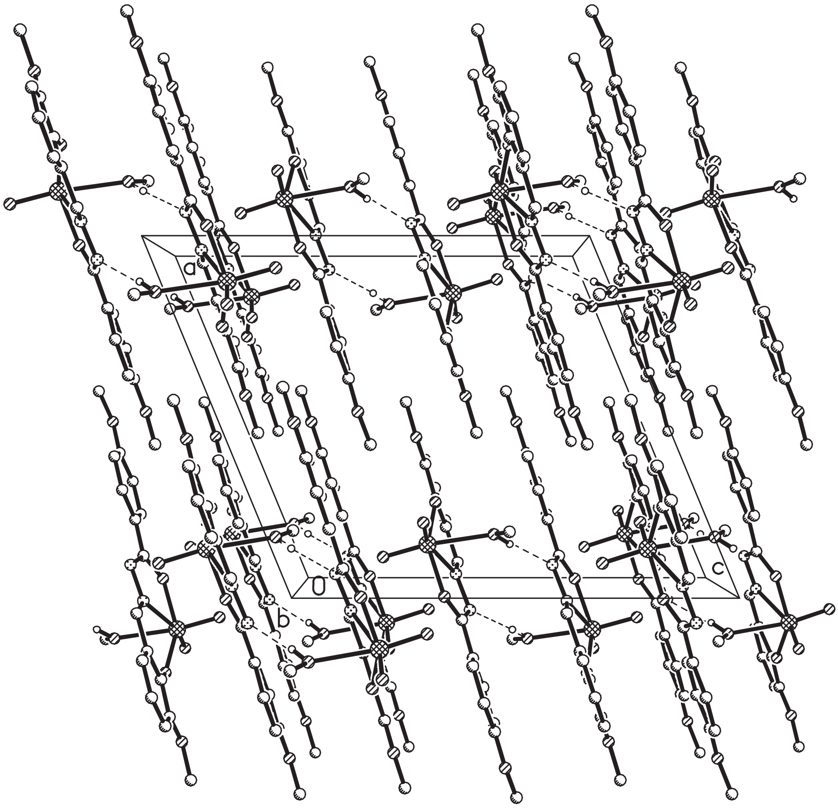


Figure 3. Molecular packing of **1** viewed along the *b*-axis. Hydrogen bonds are shown as dashed lines.

In the crystal structure of **1**, adjacent [$MoO_2L^1(CH_3OH)$] complexes are linked by two methanols through two intermolecular O6–H6A···N2 hydrogen bonds to form a dimer (figure 3). The adjacent Mo···Mo distance in **1** is 7.12 Å. In the crystal structure of **2**, adjacent [$MoO_2L^2(H_2O)$] molecules are linked by two water molecules through two intermolecular O6–H6A···O4 hydrogen bonds to form a dimer. The dimers are further linked through two intermolecular O6–H6B···O1 hydrogen bonds and two intermolecular O6–H6B···O2 hydrogen bonds to form 1-D chains (figure 4). Adjacent Mo···Mo distances in **2** are 5.28 and 9.08 Å. In addition, there are also weak $\pi\cdots\pi$ stacking interactions among C1–C6 and C9–C14 benzene rings and Mo1–O3–C8–N2–N1 chelate planes (table 4).

3.3. *IR spectra*

A weak band centered at 3434 cm^{-1} for **1** can be assigned to ν_{OH} of methanol and those centered at 3453 and 3372 cm^{-1} for **2** can be assigned to ν_{OH} of water and the hydroxyl group. The Mo=O stretches occur as a pair of sharp strong bands at 937 and 909 cm^{-1} for **1** and 945 and 915 cm^{-1} for **2**, assigned to the anti-symmetric and symmetric stretches of dioxomolybdenum(VI). Bands due to $\nu_{C=O}$ and ν_{NH} were absent in the

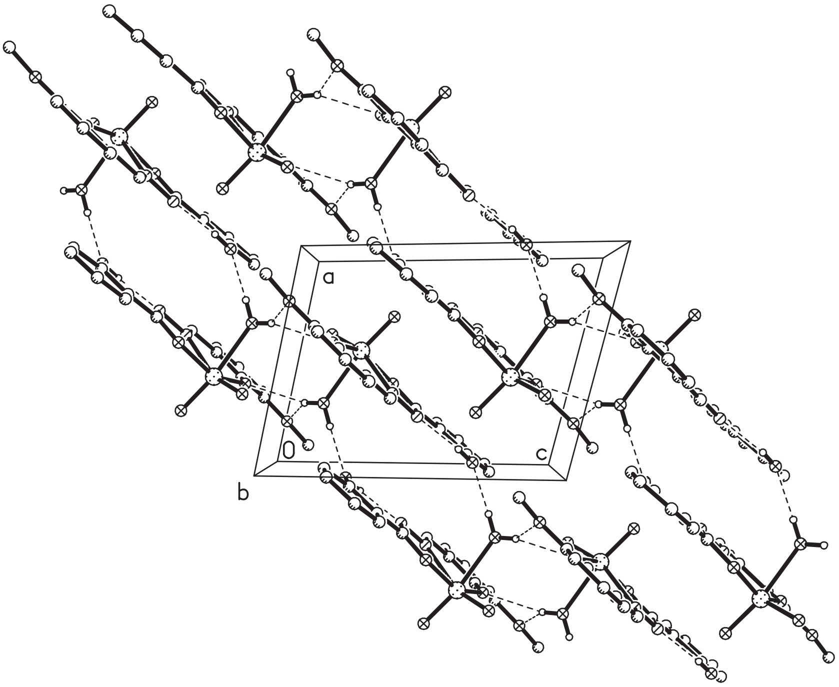


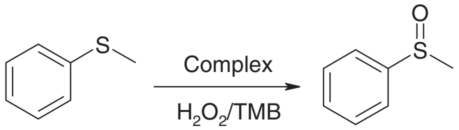
Figure 4. Molecular packing of **2** viewed along the *b*-axis. Hydrogen bonds are shown as dashed lines.

Table 4. Parameters among planes.

Cg	Distance between ring centroids (Å)	Dihedral angle (°)	Perpendicular distance of *Cg*(I) on *Cg*(J) (Å)	Perpendicular distance of *Cg*(J) on *Cg*(I) (Å)
1				
Cg(1)–*Cg*(1)$^{\mathrm{iii}}$	4.439	0.02	3.306	3.306
Cg(1)–*Cg*(2)$^{\mathrm{iv}}$	4.469	18.24	3.601	3.284
Cg(2)–*Cg*(3)$^{\mathrm{v}}$	3.783	3.55	3.506	3.494
Cg(2)–*Cg*(3)$^{\mathrm{iii}}$	3.757	0.39	3.635	3.632
2				
Cg(1)–*Cg*(1)$^{\mathrm{vi}}$	4.971	0.00	3.575	3.575
Cg(1)–*Cg*(2)$^{\mathrm{vi}}$	4.526	5.61	3.555	3.679
Cg(2)–*Cg*(3)$^{\mathrm{i}}$	4.839	7.26	3.434	3.157
Cg(2)–*Cg*(3)$^{\mathrm{i}}$	4.973	3.79	3.458	3.224
Cg(5)–*Cg*(6)$^{\mathrm{vi}}$	3.878	3.79	3.484	3.398

Symmetry codes: $^{\mathrm{i}}$ $-x$, $1-y$, $1-z$; $^{\mathrm{iii}}$ $-x$, $1-y$, $1-z$; $^{\mathrm{iv}}$ $-x$, $1/2+y$, $1/2-z$; $^{\mathrm{v}}$ $-x$, $-1/2+y$, $1/2-z$; $^{\mathrm{vi}}$ $1-x$, $1-y$, $1-z$. *Cg*(1), *Cg*(2), and *Cg*(3) are the centroids of Mo1–O3–C8–N2–N1, C1–C2–C3–C4–C5–C6, and C9–C10–C11–C12–C13–C14, respectively.

complexes and new C–O stretches appear at 1262 cm^{-1} for **1** and 1254 cm^{-1} for **2**, suggesting keto-imine tautomerization of the hydrazone ligands during coordination. Strong bands indicative of C=N–N=C in the complexes are shifted to 1609 cm^{-1} for **1** and 1611 cm^{-1} for **2**. New weak peaks at 350–800 cm^{-1} may be attributed to Mo–O and Mo–N vibrations in the complexes. IR spectra of the two complexes are similar,



Scheme 3. Oxidation with **1** and **2** as catalysts.

indicating the complexes have similar structures, as evidenced by the single-crystal X-ray determination.

3.4. *Catalytic sulfoxidation*

Using the complexes for oxidation of sulfides under homogeneous conditions in solution using methyl phenyl sulfide (thioanisol) as substrate are shown as in scheme 3. Hydrogen peroxide was used as oxidant 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 10°C. NMR was used to monitor formation of the sulfoxides with 1,3,5-trimethoxybenzene as internal standard to determine the yields. The reaction was started by 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 sulfide to the corresponding sulfoxide of about 77% for **1** and 82% for **2** within 60 min were observed. After 2 h conversions of sulfide were complete. Under the given conditions no over oxidation to the sulfone could be detected. The complexes are effective for the sulfoxidation, with **2** a little superior to **1**. Properties of the complexes in this work are a little better than those of the previously reported similar dioxomolybdenum(VI) complexes [11, 12].

4. Conclusion

Two new dioxomolybdenum(VI) complexes with similar hydrazone ligands, *N*′-(2-hydroxy-3methoxybenzylidene)-4-methoxybenzohydrazide and *N*′-(2-hydroxy-3-methoxybenzylidene)-2hydroxybenzohydrazide, have been prepared and structurally characterized. The dianionic hydrazone ligands coordinate to Mo through the phenolic O, imino N, and enolic O. Mo has octahedral coordination. Methanol and water are co-ligands during coordination. The complexes are efficient catalysts for the peroxidic oxidation of sulfides.

Supplementary material

CCDC reference numbers 854792 for **1** and 854793 for **2** contain the supplementary crystallographic data for this article. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk, or from the Cambridge Crystallographic Data Center, 12 Union

Road, Cambridge CB2 1EZ, UK; Fax: +44 1 223 336 033; E-mail: deposit@ccdc.cam.ac.uk

Acknowledgments

The authors greatly acknowledge Jingchu University of Technology for financial support.

References

[1] R.A. Lal, O.B. Chanu, R. Borthakur, M. Asthana, A. Kumar, A.K. De. *J. Coord. Chem.*, **64**, 1393 (2011).
[2] S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, K. Ghani. *Catal. Commun.*, **10**, 853 (2009).
[3] R.A. Lal, M. Chakrabarty, S. Choudhury, A. Ahmed, R. Borthakur, A. Kumar. *J. Coord. Chem.*, **63**, 163 (2010).
[4] G. Grivani, S. Tangestaninejad, A. Halili. *Inorg. Chem. Commun.*, **10**, 914 (2007).
[5] I. Sheikhsoaie, A. Rezaeffard, N. Monadi, S. Kaafi. *Polyhedron*, **28**, 733 (2009).
[6] S.N. Rao, N. Kathale, N.N. Rao, K.N. Munshi. *Inorg. Chim. Acta*, **360**, 4010 (2007).
[7] C. Karunakaran, R. Venkataramanan. *Catal. Commun.*, **7**, 236 (2006).
[8] S. Choi, J.D. Yang, M. Ji, H. Choi, M. Kee, K.H. Ahn, S.H. Byeon, W. Baik, S. Koo. *J. Org. Chem.*, **66**, 8192 (2001).
[9] R.S. Drago, D.S. Burns. *J. Catal.*, **166**, 377 (1997).
[10] P.S. Raghavan, V. Ramaswamy, T.T. Upadhya, A. Sudalai, A.V. Ramaswamy, S. Sivasanker. *J. Mol. Catal. A Chem.*, **122**, 75 (1997).
[11] R. Debel, A. Buchholz, W. Plass. *Z. Anorg. Allg. Chem.*, **634**, 2291 (2008).
[12] M. Mancka, W. Plass. *Inorg. Chem. Commun.*, **10**, 677 (2007).
[13] G.M. Sheldrick. *SHELX-97, Program for Crystal Structure Solution and Refinement,* Göttingen University, Germany (1997).
[14] G.M. Sheldrick. *SHELXTL* (*Version 5*), Siemens Industrial Automation Inc., Madison (1995).
[15] Y.-L. Zhai, X.-X. Xu, X. Wang. *Polyhedron*, **11**, 415 (1992).
[16] R. Dinda, S. Ghosh, L.R. Falvello, M. Tomas, T.C.W. Mak. *Polyhedron*, **25**, 2375 (2006).
[17] R. Dinda, S. Sengupta, S. Ghosh, H. Mayer-Figge, W.S. Sheldrick. *J. Chem. Soc., Dalton Trans.*, **23**, 4434 (2002).
[18] S. Gupta, A.K. Barik, S. Pal, A. Hazra, S. Roy, R.J. Butcher, S.K. Kar. *Polyhedron*, **26**, 133 (2007).
[19] W. Bansse, E. Ludwig, U. Schilde, E. Uhlemann, F. Weller, A. Lehmann. *Z. Anorg. Allg. Chem.*, **621**, 1275 (1995).