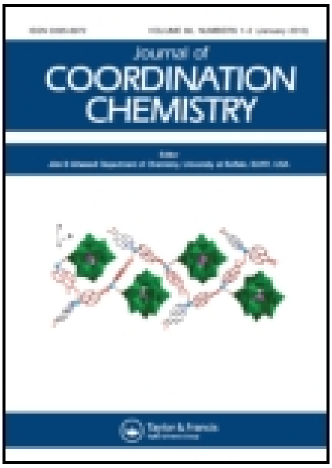
This article was downloaded by: [Northeastern University]
On: 30 December 2014, At: 21:47
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Syntheses, X-ray structures, and catalytic oxidations of dioxomolybdenum(VI) complexes with tridentate benzohydrazones

Xiao-Qiang He [a]

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

Accepted author version posted online: 12 Feb 2013.Published online: 20 Mar 2013.

To cite this article: Xiao-Qiang He (2013) Syntheses, X-ray structures, and catalytic oxidations of dioxomolybdenum(VI) complexes with tridentate benzohydrazones, Journal of Coordination Chemistry, 66:6, 966-976, DOI: 10.1080/00958972.2013.773587

To link to this article: http://dx.doi.org/10.1080/00958972.2013.773587

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. 66, No. 6, 20 March 2013, 966–976

Syntheses, X-ray structures, and catalytic oxidations of dioxomolybdenum(VI) complexes with tridentate benzohydrazones

XIAO-QIANG HE*

College of Chemical Engineering and Pharmacy, Jingchu University of Technology,
Jingmen Hubei, PR China

(*Received 13 September 2012; in final form 30 November 2012*)

Two new dioxomolybdenum(VI) complexes, $[MoO_2L^1(CH_3OH)]\cdot CH_3OH$ (**1**) and $[MoO_2L^2(CH_3OH)]$ (**2**), where L^1 and L^2 are dianionic forms of *N′*-(3-bromo-2-hydroxybenzylidene)-4-hydroxybenzohydrazide and *N′*-(2-hydroxybenzylidene)-2-hydroxy-3-methylbenzohydrazide, respectively, have been synthesized. The complexes have been characterized by elemental analyzes, IR spectra, molar conductance data, and single crystal X-ray determination. Mo in each complex is octahedral. The crystals of the complexes are stabilized by hydrogen bonds and weak $\pi \cdots \pi$ stacking interactions. The complexes function as effective olefin epoxidation catalysts with hydrogen peroxide as oxidant and sodium hydrogen carbonate as a co-catalyst at room temperature.

Keywords: Benzohydrazone; Molybdenum; Crystal structure; Hydrogen bonding; Olefin epoxidation

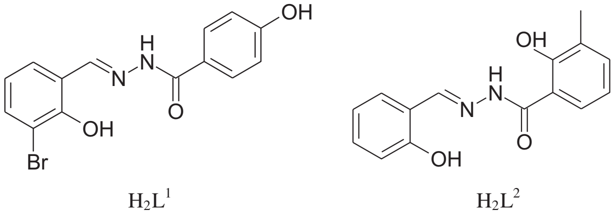
1. Introduction

Selective oxidation of hydrocarbons has attracted considerable attention in organic industry [1–3]. Molybdenum complexes have been widely used, in particular for oxidations of organic compounds [4–7]. Dioxomolybdenum complexes have been investigated as oxidation catalysts for organic substrates, particularly for epoxidation of olefins [8–11]. Synthesis, characterization, and reactivity studies of a number of dioxomolybdenum complexes with Schiff bases have been reported [12–15]. Some of the complexes possess oxygen atom transfer properties, oxidizing thiols, polyketones, and tertiary phosphines [16,17]. The catalytic abilities of dioxomolybdenum complexes with benzohydrazones have also been studied [8,18]. However, documented dioxomolybdenum complexes used as catalysts are still limited. The author reports herein the syntheses, crystal structures, and catalytic properties of two new dioxomolybdenum(VI) complexes, $[MoO_2L^1(CH_3OH)]\cdot CH_3OH$ (**1**) and $[MoO_2L^2(CH_3OH)]$ (**2**), where L^1 and L^2 are dianions of *N′*-(3-bromo-2-hydroxybenzylidene)-4-hydroxybenzohydrazide (H_2L^1; scheme 1) and *N′*-(2-hydroxybenzylidene)-2-hydroxy-3-methylbenzohydrazide (H_2L^2), respectively.

---

*Email: hexq2012@163.com

ISSN 0095-8972 print/ISSN 1029-0389 online
http://dx.doi.org/10.1080/00958972.2013.773587



Scheme 1. The benzohydrazone ligands.

2. Experimental

2.1. Materials and methods

All chemicals and solvents of analytical reagent grade were used as received. Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 elemental analyzer. Infrared spectra were carried out using a JASCO FT-IR model 420 spectrophotometer with KBr disk from 4000 to 200 cm^{-1}. GC analyzes were carried out using a Shimadzu GC-2014C gas chromatograph. Molar conductivities were carried out using a DDS-11A digital conductivity meter.

2.2. Synthesis of the benzohydrazones

H_2L^1: 3-Bromosalicylaldehyde (0.20 g, 1 mmol) dissolved in methanol (50 mL) was added to a stirred methanolic solution (30 mL) of 4-hydroxybenzohydrazide (0.15 g, 1 mmol). The reaction mixture was refluxed for 2 h on a water bath and the solvent was evaporated to give colorless crystalline products. Yields: 95%. Anal. Calcd for $C_{14}H_{11}BrN_2O_3$: C, 50.2; H, 3.3; N, 8.4%. Found: C, 50.0; H, 3.4; N, 8.4%.

H_2L^2: Salicylaldehyde (0.12 g, 1 mmol) dissolved in methanol (50 mL) was added to a stirred methanolic solution (30 mL) of 2-hydroxy-3-methylbenzohydrazide (0.17 g, 1 mmol). The reaction mixture was refluxed for 2 h on a water bath and the solvent was evaporated to give colorless crystalline products. Yields: 93%. Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.7; H, 5.2; N, 10.4%. Found: C, 66.5; H, 5.2; N, 10.3%.

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

A methanolic solution (10 mL) of $MoO_2(acac)_2$ (0.033 g, 0.1 mmol) was added to a methanolic solution (10 mL) of H_2L^1 (0.034 g, 0.1 mmol). The resulting brown solution was stirred for 10 min at reflux and then cooled to room temperature. Single crystals of **1** suitable for X-ray diffraction were formed by slow evaporation of the methanolic solution of the complex in air for 5 days. Yield: 62%. Anal. Calcd for $C_{16}H_{17}BrMoN_2O_7$: C, 36.6; H, 3.3; N, 5.3%. Found: C, 36.8; H, 3.2; N, 5.4.

2.4. Synthesis of $[MoO_2L^2(CH_3OH)]$ (2)

A methanolic solution (10 mL) of $MoO_2(acac)_2$ (0.033 g, 0.1 mmol) was added to a methanolic solution (10 mL) of H_2L^2 (0.027 g, 0.1 mmol). The resulting brown solution was stirred for 10 min at reflux and then cooled to room temperature. Single crystals of **2** suitable for X-ray diffraction were formed by slow evaporation of the methanolic solution of the complex in air for 11 days. Yield: 51%. Anal. Calcd for $C_{16}H_{16}MoN_2O_6$: C, 44.9; H, 3.8; N, 6.5%. Found: C, 44.8; H, 3.7; N, 6.7.

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. Determinations 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 [19]. The positions of almost all nonhydrogen atoms were located with direct methods. Subsequent Fourier syntheses were used to locate the remaining nonhydrogen atoms. All nonhydrogen atoms were refined anisotropically. The methanol H in **1** was located from a difference Fourier map and refined isotropically, with O−H distance restrained to 0.85(1) Å. The remaining hydrogens were placed in calculated positions and constrained to ride on their parent atoms. The analysis was performed with SHELXS-97 and SHELXL-97 programs [20,21]. 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.

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

Complex	**1**	**2**
Formula	$C_{16}H_{17}BrMoN_2O_7$	$C_{16}H_{16}MoN_2O_6$
Formula weight	525.2	428.2
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
a (Å)	16.270(2)	7.560(2)
b (Å)	8.691(1)	10.330(3)
c (Å)	14.586(1)	11.210(3)
α (°)	90	97.920(2)
β (°)	116.093(3)	98.050(2)
γ (°)	90	102.340(2)
V (Å^3)	1852.4(3)	834.0(4)
Z	4	2
λ (Å)	0.71073	0.71073
μ (MoKα) (mm^{-1})	2.907	0.822
ρ_{calcd} (g cm^{-3})	1.883	1.705
T (K)	298(2)	298(2)
F(000)	1040	432
Crystal size (mm)	0.17 × 0.15 × 0.15	0.27 × 0.23 × 0.21
θ range (°)	2.79–26.49	2.52–26.99
$h/k/l$	−20, 20/−10, 18/−18, 18	−9, 9/−13, 13/−12, 14
T (min)	0.6378	0.8085
T (max)	0.6696	0.8463
Reflections collected	3819	3522
Independent reflections	3513	2211
Data/restraints/parameters	3819/1/251	3522/1/232
Goodness of fit on F^2	1.097	1.044
R_{int}	0.0337	0.0383
Final R indices [$I > \sigma 2(I)$]	0.0244, 0.0609	0.0448, 0.1052
R indices (all data)	0.0274, 0.0625	0.0999, 0.1310
Largest peak and hole (eÅ^{-3})	0.618, −0.521	0.864, −0.739

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

1			
Bond lengths			
Mo1–O1	1.9313(16)	Mo1–O2	2.0087(15)
Mo1–N1	2.2332(18)	Mo1–O4	2.3270(17)
Mo1–O5	1.6898(19)	Mo1–O6	1.7023(17)
Bond angles			
O5–Mo1–O6	105.56(9)	O5–Mo1–O1	99.09(9)
O6–Mo1–O1	104.09(8)	O5–Mo1–O2	97.33(8)
O6–Mo1–O2	95.98(7)	O1–Mo1–O2	149.49(7)
O5–Mo1–N1	95.63(8)	O6–Mo1–N1	156.79(8)
O1–Mo1–N1	81.33(6)	O2–Mo1–N1	71.59(6)
O5–Mo1–O4	171.69(8)	O6–Mo1–O4	82.57(8)
O1–Mo1–O4	80.26(7)	O2–Mo1–O4	79.82(7)
N1–Mo1–O4	76.07(6)		
2			
Bond lengths			
Mo1–O1	1.894(4)	Mo1–O2	2.000(3)
Mo1–N1	2.214(4)	Mo1–O4	2.329(4)
Mo1–O5	1.667(4)	Mo1–O6	1.670(4)
Bond angles			
O5–Mo1–O6	105.4(2)	O5–Mo1–O1	104.01(18)
O6–Mo1–O1	99.52(18)	O5–Mo1–O2	96.51(16)
O6–Mo1–O2	96.38(18)	O1–Mo1–O2	149.53(15)
O5–Mo1–N1	157.46(17)	O6–Mo1–N1	95.15(17)
O1–Mo1–N1	81.08(14)	O2–Mo1–N1	71.70(13)
O5–Mo1–O4	83.80(16)	O6–Mo1–O4	170.22(15)
O1–Mo1–O4	81.01(15)	O2–Mo1–O4	79.06(15)
N1–Mo1–O4	75.24(13)		

Table 3. Distances (Å) and angles (°) involving hydrogen bonding of **1** and **2**.

$D-\mathrm{H}\cdots A$	$d(D-\mathrm{H})$	$d(\mathrm{H}\cdots A)$	$d(D\cdots A)$	$\angle(D-\mathrm{H}\cdots A)$
1				
$\mathrm{O4-H4}\cdots\mathrm{N2}^{\mathrm{i}}$	0.85(1)	1.88(1)	2.711(2)	167(4)
$\mathrm{O7-H7}\cdots\mathrm{O3}^{\mathrm{ii}}$	0.82	2.14	2.910(3)	157
$\mathrm{O3-H3}\cdots\mathrm{O7}^{\mathrm{iii}}$	0.82	1.92	2.729(3)	170
2				
$\mathrm{O4-H4A}\cdots\mathrm{O3}^{\mathrm{iv}}$	0.85(1)	1.94(2)	2.763(5)	163(6)
$\mathrm{O3-H3}\cdots\mathrm{N2}$	0.82	1.82	2.550(5)	147

Symmetry codes: (i) $1-x$, $1/2+y$, $1/2-z$; (ii) $2-x$, $-1/2+y$, $3/2-z$; (iii) x, $1+y$, z; (iv) $-x$, $-y$, $2-z$.

2.6. Catalytic epoxidation of olefins

To a solution of olefins (0.28 mmol), $NaHCO_3$ (0.11 mmol), and catalyst (9.4×10^{-4} mmol) in MeCN (0.5 mL) was added H_2O_2 (1.1 mmol, 30% H_2O solution) as oxidant. After the reaction was over, for products analysis, the solution was subjected to multiple ether extractions, and the extract was concentrated to 0.5 cm^3 by distillation in a rotary evaporator at room temperature and then a sample (2 μL) was taken from the solution and analyzed by GC. The retention times of the peaks were compared with those of commercial standards and chlorobenzene was used as an internal standard for GC yield calculation.

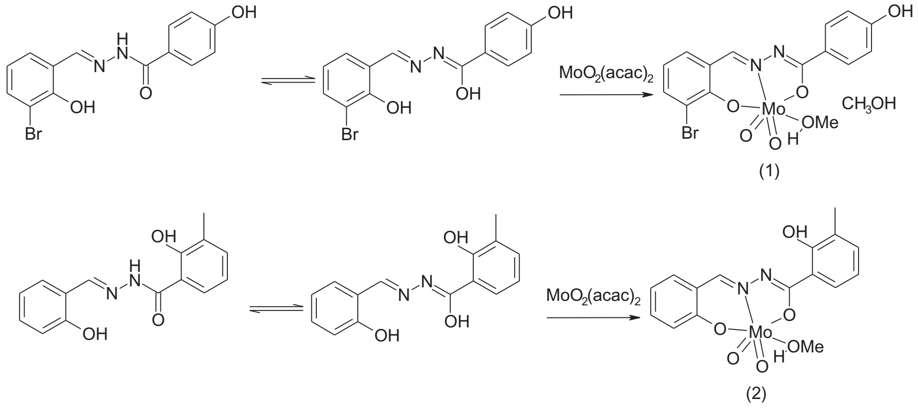
3. Results and discussion

3.1. Synthesis

The two complexes were readily prepared by reaction of $MoO_2(acac)_2$ with the benzohydrazone ligands in methanol. The reaction process of the complexes (scheme 2) is accompanied by a color change of the solution from colorless to brown. The crystals of the complexes are stable in air at room temperature and soluble in methanol, ethanol, and acetonitrile. The molar conductance values of **1** and **2** in methanol at 10^{-4} M are 8 and 11 Ω^{-1} cm^2 M^{-1}, indicating they are nonelectrolytes [22].

3.2. Crystal structure description

The molecular structures of the complexes are shown in figures 1 and 2. Complex **1** contains a dioxomolybdenum complex and a methanol. The structures of the dioxomolybdenum complexes are very similar to each other, except for the substituent groups of the benzohydrazone ligands. Beyond the basic *N′*-(2-hydroxybenzylidene) benzohydrazide skeleton, there are one bromo and one hydroxyl substituent in H_2L^1, and there are one methyl and one hydroxyl substituent in H_2L^2. The hydroxyl is present in both complexes but its position in the ring is not the same, which might influence molecular and crystal structures. In each of the complexes, the coordination geometry around Mo can be described as slightly distorted octahedron, with the equatorial plane defined by one phenolic O, one imino N, and one enolic O of the dianionic benzohydrazone, and one oxo, and with the two axial positions occupied by methanol and the other oxo. The benzohydrazone ligands coordinate meridional to Mo forming five- and six-membered chelate rings with bite angles of 71.59(6) and 81.33(6)° for **1** and 71.70(13) and 81.08(14)° for **2**. The dihedral angles between the two substituted benzene rings of the benzohydrazones are 19.7(3)° for **1** and 2.2(3)° for **2**, indicating the ligand in **1** is more twisted than in **2**. Displacements of Mo from the equatorial mean planes toward the axial oxo are 0.332(2) Å for **1** and 0.698(2) Å for **2**. The benzohydrazones are coordinated in their dianionic forms, evident from the N2–C8 and O2–C8 bond lengths with values of 1.302(3) and 1.318(3) Å for **1** and 1.285(6) and 1.295(5) Å for **2**, indicating the presence of the enolate form of the



Scheme 2. Preparation of the complexes.

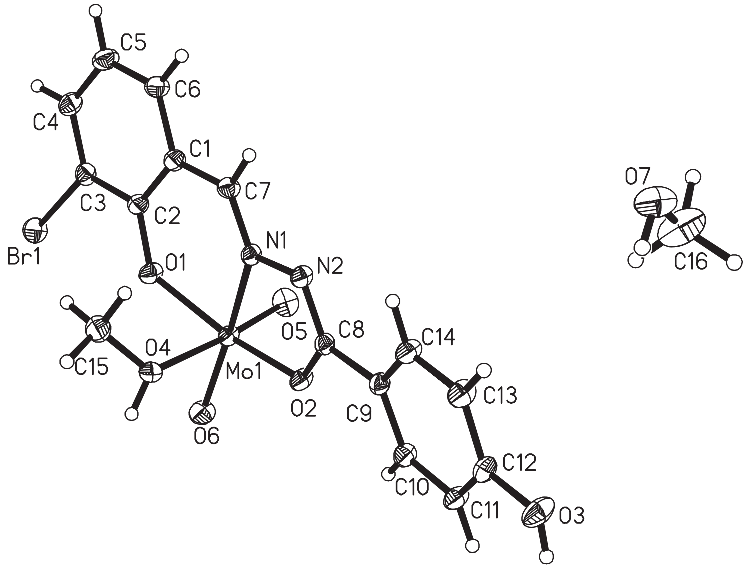


Figure 1. An ORTEP diagram of **1** with atom labeling scheme and 30% probability thermal ellipsoids for all nonhydrogen atoms.

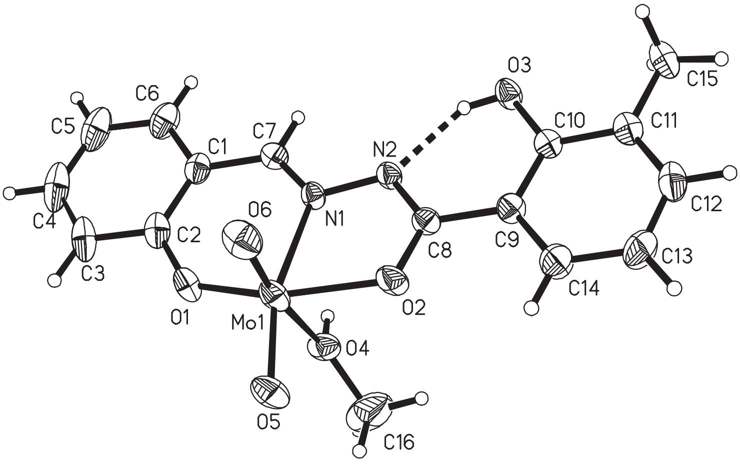


Figure 2. An ORTEP diagram of **2** with atom labeling scheme and 30% probability thermal ellipsoids for all nonhydrogen atoms. Intramolecular hydrogen bond is shown as a dashed line.

ligand amide. The Mo–O, Mo–N, and Mo=O bonds are within normal ranges and are similar to those observed in similar dioxomolybdenum(VI) complexes [23–25].

In the molecular packing structure of **1**, [MoO_2L^1] units are linked by methanols through intermolecular O–H $\cdots$ N and O–H $\cdots$ O hydrogen bonds to form 1-D chains running along the *b* axis (figure 3). In the molecular packing of **2**, adjacent [MoO_2L^2] units are linked by two methanols through two intermolecular O–H $\cdots$ O hydrogen bonds to form a dimer (figure 4). There are also weak $\pi \cdots \pi$ stacking interactions among C1–C6 and C9–C14 benzene rings, as specified in table 4 [26].

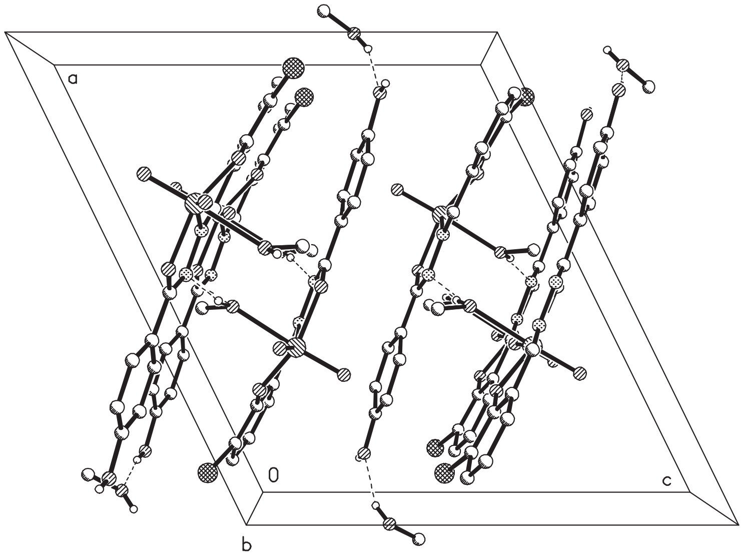


Figure 3. Packing diagram of 1-D chains of **1**, viewed along the *b* axis. Hydrogen bonds are shown as dashed lines.

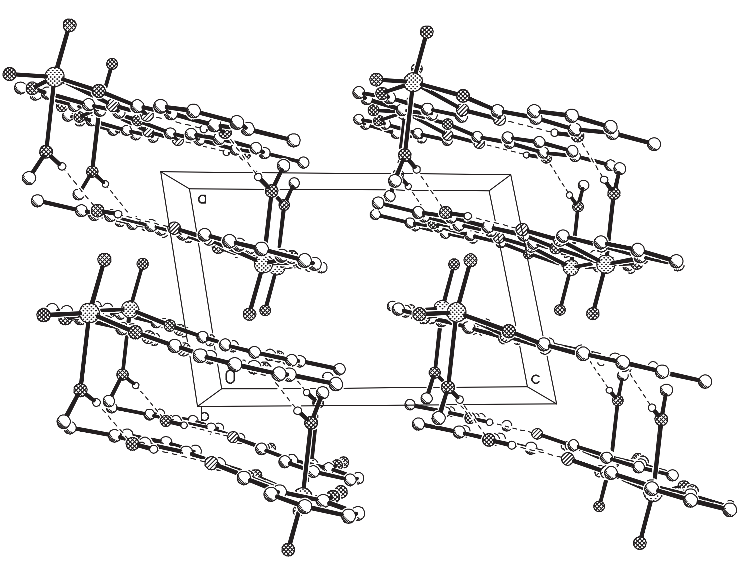


Figure 4. Packing diagram of dimers of **2**, viewed along the *b* axis. Hydrogen bonds are shown as dashed lines.

3.3. IR spectra

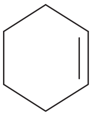
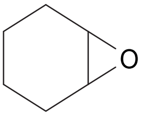
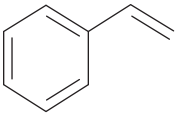
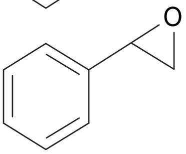
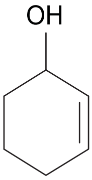
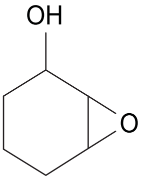
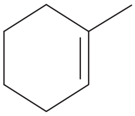
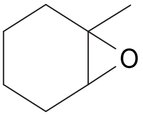
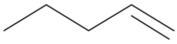
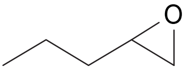
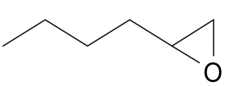
Weak and broad bands centered at 3435 cm^{-1} for **1** and 3421 cm^{-1} for **2** can be assigned to the ν_{OH} vibrations of methanol and the hydroxyl groups of the benzohydrazone ligands. The Mo=O stretching modes occur as a pair of sharp strong bands at 938 and 912 cm^{-1} for **1** and 939 and 917 cm^{-1} for **2**, which are assigned to the antisymmetric and symmetric stretching modes of the dioxomolybdenum(VI). The bands due to $\nu_{C=O}$ and ν_{NH} were

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*(2)^{v}	3.935	12.41	3.571	3.498
2				
Cg(1)-*Cg*(2)^{vi}	3.741	2.29	3.412	3.373
Cg(1)-*Cg*(2)^{vii}	4.461	2.29	3.446	3.354

Symmetry codes: (v): $1-x$, $-1/2+y$, $1/2-z$; (vi): $1-x$, $2-y$, $-z$; (vii): $2-x$, $2-y$, $-z$. *Cg*(1) and *Cg*(2) are the centroids of C1–C2–C3–C4–C5–C6 and C9–C10–C11–C12–C13–C14, respectively.

Table 5. Catalytic oxidation of olefins catalyzed by **1** and **2**[a].

Substrate	Product	Conversion (%)[b] (TON)[c]		Selectivity (%)[d]	
		**1**	95 (263)	**1**	100
		2	97 (271)	**2**	100
		**1**	92 (281)	**1**	100
		2	94 (290)	**2**	100
		**1**	97 (288)	**1**	100
		2	95 (283)	**2**	100
		**1**	92 (269)	**1**	100
		2	93 (272)	**2**	100
		**1**	96 (277)	**1**	100
		2	96 (285)	**2**	100
		**1**	98 (292)	**1**	100
		2	94 (287)	**2**	100

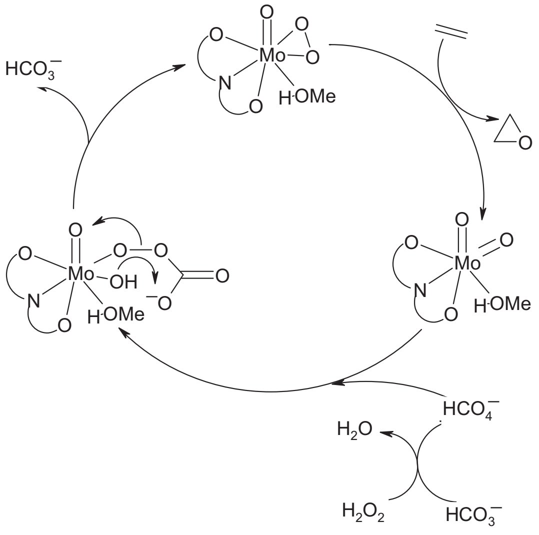
[a] The molar ratios for catalyst: substrate:$NaHCO_3:H_2O_2$ are 1 : 298 : 117 : 1170. The reactions were performed in (70 : 30) mixture of CH_3OH/CH_2Cl_2 (1.2 mL) under air at room temperature. [b] The GC conversion (%) are measured relative to the starting olefin after 74.5 min. [c] TON = (mmol of product)/mmol of catalyst. [d] Selectivity to epoxide = (epoxide%/(epoxide% + aldehyde%)) × 100.

absent in the complexes and new C–O stretches appear at 1265 cm^{-1} for **1** and 1270 cm^{-1} for **2**, suggesting keto-imine tautomerization of the benzohydrazone ligands during coordination. Strong bands indicative of C=N–N=C groups in the complexes shift to 1608 cm^{-1} for **1** and 1613 cm^{-1} for **2**. New weak peaks at 300–800 cm^{-1} may be attributed to Mo–O and Mo–N vibrations in the complexes. IR spectra of the two complexes are similar, indicating the complexes are of similar structures, as evidenced by the single crystal X-ray determination.

3.4. Catalytic properties

The complexes showed effective catalytic oxidation of various olefins to their corresponding epoxides. The details of catalytic properties with respect to epoxidation of olefins with **1** and **2** as catalysts are given in table 5. Generally, excellent epoxide yields and selectivities were observed for all aliphatic and aromatic substrates. The catalytic studies using dioxomolybdenum catalysts reveal that the efficiency of catalysts toward all substrates is similar with maximum conversion, TON, and selectivities. The mechanism (scheme 3) for the epoxidation of various olefins to epoxides using the two complexes as catalysts has been proposed by comparison with the literature [27]. When H_2O_2 was used as a sole oxidant the catalytic efficiency is not high, but when $NaHCO_3$ was added as a co-catalyst the efficiency of the system increases many fold. The key aspect of such a reaction is that H_2O_2 and hydrogen carbonate react in an equilibrium process to produce peroxymonocarbonate, HCO_4^-, which is a more reactive nucleophile than H_2O_2 and speeds up the epoxidation [28]. The basic principle of the catalytic reaction is the conversion of oxoperoxo complex to dioxo complex transferring oxo to the olefins and the conversion of dioxo complex to the oxoperoxo complex reacting with HCO_4^- to regain catalytic activity.

Comparing the catalytic properties of the complexes in the present work with those of other similar dioxomolybdenum(VI) complexes bearing benzohydrazone ligands [6,8]



Scheme 3. Probable mechanism of catalytic oxidation of olefins to epoxides.

indicates that the substituent groups of the benzohydrazone ligands have little influence to the catalytic processes.

4. Conclusions

Two new dioxomolydenum(VI) complexes with similar benzohydrazone ligands, N'-(3-bromo-2-hydroxybenzylidene)-4-hydroxybenzohydrazide and N'-(2-hydroxybenzylidene)-2-hydroxy-3-methylbenzohydrazide, have been prepared and structurally characterized using X-ray structure analysis, IR spectra, molar conductance data, and elemental analyzes. The dianionic benzohydrazones coordinate to Mo through the phenolic O, imino N, and ethanolic O. Mo is coordinated by benzohydrazone and methanol, as well as two oxo groups, forming octahedral coordination. The complexes showed effective catalytic properties in oxidation of various olefins to their corresponding epoxides. The results are in accord to those reported previously for molybdenum complexes catalyzing epoxidation of alkenes [28–31].

Supplementary material

CCDC reference numbers 901036 for **1** and 901037 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 Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

The author greatly acknowledges Jingchu University of Technology for financial support.

References

[1] P. Botella, B. Solsona, E. Garcia-Gonzalez, J.M. Gonzalez-Calbet, J.M. Lopez Nieto. *Chem. Commun.*, **47**, 5040 (2007).
[2] Q.-H. Zhang, W.-P. Deng, Y. Wang. *Chem. Commun.*, **33**, 9275 (2011).
[3] H.H. Monfared, V. Abbasi, A. Rezaei, M. Ghorbanloo, A. Aghaei. *Transition Met. Chem.*, **37**, 85 (2012).
[4] S. Tanaka, M. Annaka, K. Sakai. *Chem. Commun.*, **11**, 1653 (2012).
[5] V. Conte, B. Floris. *Dalton Trans.*, **7**, 1419 (2011).
[6] S.N. Rao, K.N. Munshi, N.N. Rao, M.M. Bhadbhade, E. Suresh. *Polyhedron*, **18**, 2491 (1999).
[7] C. Karunakaran, R. Venkataramanan. *Catal. Commun.*, **7**, 236 (2006).
[8] M. Bagherzadeh, M. Amini, H. Parastar, M. Jalali-Heravi, A. Ellern, L.K. Woo. *Inorg. Chem. Commun.*, **20**, 86 (2012).
[9] M. Herbert, E. Alvarez, D.J. Cole-Hamilton, F. Montilla, A. Galindo. *Chem. Commun.*, **32**, 5933 (2010).
[10] J. Zhao, K.R. Jain, E. Herdtweck, F.E. Keuhn. *Dalton Trans.*, **47**, 5567 (2007).
[11] M.M. Flook, A.J. Jiang, R.R. Schrock, P.M. Hoveyda. *J. Am. Chem. Soc.*, **131**, 7962 (2009).
[12] R. Debel, A. Buchholz, W. Plass. *Z. Anorg. Allg. Chem.*, **634**, 2291 (2008).
[13] M. Mancka, W. Plass. *Inorg. Chem. Commun.*, **10**, 677 (2007).
[14] Y. Li, X. Fu, B. Gong, X. Zou, X. Tu, J. Chen. *J. Mol. Catal. A: Chem.*, **322**, 55 (2010).
[15] M. Bagherzadeh, R. Latifi, L. Tahsini, V. Amani, A. Ellern, L.K. Woo. *Polyhedron*, **28**, 2517 (2009).
[16] S.N. Rao, N. Kathale, N.N. Rao, K.N. Munshi. *Inorg. Chim. Acta*, **360**, 4010 (2007).
[17] I. Sheikhshoaie, A. Rezaeifard, N. Monadi, S. Kaafi. *Polyhedron*, **28**, 733 (2009).
[18] R. Dinda, P. Sengupta, S. Ghosh, W.S. Sheldrick. *Eur. J. Inorg. Chem.*, **363**, (2003).
[19] G.M. Sheldrick. *SADABS*, University of Göttingen, Germany (1996).
[20] G.M. Sheldrick. *SHELX-97, Program for Crystal Structure Solution and Refinement*, Göttingen University, Germany (1997).
[21] G.M. Sheldrick. *SHELXTL Version 5*, Siemens Industrial Automation, Madison, WI (1995).

[22] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[23] S.-P. Gao. *J. Coord. Chem.*, **64**, 2869 (2011).
[24] S. Gupta, A.K. Barik, S. Pal, A. Hazra, S. Roy, R.J. Butcher, S.K. Kar. *Polyhedron*, **26**, 133 (2007).
[25] N.K. Ngan, K.M. Lo, C.S.R. Wong. *Polyhedron*, **33**, 235 (2012).
[26] A.L. Spec. *Acta Crystallogr.*, **D65**, 148 (2009).
[27] S.K. Maiti, S. Dinda, S. Banerjee, A.K. Mukherjee, R. Bhattacharyya. *Eur. J. Inorg. Chem.*, 2038 (2008).
[28] M. Zakeri, M. Moghadam, I. Mohammadpoor-Baltork, S. Tangestaninejad, V. Mirkhani, A.R. Khosropour. *J. Coord. Chem.*, **65**, 1144 (2012).
[29] M.R. Maurya, P. Saini, C. Haldar, A.K. Chandrakar, S. Chand. *J. Coord. Chem.*, **65**, 2903 (2012).
[30] M. Bagherzadeh, M.M. Haghdoost, A. Shahbazirad. *J. Coord. Chem.*, **65**, 591 (2012).
[31] A. Ghaffari, M. Behzad, G. Dutkiewicz, M. Kubicki, M. Salehi. *J. Coord. Chem.*, **65**, 840 (2012).