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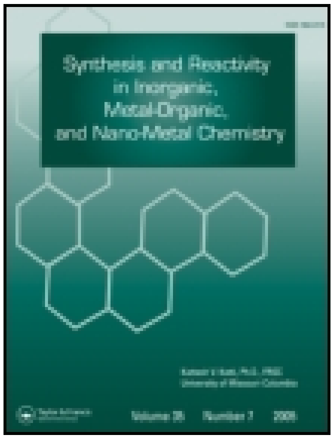

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Synthesis, Characterization, and X-Ray Structure of [cis-$MoO_2L(MeOH)$] (L = N′-(5-Chloro-2-Hydroxybenzylidene)-3-Chlorobenzohydrazide) and Its Catalytic Property

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Synthesis, Characterization, and X-Ray Structure of [*cis*-$MoO_2L(MeOH)$] (L = *N*′-(5-Chloro-2-Hydroxybenzylidene)-3-Chlorobenzohydrazide) and Its Catalytic Property

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The synthesis and characterization of [*cis*-$MoO_2L(MeOH)$] (L = *N*′-(5-chloro-2-hydroxybenzylidene)-3-chlorobenzohydrazide) are described. The dioxomolybdenum complex was prepared from 1:1 reaction mixture containing the benzohydrazone ligand and $MoO_2(acac)_2$. Orange single crystals were obtained by slow evaporation of methanolic solution containing the complex, and were characterized by elemental analysis, infrared spectroscopy, and single-crystal X-ray diffraction techniques. The geometry around the molybdenum center is distorted octahedral in which a tridentate benzohydrazone ligand with two anionic oxygens and one neutral imine nitrogen occupies meridional position. The octahedral geometry of the *cis*-dioxomolybdenum center is additionally completed by a coordinated methanol solvent molecule. The complex was tested for the homogeneous oxidation of various olefins.

Keywords: molybdenum dioxo complex, synthesis, X-ray structure, catalytic property

Introduction

Benzohydrazones prepared by the condensation of salicylaldehydes with benzohydrazides are an important class of versatile ligands.[1–3] Transition metal complexes derived from such ligands have been widely investigated due to their interesting properties, such as magnetic exchange,[4] biological activities,[1,5,6] and catalytic materials.[7,8] Molybdenum is an important metal that is capable of forming various complexes with organic ligands,[9–11] and usually shows essential catalytic properties.[12–15] Yet, molybdenum complexes derived from benzohydrazone ligands are rarely reported. Epoxides are very important and versatile intermediates for manufacturing a range of important commercial products such as pharmaceuticals and polymers. In addition, it can be easily transformed to a variety of functional groups.[16] Many transition metal complexes including molybdenum complexes have been reported for oxidation of olefins.[8,11,12,17–19] As a continuation of the work, in this report, a new *cis*-dioxomolybdenum(VI) complex is reported.

Experimental

Materials and Methods

5-Chlorosalicylaldehyde, 3-chlorobenzohydrazide, and $MoO_2(acac)_2$ of AR grade were purchased from Aldrich and used as received. CHN elemental analyses were performed with a Perkin Elmer 240C elemental analyzer. IR spectra (KBr disks) were recorded on a Perkin Elmer 257 spectrophotometer. The oxidation products were analyzed with a gas chromatograph (Shimadzu, GC-14B) equipped with a SAB-5 capillary column (phenyl methyl siloxane 30 mm × 320 mm × 0.25 mm) and a flame ionization detector. ^1H NMR spectrum was obtained in DMSO-d^6 solution with a Bruker NMR 400 (400 MHz) spectrometer. Thermal decomposition was measured on Pyris 1 thermogravimetric analyzer.

Preparation of the Molybdenum Complex

A mixture of 5-chlorosalicylaldehyde (0.78 g, 5 mmol) and 3-chlorobenzohydrazide (0.86 g, 5 mmol) in 30 mL methanol was heated to reflux for 1 h, which gave the benzohydrazone ligand H_2L. Then $MoO_2(acac)_2$ (1.63 g, 5 mmol) was added and refluxed for another 1 h. A yellow solid was obtained by concentrating the methanolic solution, washed with cold methanol and recrystallized from methanol by slow evaporation. Yield: 63%; ^1H NMR (DMSO-d^6, 400 MHz): $\delta = 3.13$ (s, 3H), 6.91(d, 1H, aromatic), 7.25–7.97(m, 6H, aromatic), 8.53 (s, 1H, -CH=N-). IR (KBr pellet): ν(C=N) 1622; $\nu(MoO_2)$ 917,

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Table 1. Crystallographic and experimental data for the complex.

Empirical formula	$C_{15}H_{12}Cl_2MoN_2O_5$
Formula weight	467.1
Temperature/K	298(2)
Wavelength (Mo$K\alpha$)/Å	0.71073
Crystal shape/color	Block/yellow
Crystal size/mm	0.23 × 0.23 × 0.22
Crystal system	Triclinic
Space group	P-1
a/Å	7.880(2)
b/Å	9.589(2)
c/Å	11.754(2)
α/°	98.149(2)
β/°	104.888(2)
γ /°	91.201(2)
V/Å^3	848.1(3)
Z	2
Calculated density/g cm^{-3}	1.829
Absorption coefficient/mm^{-1}	1.117
Theta range for data collection	2.15–25.10
Index ranges/h, k, l	−9, 8; −11, 11; −13, 12
$T_{\min}$	0.7832
$T_{\max}$	0.7911
Reflections/parameters	3006/230
Independent reflections	2151
Restraints	1
F(000)	464
Goodness of fit on F^2	1.021
R_1, wR_2 [I ≥ 2σ(I)]^a	0.0518, 0.1158
R_1, wR_2 (all data)^a	0.0890, 0.1327
Largest diff. peak and hole/e Å^{-3}	0.791, −0.553

$^aR_1 = \sum||Fo| - |Fc||/\sum|Fo|$, $wR_2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$.

886 cm^{-1}. Anal. Calcd. (%) for $C_{15}H_{12}Cl_2MoN_2O_5$: C, 38.6; H, 2.6; N, 6.0. Found (%): C, 38.5; H, 2.7; N, 5.9.

Crystal Structure Determination

Crystals suitable for X-ray measurement were grown from methanol by slow evaporation method. The single crystal of the complex was chosen and glued to thin glass fibers by epoxy glue in air for data collection. The diffraction data were collected on a Bruker Apex2 CCD with Mo $K\alpha$ radiation (λ = 0.71073 Å) at 298(2) K using the ω scan method. An empirical absorption correction was applied. The structure was solved by direct methods and difference Fourier synthesis. Crystal data collection, parameters, and refinement statistics for the complex are listed in Table 1. All of the non-H atoms were refined anisotropically. The methanol H atom was located from an electronic density map and refined with O···H distance restrained to 0.85(1) Å. All other H atoms of the complex were included in calculated positions, and assigned isotropic thermal parameters, which were set to ride on the parent atoms. All calculations were performed using the SHELXTL-97 package.[20]

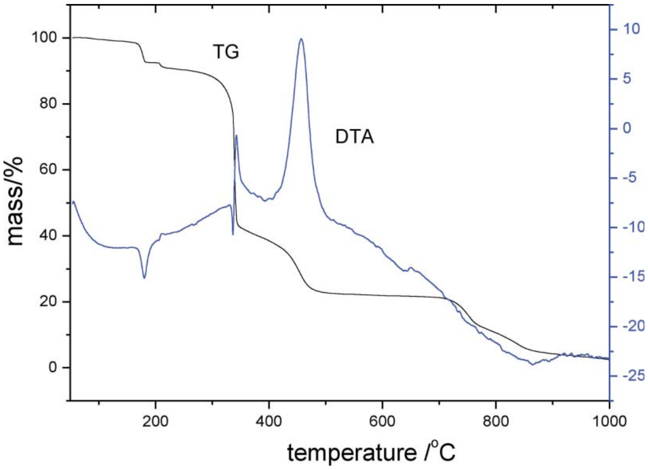


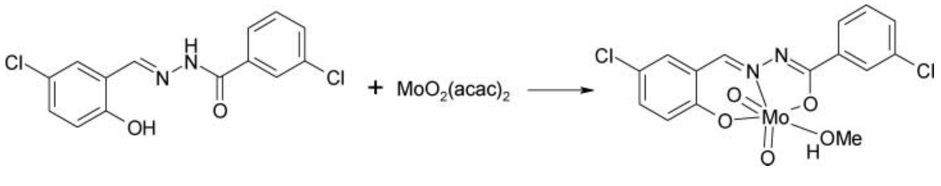
Fig. 1. TG-DTA curves of the complex.

Catalytic Oxidation Procedure

Catalytic experiments were carried out in a 50 mL glass reaction flask fitted with a water condenser. In a typical procedure, 0.032 mmol dioxo-molybdenum(VI) complex was dissolved in 10 mL CH_2Cl_2. Then 10 mmol alkene was added to the reaction mixture and 30 mmol TBHP was added. The reaction mixture was refluxed for 1 h. The reaction products were monitored at periodic time intervals using gas chromatography. The oxidation products were identified by comparison with authentic samples (retention times in GC).

Results and Discussion

The benzohydrazone ligand used for the preparation of molybdenum complex was derived from condensation of 5-chlorosalicylaldehyde and 3-chlorobenzohydrazide. The complex was prepared by simple ligand exchange reaction of the benzohydrazone ligand with $MoO_2(acac)_2$ in methanol (Scheme 1). Single crystals of the complex were successfully grown by slow evaporation of methanolic solution of the complex at room temperature.



Sch. 1. The synthesis procedure of the complex.

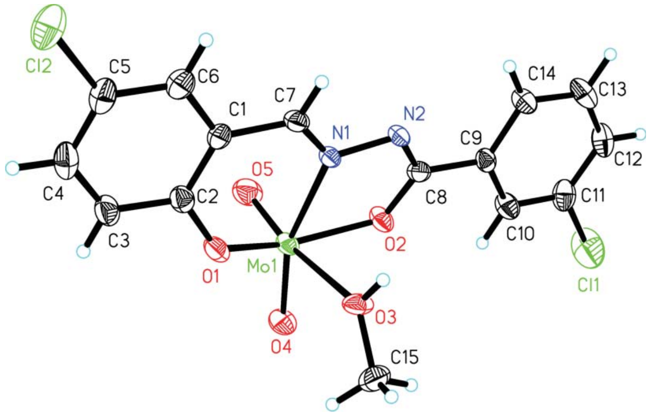


Fig. 2. ORTEP diagram (30% thermal ellipsoid) of the complex with atom labeling scheme.

The complex was characterized by IR spectroscopy. Two strong bands at 886 and 917 cm^{-1} which can be assigned as symmetric and asymmetric stretching frequencies due to *cis*-dioxo moieties indicating the existence of monomeric complex.[15] The molar conductance of the complex is 13 Ω^{-1} cm^2 mol^{-1}, indicating it is a nonelectrolyte.

Figure 1 is TG-DTG curves at a heating rate of 10°C·min^{-1}. It can be seen that there are three different decomposition stages. The first decomposition stage which occurs in the temperature range of 165–181°C, was observed as mass loss of 7.2%, corresponding to the loss of methanol ligand (calcd. 6.9%). The second stage, which occurs in the temperature range of 206–500°C, corresponds to the slow decomposition of the remainder, and the formation of MoO_2, which is stable up to 708°C, then slowly evaporated.

X-Ray Structure Description of the Complex

The molecular structure of the complex is shown in Figure 2 and the bond parameters are given in Table 2. The mononuclear complex has a distorted octahedral geometry with one nitrogen atom and five oxygen atoms. Three atoms, O1, N1, and O2 (from the tridentate ligand), and one terminal oxo atom, O4, occupy the meridional plane. The Mo1 atom lies 0.329(2) Å out from this plane in the direction of the other terminal oxygen atom O5. Both O5 and O3, the latter from the coordinated methanol molecule, occupy the axial positions forming an O3–Mo1–O5 angle of 170.34(17)° which indicate the distorted octahedral nature of the donor environment around the Mo(VI) center. The MoO_2 moiety has a *cis* configuration. The Mo1–O3 bond *trans* to the terminal oxygen atom O5 is significantly longer compared to the length of other molybdenum oxygen bonds, indicating that the methanol molecule is weakly coordinated to the metal center and can behave as a substrate-binding site. The coordinate bond parameters are consistent with those reported in the literature.[14,15] In the crystal, the molecules are linked *via* intermolecular O3–H3···N2 hydrogen bonds [O3–H3 = 0.85(1) Å, H3···$N2^i$ = 1.99(2) Å, O3···$N2^i$ = 2.826(6) Å, O3–H3···$N2^i$ = 169(7)°; symmetry code for i: 1 – *x*, 1 – *y*, – *z*], forming dimers, as shown in Figure 3.

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

Bond lengths			
Mo1-O5-	1.680(4)	Mo1-O4	1.690(4)
Mo1-O1	1.911(4)	Mo1-O2	2.004(4)
Mo1-N1	2.257(4)	Mo1-O3	2.344(4)
Bond angles			
O5-Mo1-O4	106.0(2)	O5-Mo1-O1	99.0(2)
O4-Mo1-O1	101.9(2)	O5-Mo1-O2	96.3(2)
O4-Mo1-O2	99.0(2)	O1-Mo1-O2	149.5(2)
O5-Mo1-N1	95.9(2)	O4-Mo1-N1	157.0(2)
O1-Mo1-N1	80.9(2)	O2-Mo1-N1	71.3(2)
O5-Mo1-O3	170.3(2)	O4-Mo1-O3	82.9(2)
O1-Mo1-O3	82.2(2)	O2-Mo1-O3	78.5(2)
N1-Mo1-O3	74.7(2)		

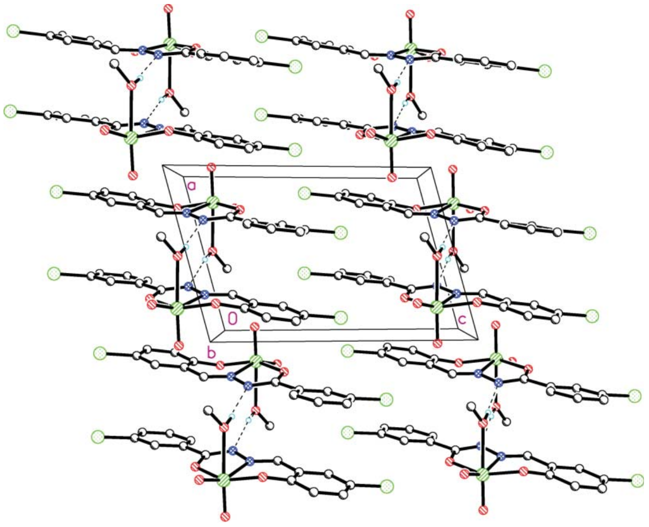
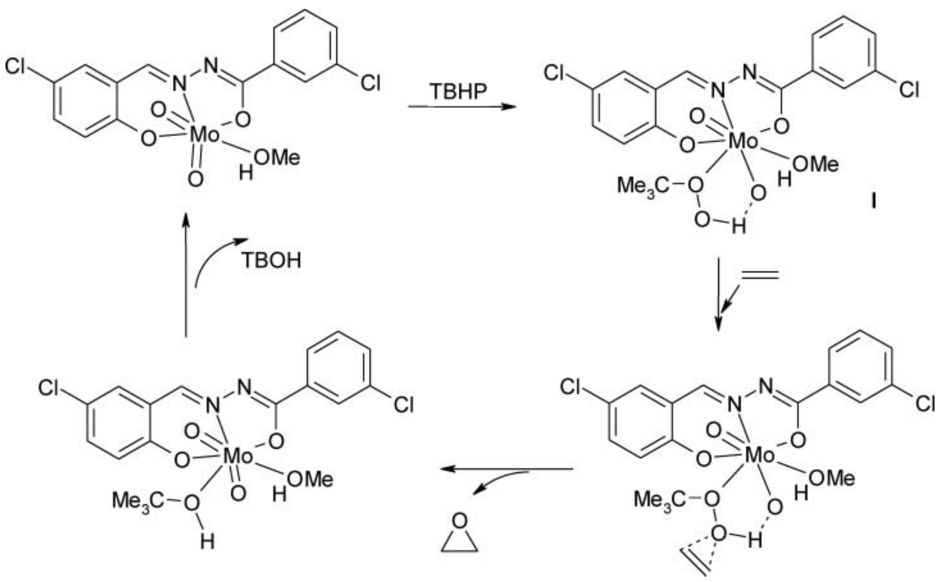


Fig. 3. Intermolecular O–H···N hydrogen bonds (dotted lines) linked dimers of the complex.

Catalytic Oxidation Results

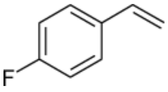
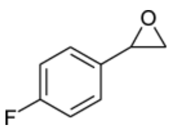
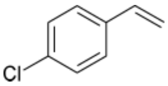
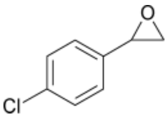
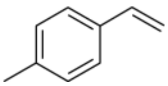
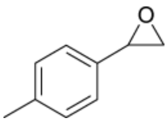
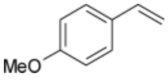
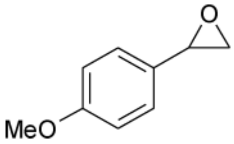
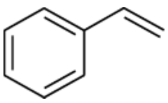
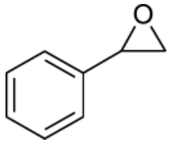
The catalytic property of the complex was investigated in the epoxidation of cyclooctene, as a model substrate, and tert-butyl hydroperoxide as the oxygen donor. In the absence of catalyst, the reactions did not proceed even under reflux. The results are presented in Table 3. Oxidation of 4-F-styrene, 4-Cl-styrene, 4-Mestyrene, and 4-OMe-styrene gave the corresponding epoxide as the sole product, while in the oxidation of styrene some benzaldehyde was detected as a by-product. From the results, it can be seen that the electron donating group in the salicylidene ring can decrease the activity of the catalyst, which results from the decreasing Lewis acidity of the molybdenum center and therefore the deduction of TBHP activation.[12] In the proposed catalytic cycle (Scheme 2), at first step, TBHP is activated by coordination to the molybdenum center and formation of hepta-coordinated molybdenum



Sch. 2. The catalytic procedure of the oxidation.

intermediate **I**. It seems that heterolytic cleavage of the TBHP occurs. Therefore catalysts with higher Lewis acidity character increase the efficiency of the coordinated peroxo group. Then olefin as a nucleophile will attack to the electrophile oxygen atom of the coordinated TBHP. A comparison of the results obtained for this work with those reported in the literature, which used TBHP as oxidizing agent reveals that reaction time is lower than other systems and higher conversion for epoxide formation will be achieved.

Table 3. Epoxidation of olefins using TBHP catalyzed by the complex in $CH_2Cl_2{}^b$.

Alkene	Conversion (%)^c	Product	Selectivity to epoxides (%)	Time (h)	TOF (h^{-1})
	37		100	1	102.5
	34		100	1	87.2
	17		100	1	45.3
	11		100	1	21.7
	23		100	1	61.9

Funding

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Supplementary Material

CCDC 946363 contains the supplementary crystallographic data for the two 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.

References

1. Patel, R. N.; Sondhiya, V. P.; Patel, D. K.; Shukla, K. K.; Singh, Y. Synthesis, crystal structure, spectroscopic and superoxide dismutase activity of copper(II) and nickel(II) complex of N'-[phenyl(pyridin-2-yl)methylidene]benzohydrazone. *Indian J. Chem. A* **2012**, *51*, 1695–1700.
2. Wang, M.-F.; Yang, Z.-Y.; Liu, Z.-C.; Li, Y.; Li, H.-G. Lanthanide complexes of 1-phenyl-3-methyl-5-hydroxypyrazole-4-carbaldehyde-(4-hydroxybenzoyl)hydrazone: Crystal structure and interaction studies with biomacromolecules. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2013**, *43*, 483–494.
3. Sathyadevi, P.; Krishnamoorthy, P.; Jayanthi, E.; Butorac, R. R.; Cowley, A. H.; Dharmaraj, N. Studies on the effect of metal ions of hydrazone complexes on interaction with nucleic acids, bovine serum albumin and antioxidant properties. *Inorg. Chim. Acta* **2012**, *384*, 83–96.
4. Bikas, R.; Hosseini-Monfared, H.; Zoppellaro, G.; Herchel, R.; Tucek, J.; Owczarzak, A. M.; Kubicki, M.; Zboril, R. Synthesis, structure, magnetic properties and theoretical calculations of methoxy bridged dinuclear iron(III) complex with hydrazone based O,N,N-donor ligand. *Dalton Trans.* **2013**, *42*, 2803–2812.
5. Mukherjee, S.; Chowdhury, S.; Ghorai, A.; Ghosh, U.; Stoeckli-Evans, H. Synthesis, structure, interaction with DNA and cytotoxicity of a luminescent copper(II) complex with a hydrazone ligand. *Polyhedron* **2013**, *51*, 228–234.
6. Aslan, H. G.; Karacan, N.; Aslan, E. Synthesis, characterization and antimicrobial activity of a new aromatic sulfonyl hydrazone derivative and its transition metal complexes. *J. Chin. Chem. Soc.* **2013**, *60*, 212–217.
7. Chakravarthy, R. D.; Suresh, K.; Ramkumar, V.; Chand, D. K. New chiral molybdenum complex catalyzed sulfide oxidation with hydrogen peroxide. *Inorg. Chim. Acta* **2011**, *376*, 57–63.
8. Barlan, A. U.; Basak, A.; Yamamoto, H. Enantioselective oxidation of olefins catalyzed by a chiral bishydroxamic acid complex of molybdenum. *Angew. Chem. Int. Ed.* **2006**, *45*, 5849–5852.
9. Amini, M.; Haghdoost, M. M.; Bagherzadeh, M. Oxido-peroxido molybdenum(VI) complexes in catalytic and stoichiometric oxidations. *Coord. Chem. Rev.* **2013**, *257*, 1093–1121.
10. Sarioz, O.; Oznergiz, S.; Kandemirli, F. Bis(amino)phosphines derived from N-phenylpiperazine and N-ethylpiperazine: Synthesis, oxidation reactions, and molybdenum complexes. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2013**, *43*, 185–195.
11. Barlan, A. U.; Basak, A.; Yamamoto, H. Enantioselective oxidation of olefins catalyzed by a chiral bishydroxamic acid complex of molybdenum. *Angew. Chem. Int. Ed.* **2006**, *45*, 5849–5852.
12. Rayati, S.; Rafiee, N.; Wojtczak, A. *cis*-Dioxo-molybdenum(VI) Schiff base complexes: Synthesis, crystal structure and catalytic performance for homogeneous oxidation of olefins. *Inorg. Chim. Acta* **2012**, *386*, 27–35.
13. Debel, R.; Buchholz, A.; Plass, W. Structural and catalytic aspects of dioxomolybdenum(VI) complexes with *w*-hydroxy functionalized *N*-salicylidene hydrazides. *Z. Anorg. Allg. Chem.* **2008**, *634*, 2291–2298.
14. Bagherzadeh, M.; Amini, M.; Parastar, H.; Jalali-Heravi, M.; Ellern, A.; Woo, L. K. Synthesis, X-ray structure and oxidation catalysis of a oxido-peroxido molybdenum(VI) complex with a tridentate Schiff base ligand. *Inorg. Chem. Commun.* **2012**, *20*, 86–89.
15. Rao, S. N.; Munshi, K. N.; Rao, N. N.; Bhadbhade, M. M.; Suresh, E. Synthesis, spectral and X-ray structural characterization of [*cis*-MoO_2(L)(solv)] (L = salicylidene salicyloyl hydrazine) and its use as catalytic oxidant. *Polyhedron* **1999**, *18*, 2491–2497.
16. Jacobsen, E. N.; Wu, M. H. In: *Comprehensive Asymmetric Catalysis II*, Jacobsen, E. N., Pfaltz, A., Yamamoto, H., editors. New York, Springer-Verlag, 1999, pp. 41–46.
17. Moradi-Shoeili, Z.; Boghaei, D. M.; Amini, M.; Bagherzadeh, M.; Notash, B. New molybdenum(VI) complex with ONS-donor thiosemicarbazone ligand: Preparation, structural characterization, and catalytic applications in olefin epoxidation. *Inorg. Chem. Commun.* **2013**, *27*, 26–30.
18. Sharma, R. K.; Pandey, A.; Gulati, S. Silica-supported molybdenum complex: A novel, selective and reusable organic-inorganic hybrid catalyst for eco-friendly oxidation of sulfides and olefins. *Polyhedron* **2012**, *45*, 86–93.
19. Gomes, A. C.; Neves, P.; Figueiredo, S.; Fernandes, J. A.; Valente, A. A.; Paz, F. A. A.; Pillinger, M.; Lopes, A. D.; Goncalves, I. S. Tris(pyrazolyl)methane molybdenum tricarbonyl complexes as catalyst precursors for olefin epoxidation. *J. Mol. Catal. A–Chem.* **2013**, *370*, 64–74.
20. Sheldrick, G. M. *SHELXTL V5.1 Software Reference Manual*; Bruker AXS, Inc., Madison, WI, 1997.