ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 7, pp. 532–538. © Pleiades Publishing, Ltd., 2019.

Synthesis, Crystal Structures, and Catalytic Properties of Dioxomolybdenum(VI) Complexes Derived from 4-Chloro-2-{[4-Diethylamino-2-Hydroxybenzylidene]amino}phenol

X. W. Zhu*

Key Laboratory of Surface and Interface Science of Henan, School of Material and Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou, 450002 P.R. China

**e-mail: zhuxuewen2017@126.com*

Received June 15, 2018; revised January 24, 2019; accepted January 30, 2019

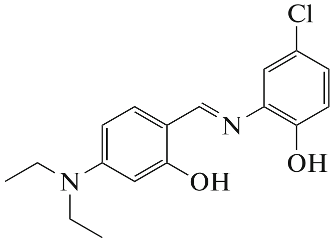
Abstract—Two new dioxomolybdenum(VI) complexes, [$MoO_2L(EtOH)$] (**I**) and [$MoO_2L(Sal)$] (**II**), where L is the dianionic form of 4-chloro-2-{[4-(diethylamino)-2-hydroxybenzylidene]amino}phenol (H_2L), Sal is 4-diethylaminosalicylaldehyde, were prepared and characterized by IR and UV-Vis spectra, as well as single crystal X-ray diffraction (CIF files CCDC nos. 1849408 (**I**) and 1849409 (**II**)). Complex **I** crystallizes as the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 7.3050(10)$, $b = 11.6969(16)$, $c = 13.3433(19)$ Å, $\alpha = 103.915(2)°$, $\beta = 102.542(2)°$, $\gamma = 105.676(2)°$, $V = 1015.8(2)$ Å^3, $Z = 2$, $R_1 = 0.0616$, $wR_2 = 0.1579$, GOOF = 1.080. Complex **II** crystallizes as the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 7.0773(11)$, $b = 12.8817(12)$, $c = 16.420(2)$ Å, $\alpha = 107.000(2)°$, $\beta = 101.478(2)°$, $\gamma = 91.416(2)°$, $V = 1397.4(3)$ Å^3, $Z = 2$, $R_1 = 0.0484$, $wR_2 = 0.1048$, GOOF = 1.015. X-ray analyses indicate that the complexes are dioxomolybdenum(VI) species with the Mo atoms in octahedral coordination. The catalytic oxidation property of the complexes with *tert*-butylhydroperoxide in CH_2Cl_2 was studied.

Keywords: Schiff base, dioxomolybdenum complex, crystal structure, catalytic property

DOI: 10.1134/S1070328419070091

INTRODUCTION

Schiff base complexes have various catalytic properties, such as ring opening polymerization of cycloalkenes [1], oxidation of hydrocarbons [2, 3], ring opening of large cycloalkanes [4–6], reduction of ketones to alcohols [7], alkylation of allylic substrates [8], improve enantioselectivity in the cyclopropanation reactions [9, 10]. The capability of molybdenum to formation of complexes with oxygen-, nitrogen-, and sulfur-containing ligands led to development of molybdenum Schiff base complexes which are efficient catalysts both in homogeneous and heterogeneous reactions [11–16]. The properties of the complexes vary obviously with the different types of ligands and coordination sites. Recently, we have reported a molybdenum complex with hydrazone ligand and its catalytic property [17]. In the present work, two new dioxomolybdenum(VI) complexes with Schiff base ligand 4-chloro-2-{[4-(diethylamino)-2-hydroxybenzylidene]amino}phenol (H_2L), [$MoO_2L(EtOH)$] (**I**) and [$MoO_2L(Sal)$] (**II**), where Sal is 4-diethylaminosalicylaldehyde, are presented.



(H_2L)

EXPERIMENTAL

Materials and methods. Sal, 2-amino-4-chlorophenol and $MoO_2(acac)_2$ were purchased from Sigma-Aldrich and used as received. All other reagents were of analytical reagent grade. Elemental analyses of C, H and N were carried out in a PerkinElmer automated model 2400 Series II CHNS/O analyzer. FT-IR spectra were obtained on a PerkinElmer 377 FT-IR spectrometer with samples prepared as KBr pellets. UV–Vis spectra were obtained on a Lambda 900 spectrometer. X-ray diffraction was carried out on a Bruker APEX II CCD diffractometer.

Synthesis of H_2L. Sal (0.01 mol, 1.93 g) and 2-amino-4-chlorophenol (0.01 mol, 1.44 g) were dissolved in ethanol (50 mL). The mixture was stirred for 30 min to give yellow solution. Then, the solvent was removed by distillation. The yellow solid was recrystallized from ethanol to give the Schiff base. The yield was 2.63 g (82%).

IR data (ν, cm^{-1}): 3345 (O–H), 1623 (C=N), 1273 (Ar–O). UV–Vis data (CH_3OH; λ_{max}, nm): 265, 373. ^{1}H NMR (500 MHz; DMSO; δ, ppm): 13.84 (s., 1H, OH), 9.78 (s., 1H, OH), 8.67 (s., 1H, CH=N), 7.35 (d., 1H, ArH), 7.28 (d., 1H, ArH), 7.03 (q., 1H, ArH), 6.91 (d., 1H, ArH), 6.30 (d., 1H, ArH), 6.01 (s., 1H, ArH), 3.38 (m., 4H, CH_2), 1.12 (m., 6H, CH_3). ^{13}C NMR (126 MHz: DMSO: δ, ppm): 164.79, 160.11, 151.77, 149.31, 136.50, 134.16, 125.36, 123.09, 118.24, 117.36, 108.95, 103.88, 97.01, 43.89, 12.56.

For $C_{17}H_{19}N_2O_2Cl$

Anal. calcd., %	C, 64.05	H, 6.01	N, 8.79
Found, %	C, 64.23	H, 5.95	N, 8.87

Synthesis of complex I. Sal (0.01 mol, 1.93 g) and 2-amino-4-chlorophenol (0.01 mol, 1.44 g) were dissolved in ethanol (50 mL). Then, $MoO_2(acac)_2$ (0.01 mol, 2.65 g) dissolved in ethanol (20 mL) was added and stirred for 1 h to give yellow solution. Single crystals of the complex, suitable for X-ray diffraction, were grown from the solution upon slowly evaporation for a few days. The yield was 1.27 g (25%).

IR data (ν, cm^{-1}): 3397 (O–H), 1614 (C=N), 1285 (Ar–O), 931 and 911 (Mo=O). UV–Vis data (CH_3OH; λ_{max}, nm): 270, 327.

For $C_{19}H_{23}N_2O_5ClMo$

Anal. calcd., %	C, 46.50	H, 4.72	N, 5.71
Found, %	C, 46.65	H, 4.83	N, 5.62

Synthesis of complex II. Sal (0.02 mol, 3.86 g) and 2-amino-4-chlorophenol (0.01 mol, 1.44 g) were dissolved in ethanol (50 mL). Then, $MoO_2(acac)_2$ (0.01 mol, 2.65 g) dissolved in ethanol (20 mL) was added and stirred for 1 h to give yellow solution. Single crystals of the complex, suitable for X-ray diffraction, were grown from the solution upon slowly evaporation for a few days. The yield was 3.13 g (49%).

IR data (ν, cm^{-1}): 1632 (C=O), 1611 (C=N), 1288 (Ar–O), 935 and 913 (Mo=O). UV–Vis data (CH_3OH: λ_{max}, nm): 270, 330, 355.

For $C_{28}H_{32}N_3O_6ClMo$

Anal. calcd., %	C, 52.71	H, 5.06	N, 6.59
Found, %	C, 52.55	H, 5.17	N, 6.70

X-ray crystallography. X-ray diffraction was carried out at a Bruker APEX II CCD area diffractometer equipped with MoK_α radiation (λ = 0.71073 Å). The collected data were reduced with SAINT [18], and multi-scan absorption correction was performed using SADABS [19]. The structures of the complexes were solved by direct method, and refined against F^2 by full-matrix least-squares method using SHELXTL [20]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data and refinement parameters for the complexes are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (nos. 1849408 (**I**) and 1849409 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Catalytic epoxidation of olefins. Epoxidation of cyclooctene, cyclohexene, 1-octene and 1-hexene catalyzed by the complexes with *tert*-butylhydroperoxide (TBHP) in CH_2Cl_2 was carried out according to the following general procedure. To a 25 mL round bottomed flask equipped with a magnetic stirring bar and immersed into water thermo-stated bath, was added 10 mL CH_2Cl_2, 1.0 mmol TBHP, 0.01 mmol catalyst and 1.0 mmol olefin. The mixture was refluxed with vigorous stirring for 2 h at an appropriately chosen temperature. The progress of the reaction was monitored by carefully with drawing aliquots of the sample at different time intervals to determine concentrations of the products by GC analysis, using *n*-hexane as an internal standard and was left to proceed until near complete conversion of TBHP. The concentration of the TBHP was determined by iodometric titration method [21]. The yield of epoxide (%) was calculated according to the starting amount of olefin. Assignments of the products were made by comparison with authentic samples. All the reactions were run in triplicates. Control experiments showed that no epoxide was formed in a measurable extent in the absence of catalyst.

RESULTS AND DISCUSSION

The ligand H_2L was readily prepared by the condensation reaction of Sal and 2-amino-4-chlorophenol in ethanol. The molybdenum(VI) complex **I** was synthesized by stirring equimolar quantities of H_2L with $MoO_2(acac)_2$ in methanol at room temperature. The molybdenum(VI) complex **II** was synthesized by stirring equimolar quantities of H_2L, Sal with $MoO_2(acac)_2$ in methanol at room temperature. In fact, complex **II** can also be obtained by reaction of equimolar quantities of complex **I** with Sal in ethanol. Single crystals of the complexes are stable in air at

Table 1. Crystallographic data and structure refinement for complexes **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	490.78	637.96
Crystal shape/color	Block/yellow	Block/yellow
T, K	298(2)	298(2)
Crystal dimensions, mm	0.19 × 0.18 × 0.18	0.31 × 0.27 × 0.23
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	7.3050(10)	7.0773(11)
b, Å	11.6969(16)	12.8817(12)
c, Å	13.3433(19)	16.420(2)
α, deg	103.915(2)	107.000(2)
β, deg	102.542(2)	101.478(2)
γ, deg	105.676(2)	91.416(2)
V, Å^3	1015.8(2)	1397.4(3)
Z	2	2
ρ_{calcd}, g cm^{-3}	1.605	1.516
$\mu(MoK_\alpha)$, mm^{-1}	0.810	0.612
$F(000)$	500	656
Measured reflections	5704	7777
Unique reflections	3671	5172
Observed reflections ($I \geq 2\sigma(I)$)	3075	4249
Min and max transmission	0.8613 and 0.8679	0.8330 and 0.8721
Parameters	260	357
Restraints	3	0
Goodness of fit on F^2	1.080	1.015
R_1, wR_2 ($I \geq 2\sigma(I)$)*	0.0616, 0.1579	0.0484, 0.1048
R_1, wR_2 (all data)*	0.0733, 0.1771	0.0636, 0.1131

* $R_1 = F_o - F_c/F_o$, $wR_2 = [\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2]^{1/2}$.

ambient condition. The complexes are soluble in methanol, ethanol, acetonitrile, DMSO, DMF, but insoluble in water. The chemical formulae of the complexes have been confirmed by elemental analyses, IR spectra, and single crystal X-ray diffraction.

The band at 1623 cm^{-1} characteristic of the azomethine group present in the free Schiff base, was shifted to lower wave numbers at 1614 cm^{-1} for **I** and 1611 cm^{-1} for **II**, indicating that the involvement the azomethine nitrogen atoms in coordination. The band at 1273 cm^{-1} in the spectrum of the Schiff base is ascribed to the phenolic C–O stretching vibration. This band is found at 1285 and 1288 cm^{-1} in the spectra of the complexes. These changes suggest that the hydroxyl groups of the Schiff bases took part in the complex formation. The Schiff base and the complex **I** exhibit broad bands at 3345 and 3397 cm^{-1}, respectively, which may be assigned to the ν(O–H). Further evidence of the bonding is also shown by the observation that new bands in the IR spectra of the metal complexes appear at 450–600 cm^{-1} assigned to Mo–N and Mo–O stretching vibrations. The Mo=O stretching mode occur as double bands at 931–935 and 911–913 cm^{-1}, assigned to the symmetric and asymmetric stretching modes of the MoO_2 moieties [22, 23].

Table 2. Selected bond distances (Å) and angles (deg) for complexes **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
I			
Mo(1)–O(1)	1.923(4)	Mo(1)–O(2)	1.988(4)
Mo(1)–O(3)	1.679(5)	Mo(1)–O(4)	1.701(4)
Mo(1)–O(5)	2.386(4)	Mo(1)–N(1)	2.266(4)
II			
Mo(1)–O(1)	1.971(3)	Mo(1)–O(2)	1.933(3)
Mo(1)–O(4)	2.398(3)	Mo(1)–O(5)	1.712(3)
Mo(1)–O(6)	1.681(3)	Mo(1)–N(1)	2.267(3)
Angle	**ω, deg**	**Angle**	**ω, deg**
I			
O(3)Mo(1)O(4)	106.1(3)	O(3)Mo(1)O(1)	99.9(3)
O(4)Mo(1)O(1)	102.4(2)	O(3)Mo(1)O(2)	99.4(2)
O(4)Mo(1)O(2)	93.6(2)	O(1)Mo(1)O(2)	150.25(19)
O(3)Mo(1)N(1)	93.1(2)	O(4)Mo(1)N(1)	159.2(2)
O(1)Mo(1)N(1)	81.61(17)	O(2)Mo(1)N(1)	74.99(16)
O(3)Mo(1)O(5)	172.3(2)	O(4)Mo(1)O(5)	81.6(2)
O(1)Mo(1)O(5)	78.88(19)	O(2)Mo(1)O(5)	78.90(18)
N(1)Mo(1)O(5)	79.21(16)		
II			
O(6)Mo(1)O(5)	105.41(15)	O(6)Mo(1)O(2)	99.50(15)
O(5)Mo(1)O(2)	100.47(14)	O(6)Mo(1)O(1)	99.36(15)
O(5)Mo(1)O(1)	96.25(14)	O(2)Mo(1)O(1)	150.40(12)
O(6)Mo(1)N(1)	93.21(14)	O(5)Mo(1)N(1)	160.51(13)
O(2)Mo(1)N(1)	81.67(12)	O(1)Mo(1)N(1)	74.68(12)
O(6)Mo(1)O(4)	171.59(13)	O(5)Mo(1)O(4)	82.98(13)
O(2)Mo(1)O(4)	79.14(12)	O(1)Mo(1)O(4)	78.87(11)
N(1)Mo(1)O(4)	78.39(11)		

Electronic absorption spectra of the Schiff base and the complexes were obtained in methanol solutions. The electronic absorption spectrum of H_2L displayed two bands at 265 and 373 nm, which are assigned for the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. In the electronic spectra of the complexes, the strong bands centered at 270 nm are attributed to the intra-ligand $\pi \rightarrow \pi^*$ absorption peak of the Schiff base ligand. The LMCT and to some extent $\pi \rightarrow \pi^*$ bands appear at about 330 nm.

The molecular structure of complex **I** is shown in Fig. 1a. The coordination geometry around the Mo atom can be described as distorted octahedron, with one imino-N and two phenolate-O of the Schiff base ligand, and one oxo group defining the equatorial plane, and with the other oxo group and one ethanol-O occupying the axial positions. The Schiff base ligand coordinates to the Mo atom in a meridional fashion forming five- and six-membered chelate rings with bite angles of 74.99(16)° and 81.61(17)°. The dihedral angle between the two benzene rings of the

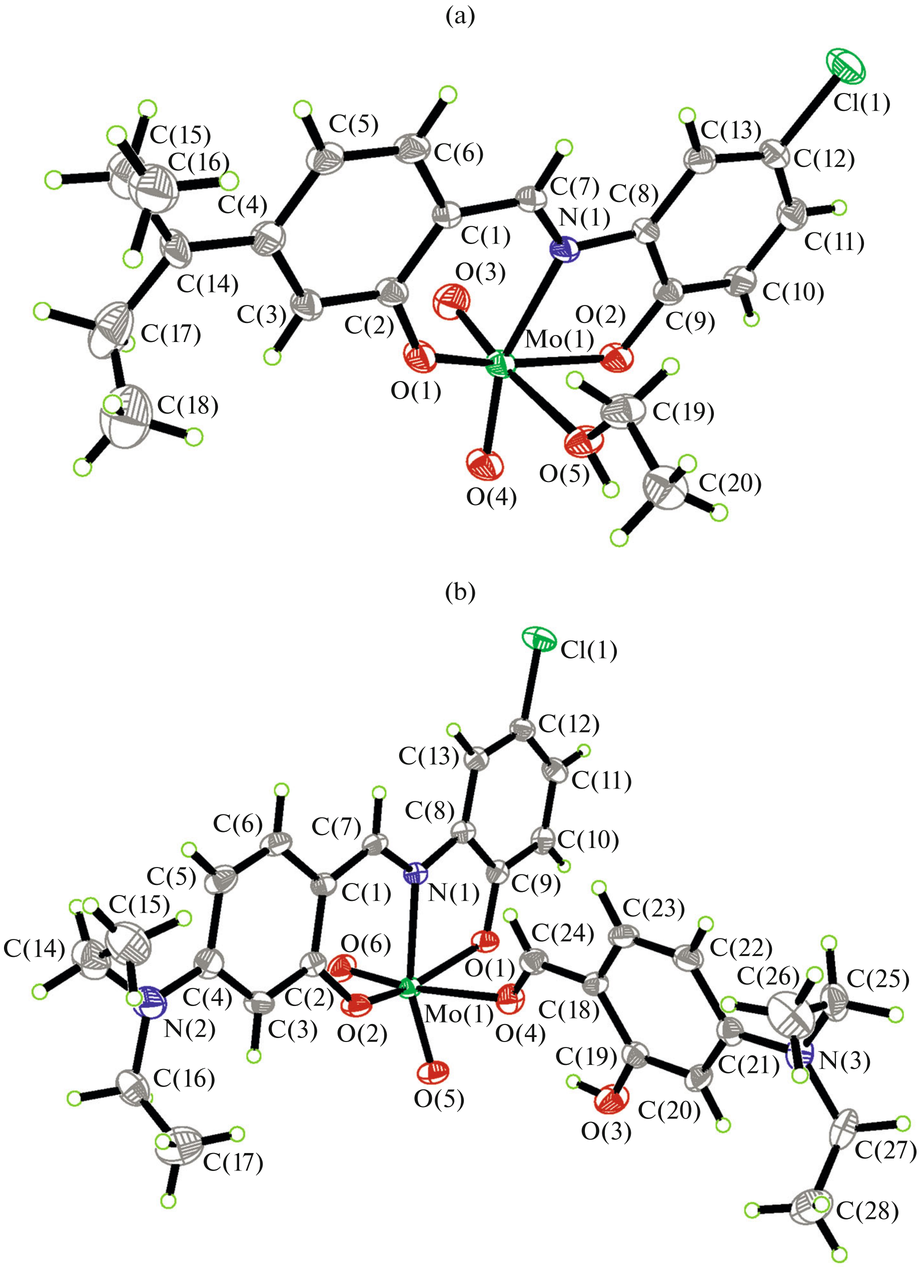


Fig. 1. A perspective view of complex **I** (a) and **II** (b) the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

Schiff base ligand is 1.9(5)°. The displacement of the Mo atom from the equatorial mean plane toward the apical oxo group is 0.343(2) Å. The Mo–O, Mo–N, and Mo=O bonds are within normal ranges and are similar to those observed in molybdenum(VI) complexes [11–16]. The torsion angles of C(4)–N(2)–C(15)–C(16) and C(4)–N(2)–C(17)–C(18) are 82.5(5)° and 86.4(5)°, respectively.

In the crystal structure of complex **I**, adjacent two [$MoO_2L(EtOH)$] molecules are linked through two intermolecular O–H···O hydrogen bonds (O(5)–H(5) 0.85(1), H(5)···O(2)^i 1.977(13), O(5)···O(2)^i 2.826(6) Å, angle O(5)–H(5)···O(2)^i 176(8)°; symmetry code for i: $1 - x$, $2 - y$, $1 - z$), to form dimers (Fig. 2).

The molecular structure of complex **II** is shown in Fig. 1b. The coordination geometry around the Mo atom can be described as distorted octahedron with one imino-N and two phenolate-O of the Schiff base ligand, and one oxo group defining the equatorial

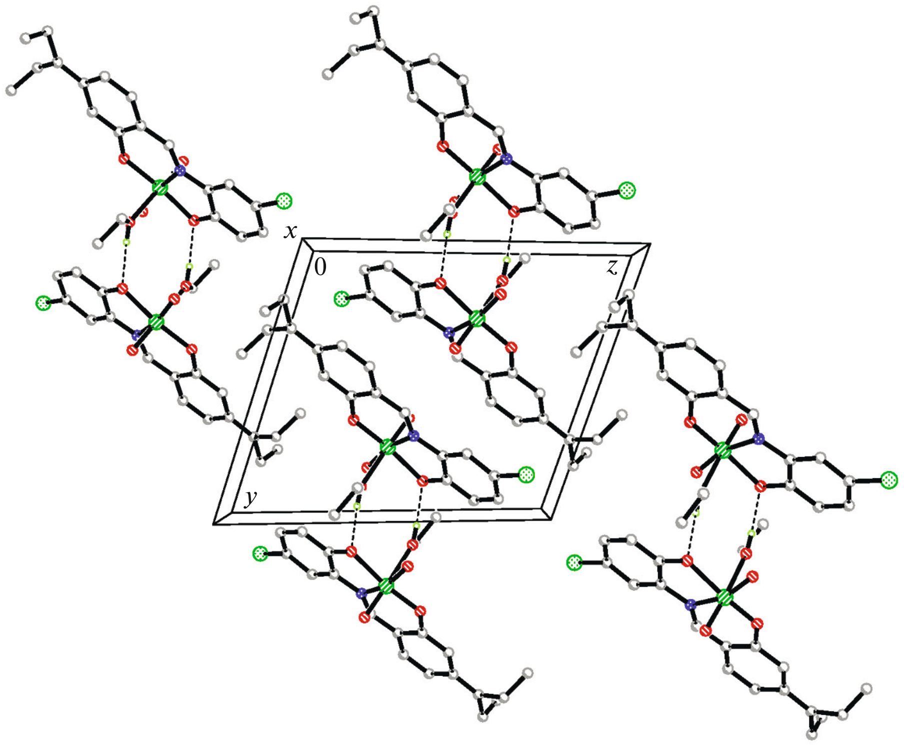


Fig. 2. The hydrogen bonds (dashed lines) linked dimers of complex **I**, viewed along the *x* axis.

plane, and with the other oxo group and one carbonyl-O of Sal ligand occupying the axial positions. The Schiff base ligand coordinates to the Mo atom in a meridional fashion forming five- and six-membered chelate rings with bite angles of 74.68(12)° and 81.67(12)°. The dihedral angle between the two benzene rings of the Schiff base ligand is 3.4(5)°. The displacement of the Mo atom from the equatorial mean plane toward the apical oxo group is 0.333(2) Å. The Mo–O, Mo–N, and Mo=O bonds are within normal ranges and are similar to those of complex **I** and other molybdenum(VI) complexes [11–16]. The torsion angles of C(4)–N(2)–C(14)–C(15), C(4)–N(2)–C(16)–C(17), C(21)–N(3)–C(25)–C(26) and C(21)–N(3)–C(27)–C(28) are 79.1(5)°, 88.5(5)°, 79.5(5)° and 84.4(5)°, respectively. In the crystal structure of complex **II**, molecules are stack along the *x* axis (Fig. 3).

Table 3. Epoxide yields (%) for the catalytic processes at different temperatures

Substrate	25°C		45°C		65°C	
	I	**II**	**I**	**II**	**I**	**II**
Cyclooctene	83	72	90	81	98	92
Cyclohexene	72	66	80	72	95	87
1-Hexene	66	61	75	70	82	83
1-Octene	53	47	58	55	73	71

Catalytic property of the complexes was investigated in the epoxidation of cyclooctene, cyclohexene, 1-octene and 1-hexene with TBHP and CH_2Cl_2 as a solvent at different temperatures 25, 45 and 65°C. The catalytic reactions were initially performed in common atmosphere in order to test the performance of the system under the easiest possible reaction conditions. A substrate, oxidant, and catalyst ratio of 100 : 100 : 1 was used. In general, the epoxide yields are higher for cyclic olefins than those for terminal olefins. As seen in Table 3, the order of increasing reactivity based on yield% were as cyclooctene > cyclohexene > 1-hexene > 1-octene. In addition, the epoxide yields increase with the rise in temperature. Except for 1-hexene at 65°C, complex **I** has better catalytic property than complex **II**.

Thus two new dioxomolybdenum(VI) complexes derived from the Schiff base ligand 4-chloro-2-{[4-(diethylamino)-2-hydroxybenzylidene]amino}phenol have been

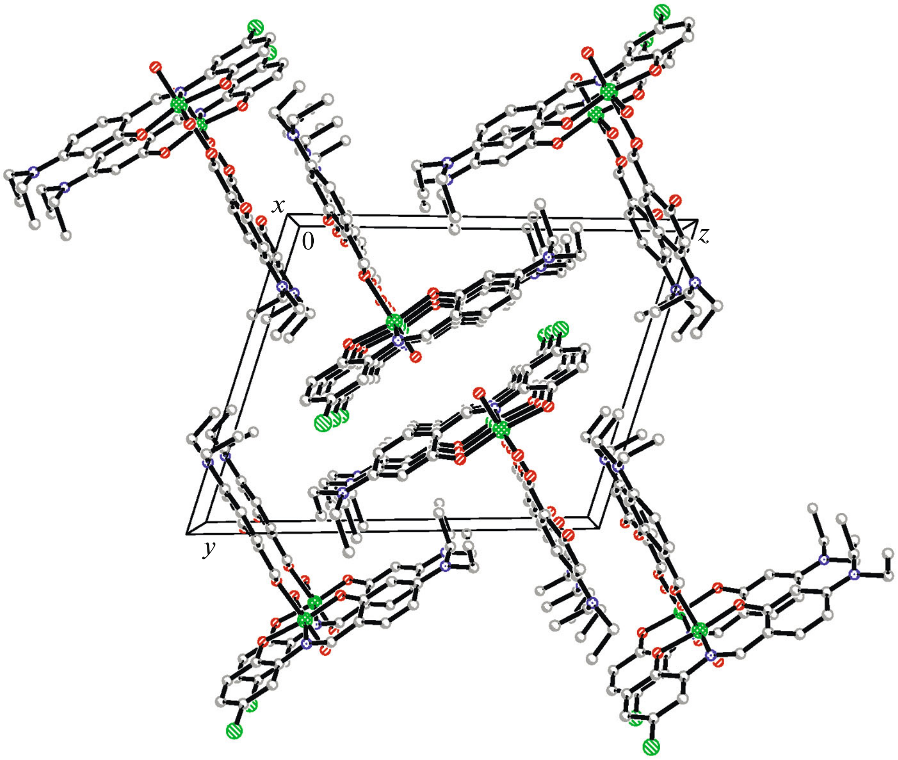


Fig. 3. The molecular packing diagram of complex **II**, viewed along the *x* axis.

prepared and structurally characterized. The Mo atoms in the complexes are in octahedral coordination. Both complexes have effective catalytic properties on cyclooctene.

REFERENCES

1. Huang, D., Wang, C., and Song, Y., *Russ. J. Gen. Chem.*, 2013, vol. 83, no. 12, p. 2361.
2. Biswas, S., Dutta, A., Dolai, M., et al., *RSC Adv.*, 2014, vol. 4, no. 65, p. 34248.
3. Bahramian, B., Ardejani, F.D., Mirkhani, V., et al., *Appl. Catal., A*, 2008, vol. 345, no. 1, p. 97.
4. Schriescheim, A., Muller, R.J., and Rowe, C.A., *J. Am. Chem. Soc.*, 1962, vol. 84, no. 16, p. 3164.
5. Farzaneh, F., Ghiasi, M., Ghandi, M., et al., *J. Porous Mater.*, 2013, vol. 20, no. 1, p. 267.
6. Pamin, K., Pozzi, G., Tabor, E., et al., *Catal. Commun.*, 2013, vol. 39, no. 17, p. 102.
7. Ventakachalam, G. and Ramesh, R., *Inorg. Chem. Commun.*, 2005, vol. 8, no. 11, p. 1009.
8. Pou, D., Platero-Prats, A.E., Perez, S., et al., *J. Organomet. Chem.*, 2007, vol. 692, no. 22, p. 5017.
9. Koz, G., Astley, D., and Astley, S.T., *Turk. J. Chem.*, 2011, vol. 35, no. 4, p. 553.
10. Masterson, D.S., Hobbs, T.L., and Glatzhofer, D.T., *J. Mol. Catal., A*, 1999, vol. 145, no. 1, p. 75.
11. Bagherzadeh, M., Latifi, R., Tahsini, L., et al., *Polyhedron*, 2009, vol. 28, no. 12, p. 2517.
12. Moradi-Shoeili, Z., Zare, M., Bagherzadeh, M., et al., *J. Coord. Chem.*, 2015, vol. 68, no. 3, p. 548.
13. Bagherzadeh, M., Amini, M., Parastar, H., et al., *Inorg. Chem. Commun.*, 2012, vol. 20, no. 1, p. 86.
14. Aziz, A.A.A., *J. Mol. Struct.*, 2010, vol. 979, no. 1, p. 77.
15. Chakravarthy, R.D., Suresh, K., Ramkumar, V., et al., *Inorg. Chim. Acta*, 2011, vol. 376, no. 1, p. 57.
16. Rayati, S., Rafiee, N., and Wojtczak, A., *Inorg. Chim. Acta*, 2012, vol. 386, no. 1, p. 27.
17. Zhu, X.W., *Russ. J. Coord. Chem.*, 2018, vol. 44, no. 7, p. 421. https://doi.org/10.1134/S1070328418070084
18. *SMART (version 5.625) and SAINT (version 6.01)*, Madison: Bruker AXS Inc., 2007.
19. Sheldrick, G.M., *SADABS, Program for Empirical Absorption Correction of Area Detector*, Göttingen: Univ. of Göttingen, 1996.
20. Sheldrick, G.M., *SHELXTL, Version 5.1, Software Reference Manual*, Madison: Bruker AXS Inc., 1997.
21. Brill, W.F., *J. Am. Chem. Soc.*, 1963, vol. 85, no. 3, p. 141.
22. Rao, S.N., Munshi, K.N., Rao, N.N., et al., *Polyhedron*, 1999, vol. 18, no. 19, p. 2491.
23. El-Medani, S.M., Aboaly, M.M., Abdalla, H.H., et al., *Spectrosc. Lett.*, 2004, vol. 37, no. 6, p. 619.