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Syntheses, structure, redox and catalytic epoxidation properties of dioxomolybdenum(VI) complexes with Schiff base ligands derived from tris(hydroxymethyl)amino methane

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Abstract

Five kinds of dioxomolybdenum(VI) complexes with Schiff base ligands derived from tris(hydroxymethyl)amino methane are prepared and structurally characterized by X-ray crystallography, which reveals that these complexes adopt a distorted octahedral six-coordinate configuration formed by the tridentate Schiff base ligand, one coordinating water and two binding oxygen atoms. These complexes show good catalytic activities and selectivity in the epoxidation of cyclohexene with *t*-butylhydroperoxide, especially for complex **4**, which could give a nearly 100% of epoxidation conversion and selectivity. Introduction of the electron-withdrawing group to the salicylidene ring of complex strongly increases the effectiveness of a catalyst, but decreases the redox stability of a complex.

Keywords: Epoxidation; Homogeneous catalysis; Dioxomolybdenum(VI) complexes; Tris(hydroxymethyl)amino methane; Schiff base ligands

1. Introduction

Because of their versatility as intermediates, epoxides are of great value in both synthetic organic chemistry and chemical technology [1]. They can be formed from corresponding olefins by oxidation with various oxygen sources in the presence of catalyst [2,3]. Molybdenum complexes are considered to be very effective catalysts for epoxidation with alkyl hydroperoxides as oxidants [4]. Although recently reported some oxodiperoxo molybdenum(VI) complexes show very pronounced efficiency epoxidation of olefinic compounds at room temperature [5,6], these catalysts suffer the disadvantages due to the complicated preparation procedure and high cost. Whereas dioxomolybdenum(VI) complexes are more easy to be prepared, synthesis of new efficient, selective dioxomolybdenum(VI) catalysts is still a subject of practical and theoretical interest [7]. Tris(hydroxymethyl)amino methane (THAM) has been widely used in biochemistry, biology, physiology, and medicine, as an inexpensive pH buffer in the physiological pH range [8], and some metal complexes with Schiff base ligands derived from it have been reported [9–12], but to the best of our knowledge, there are no reports on their dioxomolybdenum(VI) complexes used as catalysts in epoxidation of alkenes.

In this paper, we reported five kinds of easily prepared dioxomolybdenum(VI) complexes with Schiff base ligands derived from THAM and salicylaldehyde with different substituents (**1**–**4**) and 2-hydroxynaphthaldehyde (**5**) (Scheme 1), and their catalytic applications in the epoxidation of cyclohexene with *tert*-butyl hydroperoxide (TBHP). These catalysts will be promising due to their available free hydroxymethyl groups which could make them suitable for attachment to silica surfaces, converting them to very specific heterogeneous catalysts.

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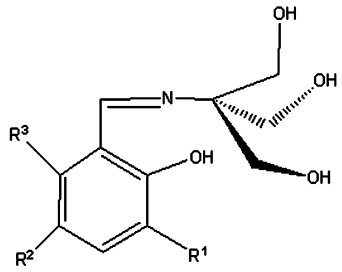


R^1	R^2	R^3	Ligand	Complexes
H	H	H	H_4L^1	**1** $[MoO_2(H_2L^1)(MeOH)]$
OMe	H	H	H_4L^2	**2*** $[MoO_2(H_2L^2)(H_2O)]$
OEt	H	H	H_4L^3	**3** $[MoO_2(H_2L^3)(H_2O)]$
H	NO_2	H	H_4L^4	**4*** $[MoO_2(H_2L^4)(H_2O)]$
H	C_4H_4		H_4L^5	**5*** $[MoO_2(H_2L^5)(H_2O)]$

Scheme 1. Ligands used and complexes synthesized. (*) indicates a single-crystal structure determination.

2. Experimental

2.1. Materials and methods

Salicylaldehyde and THAM were obtained commercially, distilled and recrystallized respectively prior to use. 3-Methoxy-2-hydroxy-benzaldehyde, 3-ethoxysalicylaldehyde, 5-nitrosalicylaldehyde, and 2-hydroxy-1-napthaldehyde were purchased from Alfa Aesar. Analytical grade L-ascorbic acid was obtained from local source and used without further purification prior to use. $MoO_2(acac)_2$ was prepared by a reported procedure [13].

C, H and N elemental analysis were carried out on a Perkin-Elmer 2400 elemental instrument. Mo content of the complexes was measured by using instrument TPS-7000 ICP scanning spectra. Infrared spectra were recorded on Spectrum GX using polystyrene as a standard (KBr pellet). Fourier transform Raman (FT-Raman) spectra were undertaken in a Bruker RFS100/S apparatus using a laser source of Nd/YAG $\lambda = 1064$ nm of 200 mW and a Ge detector at 77 K. ^{1}H NMR and ^{13}C NMR were recorded at 298 K in DMSO-d_6 using a Bruker AV-300 spectrometer. UV–vis spectrophotometric experiments were performed on a UV-8500 spectrometer (made in Shanghai, China). Cyclic voltammogram (CV) measurements were performed using a Fuso HECS 321B potential sweep unit with DMF solutions containing Bu_4NClO_4 (TBAP) (0.1 M) as a supporting electrolyte at a scan rate of 100 mV s^{-1}. Three-electrochemical cell was a three-electrode system consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode.

2.2. X-ray crystallography

Standard procedures were used for mounting the crystals on a Bruker Apex-II area-detector diffractometer. As the crystals were found to be stable, no special protection was employed. Intensity data were collected using Mo Kα radiation ($\lambda = 0.71073$ Å) under 50 kV, 25 mA and by a ϕ- and ω-scan mode at 295(2) K. The SAINT and SADABS program in the APPEX2 software package was used for the integration and absorption corrections [14]. The structure was solved by direct methods using SHELXS-97 program of the APPEX2 software package and refined on F^2 with XSHELL 6.3.1, all non-hydrogen atoms being modeled anisotropically. The disorder H atoms of water in complex **5** were found in a difference Fourier map and refined with the following restraints: H···O = 0.85(2), H···H = 1.38(2) Å, whilst maintaining a H–O–H bond angle of 107.5°. The other H atoms were positioned geometrically and treated as riding on their parent atoms, with C–H distances of 0.93 Å (aromatic), 0.97 Å (methylene) and 0.96 Å (methyl), and with $U_{iso}(H) = 1.5\,U_{eq}(C)$ for methyl H atoms and $1.2\,U_{eq}(C)$ for other H atoms. Other details of collection and refinement are provided in Table 1.

CCDC reference numbers 623603 and 623604.

2.3. Synthesis of Schiff bases

H_4L^1. To THAM(1.210 g, 10 mmol) in methanol (40 ml) was added salicylaldehyde (1.221 g, 10 mmol) in methanol (20 ml). The deep yellow solution which resulted was heated at 80 °C for 4 h, concentrated and cooled to room temperature, and the yellow solid yielded after the addition of adequate diethyl ether was filtered, washed with methanol and diethyl ether respectively, recrystallized in methanol and dried in vacuo to obtain *H_4L^1* (2.03 g, 90%). Found: C, 58.5; H, 6.6; N, 6.0. Calc. for $C_{11}H_{15}NO_4$: C, 58.7; H, 6.7; N, 6.2%: mp 150–151 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.55 (s, 1H, imine), 7.42–6.76 (m, 4H, Ph), 4.76 (s, 1H, Ph–O*H*), 3.61 (s, 6H, C*H*$_2$OH), 3.36 (s, 3H, CH$_2$O*H*). IR (KBr matrix, in cm^{-1}) ν(OH) 3321, ν(C=N) 1636; FT-Raman (cm^{-1}) ν(OH) 3311, ν(C=N) 1636. H_4L^2–H_4L^5 were synthesized and purified in a similar method as for H_4L^1.

H_4L^2. (Found: C, 56.3; H, 6.7; N, 5.5. Calc. for $C_{12}H_{17}NO_5$: C, 56.5; H, 6.7; N, 5.5): mp 188–189 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.55 (s, 1H, imine), 6.96 (m, 2H, Ph), 6.62 (d, 1H, Ph), 4.87 (s, 1H, Ph–O*H*), 3.73 (s, 3H, OCH$_3$), 3.60 (s, 6H, C*H*$_2$OH), 3.36 (s, 3H, CH$_2$O*H*). IR (KBr matrix, in cm^{-1}) ν(OH) 3340, 3199; ν(C=N) 1642; FT-Raman (cm^{-1}) ν(C=N) 1645.

H_4L^3. (Found: C, 57.8; H, 7.0; N, 5.2. Calc. for $C_{13}H_{19}NO_5$: C, 58.0; H, 7.1; N, 5.2): mp 169–170 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.46 (d, 1H, imine), 6.87–6.96 (m, 2H, Ph), 6.55 (t, 1H, Ph), 4.85 (t, 1H, Ph–O*H*), 3.94–4.01 (m, 2H, OC*H*$_2$CH$_3$), 3.60 (d, 6H, C*H*$_2$OH), 3.39 (s, 3H, CH$_2$O*H*), 1.30 (t, 3H, OCH$_2$C*H*$_3$). IR (KBr matrix, in cm^{-1}) ν(OH) 3300; ν(C=N) 1631; FT-Raman (cm^{-1}) ν(C=N) 1626.

H_4L^4. (Found: C, 48.9; H, 5.2; N, 10.4. Calc. for $C_{11}H_{14}N_2O_6$: C, 48.9; H, 5.2; N, 10.4): mp 237 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.74 (d, 1H, imine), 8.56 (d, 1H, Ph), 7.98–8.03 (m, 1H, Ph), 6.50 (d, 1H, Ph), 5.27 (s, 1H, Ph–O*H*), 3.63 (d, 6H, C*H*$_2$OH), 3.41 (s, 3H, CH$_2$O*H*). IR (KBr matrix, in cm^{-1}) ν(OH) 3488, 3429, 3256; ν(C=N) 1653; FT-Raman (cm^{-1}) ν(C=N) 1657.

H_4L^5

Table 1
Summary of crystallographic data and parameters for complexes **4** and **5**

	Complex	
	4	**5**
Empirical formula	$C_{11}H_{14}MoN_2O_9$	$C_{15}H_{19}MoNO_8$
Formula weight	414.18	437.25
Temperature	295(2)	295(2)
μ(Mo Kα) (mm^{-1})	0.71073	0.71073
Crystal system, space group	Monoclinic $P2_1/c$	Orthorhombic $P2_12_12_1$
Unit cell dimensions	$a = 13.9002(5)$ Å, $\alpha = 90°$, $b = 8.4501(3)$ Å, $\beta = 113.3°$, $c = 13.2189(5)$ Å, $\gamma = 90°$	$a = 8.0627(5)$ Å, $\alpha = 90°$, $b = 11.6897(7)$ Å, $\beta = 90°$, $c = 17.7100(11)$ Å, $\gamma = 90°$
Cell volume ($Å^3$)	1426.01(9)	1669.18(18)
Z, D_x/Mg (m^{-3})	4, 1.929	4, 1.740
$F(0\,0\,0)$	832	888
Crystal size (mm)	$0.23 \times 0.17 \times 0.10$	$0.19 \times 0.14 \times 0.10$
θ (°)	2.89–25.49	2.09–26.00
Reflections collected/unique	8642/2619 [$R_{int} = 0.0276$]	10,924/3216 [$R_{int} = 0.0317$]
Data/restraints/parameters	2619/2/215	3216/6/240
Goodness-of-fit on F^2	1.002	1.008
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0243$, $wR_2 = 0.0639$	$R_1 = 0.0250$, $wR_2 = 0.0538$
R indices (all data)	$R_1 = 0.0315$, $wR_2 = 0.0659$	$R_1 = 0.0291$, $wR_2 = 0.0549$

. (Found: C, 65.3; H, 6.1; N, 5.5. Calc. for $C_{15}H_{17}NO_4$: C, 65.4; H, 6.2; N, 5.1): mp 170–172 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.90 (d, 1H, imine), 7.95 (d, 1H, Ar–H), 7.66 (d, 1H, Ar–H), 7.60 (d, 1H, Ar–H), 7.40 (t, 1H, Ar–H), 7.15 (t, 1H, Ar–H), 6.64 (d, 1H, Ar–H), 5.13 (s, 3H, CH_2OH), 3.65 (s, 6H, CH_2OH). IR (KBr matrix, in cm^{-1}) ν(OH) 3326; ν(C=N) 1634; FT-Raman (cm^{-1}) ν(C=N) 1614.

2.4. Synthesis of molybdenum complexes

[$MoO_2(H_2L^1)(MeOH)$] **1**. H_4L^1 (2.830 g, 12.57 mmol) was dissolved in ca. 75 ml of methanol. After complete dissolution, $MoO_2(acac)_2$ (4.120 g, 12.57 mmol) was added to the yellow solution. The mixture was allowed to react at room temperature for 1 day, and then the volume was reduced to ca. 10 ml and 20 ml of diethyl ether were added to precipitate the compound as a yellow solid. The solid was washed twice with diethyl ether and dried under vacuum. Yield 3.77 g (78%). Anal. Calc. for $C_{12}H_{17}MoNO_7$: C, 37.61; H, 4.47; Mo, 25.04; N, 3.66. Found: C, 37.20; H, 4.58; Mo, 24.90; N, 3.28. IR (KBr matrix, in cm^{-1}): ν(OH) 3517, 3305; ν(C=N) 1627; ν_s(M=O) 927; ν_{as}(M=O) 895. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.49 (s, 1H, imine), 7.62–6.88 (m, 4H, Ph), 5.01 (t, 2H, free CH_2OH), 4.44 (s, 2H, bound CH_2O^-), 3.74–3.57 (m, 4H, free CH_2OH). ^{13}C NMR: δ 163.6 (imine), 159.8–119.0 (aromatic), 76.8 (bound CH_2O^-), 61.0 (free CH_2OH), 53.7 (tertiary C). UV–vis (DMF): λ (nm) (ε, $M^{-1}\,cm^{-1}$) 270.5 (12,710) and 345.5 (3478). Complexes **2**–**5** were synthesized and purified as for **1**.

[$MoO_2(H_2L^2)(H_2O)$] **2**. Yield 4.54 g (90%); found C, 36.70; H, 4.40; Mo, 23.37; N, 3.41. $C_{12}H_{17}MoNO_8$ requires C, 36.10; H, 4.29; Mo, 24.03; N, 3.51; IR (KBr matrix, in cm^{-1}): ν(OH) 3467, 3341; ν(C=N) 1625; ν_s(M=O) 933; ν_{as}(M=O) 901. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.47 (s, 1H, C*H*=N), 7.18 (t, H, Ar–*H*), 6.89 (t, 1H, Ar–H), 4.42 (s, 2H, bound CH_2O^-), 3.79 (s, 3H, –OCH_3), 3.74–3.57 (m, 4H, free CH_2OH). ^{13}C NMR: δ 163.7 (imine), 151.5–118.0 (aromatic), 76.9 (bound CH_2O^-), 60.8 (free CH_2OH), 56.2 (OCH_3), 53.3 (tertiary C). UV–vis (DMF): λ (nm) (ε, $M^{-1}\,cm^{-1}$) 283 (14,970) and 366.5 (3474).

[$MoO_2(H_2L^3)(H_2O)$] **3**. Yield 4.64 g (89%); found C, 38.24; H, 4.68; Mo, 23.14; N, 3.10. $C_{13}H_{19}MoNO_8$ requires C, 37.78; H, 4.63; Mo, 23.22; N, 3.39; IR (KBr matrix, in cm^{-1}): ν(OH) 3427; ν(C=N) 1629; ν_s(M=O) 930; ν_{as}(M=O) 904. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.46 (s, 1H, C*H*=N), 7.16 (t, 2H, Ar–*H*), 6.86 (t, 1H, Ar–H); 4.41 (s, 2H, bound CH_2O^-), 4.05 (m, 2H, –OCH_2CH_3), 3.69 (m, 4H, free CH_2OH), 1.33 (t, 3H, –OCH_2CH_3). ^{13}C NMR: δ 163.8 (imine), 148.3–118.1 (aromatic), 76.9 (bound CH_2O^-), 65.0 (–OCH_2CH_3), 60.8 (free CH_2OH), 53.3 (tertiary C), 16.2 (–OCH_2CH_3). UV–vis (DMF): λ (nm) (ε, $M^{-1}\,cm^{-1}$) 282.5 (12,082) and 364.5 (2724).

[$MoO_2(H_2L^4)(H_2O)$] **4**. Yield 4.94 g (95%); found C, 31.60; H, 3.62; Mo, 22.85; N, 6.83. $C_{11}H_{14}MoN_2O_9$ requires C, 31.90; H, 3.41; Mo, 23.16; N, 6.76; IR (KBr matrix, in cm^{-1}): ν(OH) 3563, 3425; ν(C=N) 1640; ν_s(M=O) 937; ν_{as}(M=O) 908. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.67 (s, 1H, C*H*=N), 8.72 (d, 1H, Ar–H), 8.30 (m, 1H, Ar–H), 7.04 (d, 1H, Ar–H), 4.55 (s, 2H, bound CH_2O^-), 3.79–3.58 (m, 4H, free CH_2OH). ^{13}C NMR: δ 164.1 (imine), 163.9–116.9 (aromatic), 76.6 (bound CH_2O^-), 60.8 (free CH_2OH), 53.4 (tertiary C). UV–vis (DMF): λ (nm) (ε, $M^{-1}\,cm^{-1}$) 268.5 (12,123) and 342.0 (4494).

[$MoO_2(H_2L^5)(H_2O)$] **5**. Yield 4.87 g (92%); found C, 43.50; H, 4.18; Mo, 22.21; N, 3.26. $C_{15}H_{19}MoNO_8$ requires C, 42.97; H, 4.09; Mo, 22.88; N, 3.34; IR (KBr matrix, in cm^{-1}): ν(OH) 3238; ν(C=N) 1607; ν_s(M=O) 942; ν_{as}(M=O) 890. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.15 (s, 1H, C*H*=N), 8.26 (d, 1H, Ar–*H*), 8.05 (d, 1H, Ar–*H*), 7.91 (d, 1H, Ar–*H*), 7.64 (t, 1H, Ar–*H*), 7.44 (t, 1H, Ar–*H*), 7.16 (d, 1H, Ar–*H*), 4.48 (s, 2H, CH_2O–), 3.88–3.64 (m, 4H, free CH_2OH). ^{13}C NMR: δ 163.7 (imine), 158.8–114.7(aromatic), 76.9 (bound CH_2O^-), 62.4 (free CH_2OH), 53.7 (tertiary C). UV–vis (DMF): λ (nm) (ε, $M^{-1}\,cm^{-1}$) 270.0 (10,129) and 379.0 (3896).

The *cis*-dioxomolybdenum(VI) complexes **1**–**5** were generally recrystallized from methanol containing a little water. Single

crystals of **2**, **4** and **5** suitable for X-ray diffraction analysis were obtained by evaporation at room temperature after several days, and the structure of **2** has been reported by us [15].

2.5. Catalytic epoxidations of cyclohexene by complexes 1–5

Epoxidation of cyclohexene by dioxomolybdenum(VI) Schiff base complexes with TBHP was carried out according to the following general procedure: a mixture of catalyst (0.003 mmol), cyclohexene (6.56 g, 0.08 mol) and 1,2-dichloroethane (5 ml) was placed in a three-necked round-bottomed flask equipped with a condenser and a magnetic stirrer. The mixture was stirred for 5 min at 353 K and then 2 ml (ca. 0.02 mol) anhydrous *t*-butylhydroperoxide (TBHP) was added. The reaction was monitored at certain time intervals to determine the concentrations of TBHP and 1,2-epoxycyclohexene by GC and was left to proceed until near complete conversion of TBHP.

3. Results and discussion

3.1. Single-crystal X-ray diffraction analysis

X-ray diffraction data for **4** and **5** were collected using a Bruker Apex-II area-detector diffractometer. Selected crystallographic data and selected bond distances (Å) and angles (°) for the primary coordination spheres of the complexes are summarized in Tables 1–3, respectively. Figs. 1 and 2 are the molecular structure of **4** and **5**, respectively.

Table 2
Selected bond distances (Å) and angles (°) for the primary coordination spheres of complex **4**

Mo1–N1	2.282 (2)	Mo1–O7	1.690 (2)
Mo1–O1	1.961 (2)	Mo1–O8	1.706 (2)
Mo1–O2	1.937 (2)	Mo1–O9	2.334 (2)
N1–Mo1–O9	81.74 (7)	O7–Mo1–O1	96.76 (10)
O1–Mo1–N1	81.13 (7)	O7–Mo1–O2	98.74 (9)
O1–Mo1–O9	79.21 (8)	O7–Mo1–O8	106.17 (10)
O2–Mo1–N1	74.38 (7)	O7–Mo1–O9	172.37 (9)
O2–Mo1–O1	151.17 (8)	O8–Mo1–O1	102.61 (9)
O2–Mo1–O9	82.39 (7)	O8–Mo1–O2	96.22 (8)
O7–Mo1–N1	91.27 (9)	O8–Mo1–O9	81.13 (9)

Table 3
Selected bond distances (Å) and angles (°) for the primary coordination spheres of complex **5**

Mo1–N1	2.270 (2)	Mo1–O5	2.352 (2)
Mo1–O1	1.939 (2)	Mo1–O6	1.711 (2)
Mo1–O2	1.936 (2)	Mo1–O7	1.700 (2)
N1–Mo1–O5	78.24 (8)	O6–Mo1–O2	96.14 (11)
O1–Mo1–N1	80.17 (8)	O6–Mo1–O5	83.93 (9)
O1–Mo1–O5	78.95 (9)	O7–Mo1–N1	91.42 (9)
O2–Mo1–N1	74.81 (8)	O7–Mo1–O1	97.96 (10)
O2–Mo1–O1	150.52 (9)	O7–Mo1–O2	98.00 (10)
O2–Mo1–O5	80.89 (8)	O7–Mo1–O5	169.55 (9)
O6–Mo1–N1	161.03 (10)	O7–Mo1–O6	106.52 (10)
O6–Mo1–O1	102.84 (11)		

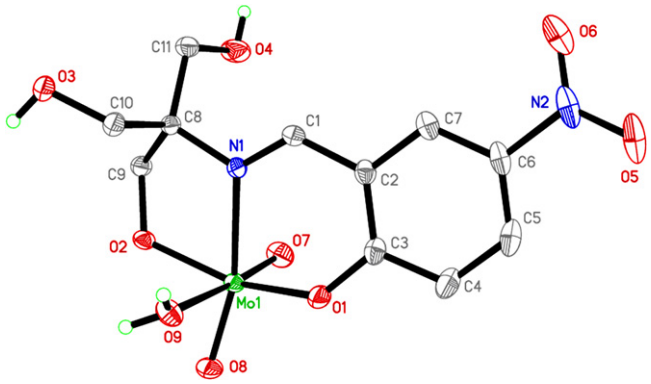


Fig. 1. The molecular structure of **4**, showing 30% probability displacement ellipsoids. All H atoms on carbon have been omitted for clarity.

Complex **4** adopts a distorted octahedral geometry. The azomethine N atom, phenolate O atom (O_{ph}) and one of the alkoxo O atoms (O_{alk}) of the Schiff base bind to the metal. In the coordination polyhedron, the O2 (alkoxo), O1 (phenolate), N1 (imino) and O8 (from *cis*-MoO_2) are nearly coplanar, with a mean deviation of 0.0056(2) Å. The distance of the Mo atom to the plane is 0.2296(2) Å. Atoms O7 (from *cis*-MoO_2) and O9 (from water), coordinating with Mo, lie above and below the plane. Both the Mo=O distances and the O=Mo=O angle are in the usual range for *cis*-MoO_2 complexes [16]. The imine N atom is *trans* to one Mo=O.

Similarly, complex **5** also has a distorted octahedral six-coordinate configuration formed by the tridentate Schiff base ligand, one coordinating water and two binding oxygen atoms. In the coordination polyhedron, the O1 (phenolate), O2 (alkoxo), N1 (imino) and O6 (from *cis*-MoO_2) are nearly coplanar, with a mean deviation of 0.0043(2) Å. The distance of the Mo atom to the plane is 0.3084(2) Å. Atoms O7 (from *cis*-MoO_2) and O5 (from water), coordinating with Mo, lie above and below the plane. In addition, one uncoordinated disorder water solvent molecular is present in complex **5**, which is not found in complex **4**.

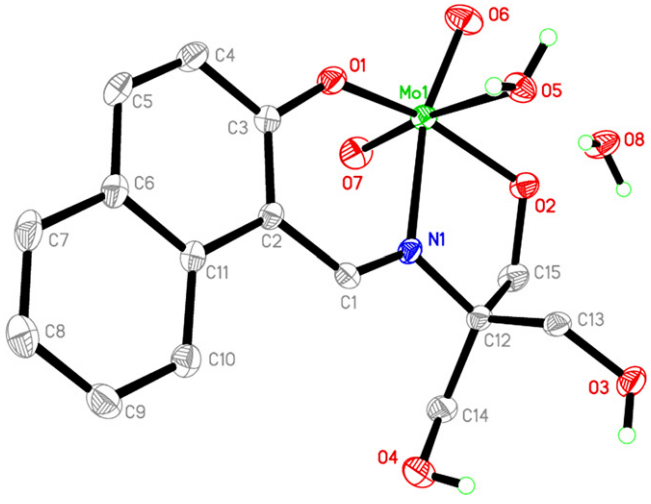


Fig. 2. The molecular structure of **5**, showing 30% probability displacement ellipsoids. All H atoms on carbon have been omitted for clarity.

3.2. Electronic and IR spectra

The electronic spectra of all the complexes were recorded in 10^{-3} M DMF solution at room temperature. The spectra of these complexes exhibit two absorption bands in the regions 268–283 and 342–379 nm. The first band is attributed to $\pi \rightarrow \pi^*$ transitions of imino group and the second should be due to the ligand to metal charge transfer (LMCT) transition of phenolate O to Mo centre as a consequence of coordination of phenolate O atom to Mo center [17]. The LMCT wavelength is in the order: **5** > **2** > **3** > **1** > **4**. In IR spectra of complexes **1**–**5**, the imino(C=N) bands are all shifted to lower wave numbers compared to the free ligand due to coordination of the metal to the imine nitrogen [18]. In all cases two bands in the region 890–910 and 920–940 cm^{-1}, which may be assigned to the symmetric and asymmetric stretching modes of the Mo=O double bonds were observed in IR spectra of complexes, indicated the presence of oxo-molybdenum centres [19].

3.3. Electrochemical studies

The electrochemical properties of *cis*-dioxomolybdenum(VI) complexes **1**–**5** were examined with cyclic voltammetry in DMF solution with 0.001 M concentration of the complexes, using glassy carbon working and an Ag/AgCl reference electrode, in the potential range −2.0 to 0 V. The result was illustrated in Fig. 3 for complex **1**.

All the complexes showed quasi-reversible redox behaviour corresponding to a Mo(VI)/Mo(V) couple in the potential range −700 to −900 mV. The quasi-reversible behaviour observed with these complexes may indicate a fast chemical complication including decomposition, coupled with the primary electron-transfer step [20]. Thus the studies indicated that these ligands (H_4L^n, n = 1–5) can provide environment suitable for stabilizing higher oxidation state of metal ions, such as Mo(VI), probably due to the availability of several oxo-donor groups. The calculated $E_{1/2}$ values for the Mo(VI)/Mo(V) couple of these complexes are in the range −820 to −780 mV with respect to Ag/AgCl, and in the order: **4** (−784 mV) > **1** (−788 mV) > **3** (−796 mV) > **2** (−800 mV) > **5** (−811 mV), which indicated that the stabilization of these complexes in higher oxidation state should be in the reverse order. In fact, the $E_{1/2}$ values for the Mo(VI)/Mo(V) couple are positively related to the LMCT transition frequencies (i.e. energy) in the electronic spectra; the higher the LMCT transition frequency is, the more difficult the reduction of the complex is, or the higher the redox stability of the complex is. If a straight line is fitted to the relation between LMCT frequencies and $E_{1/2}$ values for the five complexes, an equation $y = 86136x - 1035.8$ could be obtained, where x is representative for LMCT frequencies (nm^{-1}) and y for $E_{1/2}$ values (mV). The correlation factor (R^2) for this fitted straight line is 0.9529. But it had to be admitted that the validity of this equation should be further examined for other complexes.

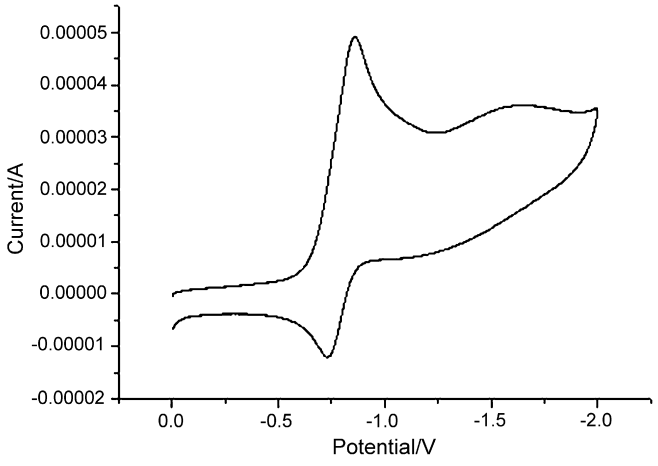


Fig. 3. Cyclic voltammogram of complex **1** (1×10^{-3} M) in DMF containing 0.1 M TBAP; scan rate = 100 mV s^{-1}.

3.4. Chemical redox in solution

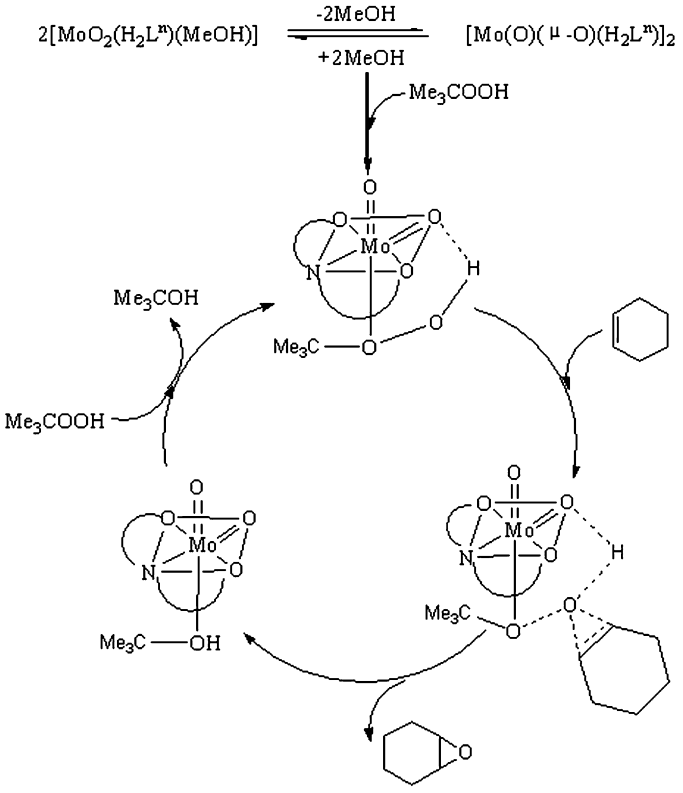
Solution redox reactivity of complexes from **1** to **5** was studied using L-ascorbic acid as reducing agent at a 1:2 mole ratio under deoxygenated conditions and was monitored by absorption spectra. To our surprise, no obvious change in absorption spectra was found during the whole monitoring time (1 day), whether for the complex **4** which was relatively easy to be reduced or for **5** which was relatively difficult to be done. The reason is probably due to the fact that Mo complexes react with radicals formed in the oxidation reaction [21].

3.5. Catalytic epoxidation of cyclohexene

Although the mechanism of epoxidation of olefins is still controversially discussed, Sobczak's [22,23] ideas should be accepted on the basis of structurally analogy of catalysts. According to Sobczak, the suggested mechanism was given in Scheme 2. These are the essential stages of the process:

1. Formation of the intermediate complex $[Mo(O)_2(H_2L^n)(t\text{-BuOOH})]$ and activation of TBHP molecule (coordination via the peroxo oxygen bonded to the molybdenum atom and formation of a hydrogen bonding with one of the terminal oxygens).
2. Interaction between the cyclohexene and TBHP molecule, activated in the coordination sphere of the molybdenum complex.
3. Formation of epoxide and conversion of TBHP into *t*-BuOH, which remains in the coordination sphere.
4. Substitution of *t*-BuOH by TBHP and reproduction of the intermediate complex $[Mo(O)_2(H_2L^n)(t\text{-BuOOH})]$.

These compounds were selected for the study of catalytic epoxidation of olefins by organic hydroperoxides because of unique structure. The coordination sphere of these six-coordinated molybdenum(VI) complex contain: (1) a dianionic tridentate salycylideneiminophenolate chelating ligand coordinating via two oxygens and one nitrogen; (2) a labile coordinated water molecule(or other solvent molecule); (3) two terminally bonded oxygens in a *cis* arrangement. This structure meets all the requirements for an active catalyst in the epoxidation



Scheme 2. Suggested mechanism of cyclohexene epoxidation with TBHP catalysed by complexes **1**–**5**.

reaction: the presence of one labile ligand (ethanol), through which the substitution reaction of the organic hydroperoxide molecule may proceed easily [22], and a stable remaining molybdenum-oxygen (and/or nitrogen) bonding (resistant to reactions involving ROOH or radicals formed in the side process of free-radical decomposition of hydroperoxide) [23].

The catalytic activities of dioxomolybdenum(VI) complexes **1**–**5** were determined by the yield at epoxidation of cyclohexene using TBHP as oxidant. The yields in the reactions are expressed as $Y = (C_{epox}/C_{TBHP}) \times 100\%$ where C_{epox} and C_{TBHP} (mol l^{-1}) are the concentration of epoxide formed and initial concentration of TBHP, respectively. The selectivity with respect to the TBHP reacted was calculated by the ratio $S = (C_{epox}/(C_{TBHP} - C)) \times 100$, where C is the final TBHP concentration. In most cases, the latter was found to be close to 100%. An excess of cyclohexene with respect to TBHP (molar ratio of 4–5) was used in order to obtain high TBHP conversions and selectivity with respect to cyclohexene epoxide.

The kinetic curves of the cyclohexene oxide yield in the presence of the various molybdenum complexes as catalysts at 353 K are shown in Fig. 4. For $MoO_2(acac)_2$ and complex **4**, very high cyclohexene oxide yield were reached within shorter reaction times, compared to other molybdenum complexes (**1**, **2**, **3** and **5**). The order of catalytic activities is **4** ≈ $MoO_2(acac)_2$ > **1** > **2** > **3** > **5**. This result indicates that introduction of the electron-withdrawing group to the salicylidene ring strongly increases the effectiveness of a catalyst, whilst the electron-donating one decreases the activities. The reason may

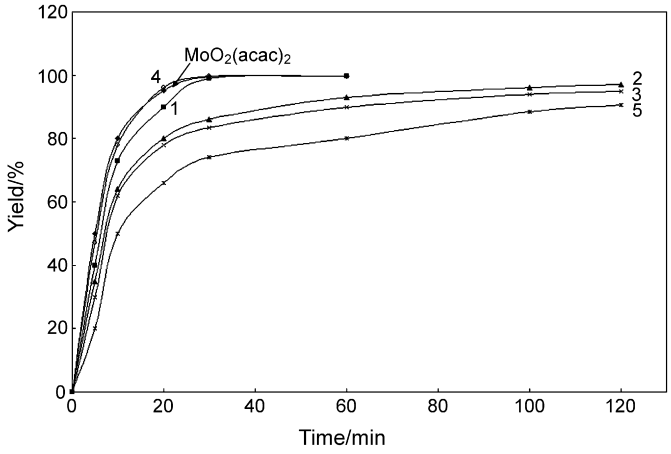


Fig. 4. Kinetic curves for the cyclohexene oxide yield in the presence of various molybdenum complexes as catalysts at 353 K. (♦) $MoO_2(acac)_2$; (■) complex **1**; (▲) complex **2**; (×) complex **3**; (◯) complex **4**; (*) complex **5**.

be that the electron-withdrawing group could increase the Lewis acidity, and therefore the catalytic activities of epoxidation [24]. Complex **4** may be considered to be the best catalyst in this reaction among these complexes. The catalytic activity of complex **3** is lower than that of complex **2**. The reason may be ascribed to the crowding of the larger substitutes in the 3-position, which might result in tilting of the aromatic ring out of planar arrangement [25].

In order to gain a better insight into the catalytic activity of complex **4** in epoxidation of cyclohexene, the effect of the reaction temperature, solvent and the olefin:oxidant ratio was investigated and the results were summarized in Table 4.

In Table 4, from entry 1 to 4, the epoxy-compound yield sharply decreased with decreasing temperature, showing that the epoxycyclohexene yield strongly depends on the reaction temperature. At 303 K, we observed no epoxy-compounds. As we obtained 1.5% epoxide yield at 313 K, it may be presumed that the reaction starts at about 313 K; at 353 K the yield increased up to 100%.

Comparing entry 1 with 5, it was found that the absence of solvent (1,2-dichloroethane) during the epoxidation of cyclohexene at 353 K led to a decrease in the epoxycyclohexene yield from 100% with the solvent to 68% without it. The result indicated that chlorinated solvents facilitate epoxidation [26].

Table 4
The effect of the reaction condition on complex **4** catalysed epoxidation of cyclohexene[a]

Entry	Temperature (K)	Solvent[b] (ml)	Olefin:oxidant ratio	Yield (%)
1	353	5	4:1	100
2	333	5	4:1	25
3	313	5	4:1	1.5
4	303	5	4:1	0
5	353	0	4:1	68
6	353	5	3:1	95
7	353	5	2:1	87
8	353	5	3:2	65

[a] 0.003 mmol catalyst; 0.08 mol cyclohexene; 60 min.
[b] The used solvent is 1,2-dichloroethane ($ClCH_2CH_2Cl$).

From entry 6 to 8, the influence of the olefin:oxidant ratio on the epoxycyclohexene yield was investigated. The cyclohexene:TBHP molar ratio of 3:1 gave a 95% yield of epoxide, whilst a significant decrease in the epoxycyclohexene yield was observed for the decrease in ratio of 2:1 and 3:2.

In next work, these catalysts will be tried to attach to silica surfaces, and the recovery of catalysts will be investigated.

4. Conclusions

This set of dioxomolybdenum(VI) complexes with Schiff base ligands derived from tris(hydroxymethyl)amino methane exhibit good catalytic activities and selectivity in the epoxidation of cyclohexene with *t*-butylhydroperoxide. The electron-withdrawing group on the salicylidene ring of complex is advantageous over electron-donating one on the effectiveness of a catalyst but disadvantageous on the redox stability of a complex.

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References

[1] S.M. Bruno, J.A. Fernandes, L.S. Martins, I.S. Gonçalves, M. Pillinger, P. Ribeiro-Claro, J. Rocha, A.A. Valente, Catal. Today 114 (2006) 263.
[2] K.A. Jorgensen, Chem. Rev. 89 (1989) 431.
[3] E.P. Talsi, K.V. Shalyaev, K.I. Zamaraev, J. Mol. Catal. A: Chem. 83 (1993) 347.
[4] S.V. Kotov, T.M. Kolev, M.G. Georgieva, J. Mol. Catal. A: Chem. 195 (2003) 83.
[5] N. Gharah, S. Chakraborty, A.K. Mukherjee, R. Bhattacharyya, Chem. Commun. 22 (2004) 2630.
[6] J.-M. Bregeault, M. Vennat, L. Salles, J.-Y. Piquemal, Y. Mahha, E. Briot, P.C. Bakala, A. Atlamsani, R. Thouvenot, J. Mol. Chem. A: Chem. 250 (2006) 177.
[7] M. Masteri-parahani, F. Farzaneh, M. Ghandi, J. Mol. Catal. A: Chem. 192 (2003) 103.
[8] W.A. Bubb, H.A. Berthon, P.W. Kuchel, Bioorg. Chem. 23 (1995) 119.
[9] C.P. Rao, A. Sreedhara, P.V. Rao, M.B. Verghese, K. Rissanen, E. Kolehmainen, N.K. Lokanath, M.A. Sridhar, J.S. Prasad, J. Chem. Soc., Dalton Trans. 14 (1998) 2383.
[10] P.V. Rao, C.P. Rao, A. Sreedhara, E.K. Wegelius, K. Rissanen, E. Kolehmainen, J. Chem. Soc., Dalton Trans. 7 (2000) 1213.
[11] M. Dey, C.P. Rao, P.K. Saarenketo, K. Rissanen, Inorg. Chem. Commun. 5 (2002) 380.
[12] M. Dey, C.P. Rao, P.K. Saarenketo, K. Rissanen, E. Kolehmainen, P. Guionneau, Polyhedron 22 (2003) 3515.
[13] G.J. Chen, J.W. Madonald, W.E. Newton, Inorg. Chem. 15 (1976) 2612.
[14] Bruker, APEX2 Version 1.22, Bruker AXS Inc., Madison, WI, USA, 2004.
[15] Y. Sui, X.N. Fang, Q.Y. Luo, H.M. Chen, M.Q. Zhou, Acta Crystallogr. E 62 (2006) m1994–m1996.
[16] H.R. Holm, Chem. Rev. 87 (1987) 1401.
[17] J. Topich, Inorg. Chem. 20 (1981) 3704.
[18] K. Ambroziak, R. Pelech, E. Milchert, T. Dziembowska, Z. Rozwadowski, J. Mol. Chem. A: Chem. 211 (2004) 9.
[19] Z. Petrovski, M. Pillinger, A.A. Valente, I.S. Goncalves, A. Hazell, C.C. Romao, J. Mol. Catal. A: Chem. 227 (2005) 67.
[20] A. Mukhopadhyay, A. Karkamkar, E. Kolehmainen, C.P. Rao, Carbohydr. Res. 311 (1998) 147.
[21] C. Chatgilialoglu, D. Crich, M. Komatsu, I. Ryu, Chem. Rev. 99 (1999) 1991.
[22] J. Sobczak, J.J. Ziolkowski, J. Mol. Catal. 13 (1981) 11.
[23] J.M. Sobczak, J.J. Ziolkowski, Appl. Catal. A: Gen. 248 (2003) 261.
[24] R.A. Sheldon, J.A.V. Doorn, J. Catal. 31 (1973) 427.
[25] G. Asgedom, A. Sreedhara, C.P. Rao, Polyhedron 14 (1995) 1873.
[26] B.C. Reichardt, Solvents and Solvent Effect in Organic Chemistry, VCH, Weinhem, 1998.