

Effect of single-wall carbon nanotubes on direct epoxidation of cyclohexene catalyzed by new derivatives of *cis*-dioxomolybdenum(VI) complexes with bis-bidentate Schiff-base containing aromatic nitrogen–nitrogen linkers

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Abstract

The synthesis and characterisation of three dimeric *cis*-dioxomolybdenum(VI) complexes involving Schiff-base ligands is described. Ligands were obtained by condensation of salicylaldehyde with aromatic nitrogen–nitrogen linkers (4,4'-diaminodiphenylmethane; 4,4'-diaminodiphenylether; 4,4'-diaminodiphenylsulfone). [MoO₂(acac)₂] reacted with the prepared ligands; bis[(*N,O*-salicylidene)-4,4'-diaminodiphenyl]methane, H₂L¹; bis[(*N,O*-salicylidene)-4,4'-diaminodiphenyl]ether, H₂L²; bis[(*N,O*-salicylidene)-4,4'-diaminodiphenyl]sulfone, H₂L³; forming six-coordinated *cis*-dioxoMo(VI) complexes; [MoO₂L¹⁻³]₂. The yellow colored, non-electrolytic and diamagnetic compounds were characterized by elemental analyses and spectroscopic techniques (IR, ¹H NMR and UV–vis). These complexes show good catalytic activity and selectivity in the epoxidation of cyclohexene with *t*-butylhydroperoxide (TBHP), especially for complex [MoO₂L³]₂, which could give a nearly 88% of epoxidation conversion and 94% of selectivity. Introduction of the electron-withdrawing group to the aromatic nitrogen–nitrogen linkers of complex strongly increases the effectiveness of a catalyst. The addition of single-wall carbon nanotubes (SWNT) can enhance the activity of the Mo complexes and the selectivity toward epoxide. It is also better for the recycling of the Mo complex, the catalytic activity and the selectivity toward which still held at a high level after four times using.

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Keywords: Single-wall nanotube; Epoxidation; Cyclohexene; Dioxomolybdenum(VI)

1. Introduction

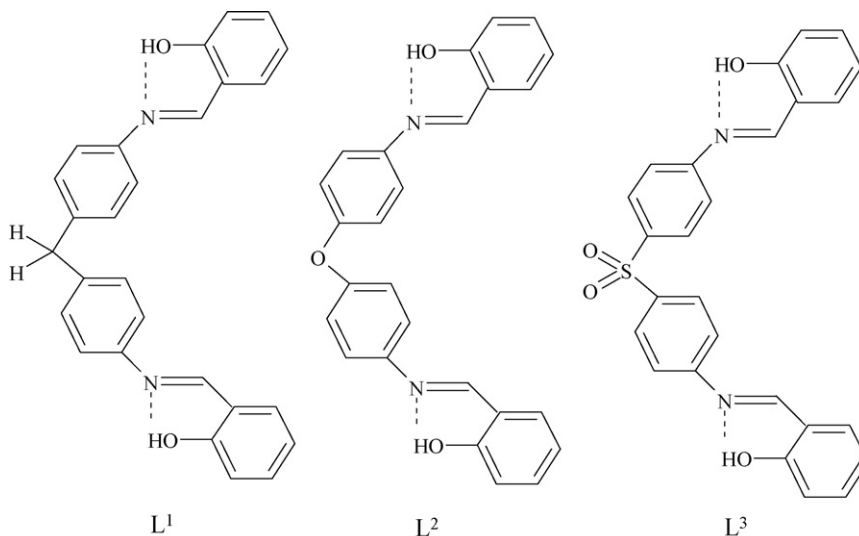
The coordination chemistry of molybdenum(VI) has attracted considerable interest due to its biological importance [1] as well as for the importance of molybdenum(VI) complexes as catalysts in various oxidations reactions [2,3], such as epoxidation and hydroxylation of olefins [4], oxidation of alcohols [5], and as catalysts of oxygen atom transfer reactions [6]. Molybdenum complexes are considered to be very effective catalysts for epoxidation with alkyl hydroperoxides as oxidants [7]. Although recently reported oxodiperoxo molybdenum(VI) complexes show very pronounced efficiency for the epoxidation of olefinic compounds at room temperature [8,9], these catalysts

suffer from 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 [10].

Epoxides are useful compounds that have found applications in diverse areas. Many different methods for the preparation of epoxides have been developed, but the most extensive industrial method is the oxidation of alkenes to the corresponding epoxide in liquid phase with organic hydroperoxides in the presence of a catalyst. Indeed, hydrocarbon-soluble transition metal complexes can be employed as homogeneous catalysts. Epoxide selectivity depends on the Lewis acidity and the oxidation state of the metals [4,11]. High surface area carbons have been the supports of choice for many noble metals and Lewis acids to convert a homogeneous into a heterogeneous process [12,13]. A special type of carbon that has attracted much current interest is carbon nanotubes [14,15] and in particular single-walled

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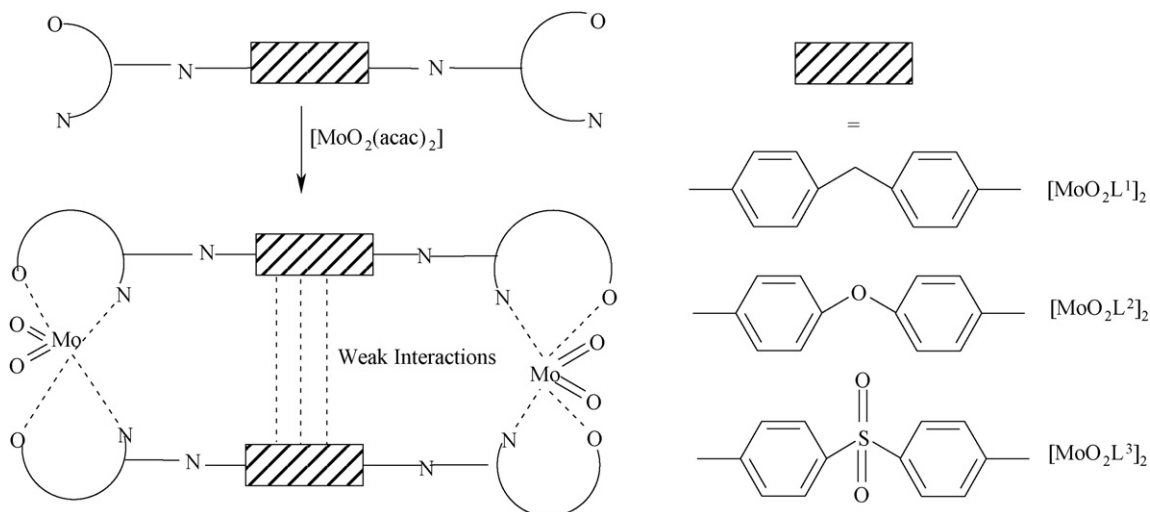
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Scheme 1. Molecular structure of H_2L^1 - H_2L^3 .

carbon nanotubes (SWNTs) [16,17]. Besides chemical composition (SWNTs are considered a new allotropic form of elemental carbon, while active carbons contain H as well as significant percentages of O, N, and S depending on the source [12,13]), the major difference between carbon nanotubes and active carbons is the well-defined structure of the former that contains exclusively fibers or bundles of fibers of several micrometers in length. In particular, the sample of SWNTs used in the present work is formed exclusively by nanotubes of 1–2 nm in diameter and bundles of them with lengths of 5–30 μm , having a specific surface area of 400 $\text{m}^2 \text{g}^{-1}$. While this area is far from the maximum specific area achievable in activated carbons, the special structured topology of the SWNT surface introducing a characteristic periodicity and regularity may play a positive role when these materials are used as supports in heterogeneous catalysis. However, to our knowledge, there is lack of report on epoxidation by using SWNTs supported homogeneous catalyst. Both the

effect of SWNTs as support on the oxidative activity and selectivity of homogeneous catalyst and the stability of SWNTs as carbon materials at mild oxidation conditions are still uncertain.

In this paper, we reported three kinds of easily prepared dioxomolybdenum(VI) complexes; $[\text{MoO}_2\text{L}^1]_2$, $[\text{MoO}_2\text{L}^2]_2$, $[\text{MoO}_2\text{L}^3]_2$; with Schiff-base ligands derived from aromatic nitrogen–nitrogen linkers (4,4'-diaminodiphenylmethane; 4,4'-diaminodiphenylether; 4,4'-diaminodiphenylsulfone) and salicylaldehyde; bis[(*N,O*-salicylidene)-4,4'-diaminodiphenyl] methane, H_2L^1 ; bis[(*N,O*-salicylidene)-4,4'-diaminodiphenyl] ether, H_2L^2 ; bis[(*N,O*-salicylidene)-4,4'-diaminodiphenyl] sulfone, H_2L^3 (Schemes 1 and 2), and their catalytic applications in the epoxidation of cyclohexene with *tert*-butylhydroperoxide (TBHP). Also, we reported new advances in the epoxidation of cyclohexene catalyzed by new bis-bidentate Schiff-base Mo(VI) complexes with additive SWNTs under mild reaction conditions.

Scheme 2. π - π interaction operating between the bridging aromatic groups.

2. Experimental

2.1. Materials

All chemicals and solvents used in the syntheses were reagent grade and were used without further purification. For the spectroscopic measurements, H₂O was distilled and organic solvents were purified according to the literature method. Cyclohexene, bridging diamine (4,4'-diaminodiphenylmethane; 4,4'-diaminodiphenylether; 4,4'-diaminodiphenylsulfone) and *tert*-butylhydroperoxide (TBHP, 80% in di-tertiary butyl peroxide) were purchased from Merck Chemical Company. Cyclohexene was distilled under nitrogen and stored over molecular sieves (4 Å). Isooctane was used as an internal standard for the quantitative analysis of the product using gas chromatography. Epoxycyclohexane was identified by comparisons of their retention times with those of the corresponding pure compounds (obtained from Merck). [MoO₂(acac)₂] was prepared by a known method [18]. single-wall carbon nanotube (90% SWNTs; 95% CNTs; diameter: 1–2 nm; length: 5–30 μm; SSA: >400 m² g⁻¹; color: black) was purchased from Nanostructured & Amorphous Materials, Inc.

2.2. Physical measurements

Electronic absorption spectra were obtained with a Shimadzu UV–Vis scanning spectrophotometer (Model 2101 PC), IR spectra with a Shimadzu Varian 4300 spectrophotometer, and conductance measurements with a Metrohm Herisau conductometer E 518. Elemental analyses were obtained with a Carlo Erba Model EA 1108 analyzer. The molybdenum contents of the samples were measured by Atomic Absorption Spectrophotometry (AAS-Perkin-Elmer 4100-1319). ¹H NMR (400 MHz) spectra were measured in CDCl₃ solutions and referenced to the solvent signals. The stability of the supported catalyst was checked after the reaction by AAS and possible leaching of the complex was investigated by AAS in the reaction solution after filtration of the SWNTs. The products were analyzed by GC–MS, using a Philips Pu 4400 Chromatography (1.5 m, 3% OV-17 Column), Varian 3400 Chromatography (25 m, DB-5 Column) coupled with a QP Finnegan MAT INCOF 50, 70 eV.

2.3. Preparation of bis-bidentate Schiff-base ligands

The bis-bidentate ligands were prepared by a usual Schiff-base condensation in methanol (50 ml) of salicylaldehyde (10 mmol, 1.22 g) with bridging diamine (4,4'-diaminodiphenylmethane, 5 mmol, 0.99 g for H₂L¹; 4,4'-diaminodiphenylether, 5 mmol, 1.00 g for H₂L²; 4,4'-diaminodiphenylsulfon, 5 mmol, 1.24 g for H₂L³) [19]. The solutions were stirred and refluxed for 12 h. Yellow precipitates were filtered, washed by a small amount of methanol and dried in vacuo. H₂L¹: yield 95%, mp 212–214 °C. Anal. calcd. for C₂₇H₂₂N₂O₂: C, 79.78; H, 5.46; N, 6.89. Found: C, 79.61; H, 5.33; N, 6.97%. Main IR (KBr, cm⁻¹): 1617 (C=N), 1614

(C=C), 1308 and 1290 (C–O). ¹H NMR (400 MHz, CDCl₃, internal reference TMS): δ 13.18 (2H, s, O···H···N), 8.55 (2H, s, CH=N), 7.37–7.28 (4H, m, sal-ald), 7.29 (4H, ddd, aminophenyl), 7.08 (4H, ddd, aminophenyl), 7.01 (2H, d, sal-ald), 6.90 (2H, td, sal-ald). H₂L²: yield 92%, mp 214–216 °C. Anal. calcd. for C₂₆H₂₀N₂O₃: C, 76.46; H, 4.94; N, 6.86. Found: C, 76.30; H, 4.81; N, 6.94%. Main IR (KBr, cm⁻¹): 1623 (C=N), 1616 (C=C), 1310 and 1294 (C–O). ¹H NMR (400 MHz, CDCl₃, internal reference TMS): δ 13.24 (2H, s, O···H···N), 8.65 (2H, s, CH=N), 7.42–7.36 (4H, m, sal-ald), 7.31 (4H, ddd, aminophenyl), 7.09 (4H, ddd, aminophenyl), 7.03 (2H, d, sal-ald), 6.95 (2H, td, sal-ald). H₂L³: yield 90%, mp 240–242 °C. Anal. calcd. for C₂₆H₂₀N₂O₄S: C, 68.41; H, 4.42; N, 6.14. Found: C, 68.29; H, 4.31; N, 6.25%. Main IR (KBr, cm⁻¹): 1627 (C=N), 1618 (C=C), 1310 and 1298 (C–O). ¹H NMR (400 MHz, CDCl₃, internal reference TMS): δ 13.37 (2H, s, O···H···N), 8.85 (2H, s, CH=N), 7.52–7.46 (4H, m, sal-ald), 7.32 (4H, ddd, aminophenyl), 7.10 (4H, ddd, aminophenyl), 7.08 (2H, d, sal-ald), 6.70 (2H, td, sal-ald).

2.4. Synthesis of dioxomolybdenum(VI) complexes; [MoO₂L^{1–3}]₂

The preparation of three complexes is identical, and the synthetic process is the following: to a solution of ligand H₂L¹ (2.03 g, 5 mmol), H₂L² (2.04 g, 5 mmol) or H₂L³ (2.28 g, 5 mmol) in chloroform (25 ml) was added a methanol suspension (25 ml) of [MoO₂(acac)₂] (5 mmol, 1.64 g). After 24 h, yellowish precipitations were filtered and washed with mixture of chloroform and methanol twice and dried in vacuo. [MoO₂L¹]₂: yield 85%, mp > 250 °C, Λ_M, 10 (Ω⁻¹ cm² mol⁻¹). Anal. calcd. for Mo₂C₅₄H₄₀N₄O₈: C, 60.91; H, 3.79; N, 5.26; Mo, 18.02. Found: C, 60.78; H, 3.62; N, 5.33; Mo, 17.87%. Main IR (KBr, cm⁻¹): 1615 (C=N), 1615 (C=C), 1310 and 1293 (C–O), 920, 892 (Mo=O), 504 (Mo–O), 445 (Mo–N). ¹H NMR (400 MHz, CDCl₃, internal reference TMS): 9.25 (2H, s, CH=N), 7.40–7.31 (4H, m, sal-ald), 7.30 (4H, ddd, aminophenyl), 7.10 (4H, ddd, aminophenyl), 7.05 (2H, d, sal-ald), 6.97 (2H, td, sal-ald). [MoO₂L²]₂: yield 80%, mp 200 °C, Λ_M, 12 (Ω⁻¹ cm² mol⁻¹). Anal. calcd. for Mo₂C₅₂H₃₆N₄O₁₀: C, 58.44; H, 3.40; N, 5.24; Mo, 17.95. Found: C, 58.30; H, 3.31; N, 5.35; Mo, 17.80%. Main IR (KBr, cm⁻¹): 1620 (C=N), 1618 (C=C), 1312 and 1295 (C–O), 924, 896 (Mo=O), 506 (Mo–O), 450 (Mo–N). ¹H NMR (400 MHz, CDCl₃, internal reference TMS): 9.35 (2H, s, CH=N), 7.44–7.38 (4H, m, sal-ald), 7.36 (4H, ddd, aminophenyl), 7.12 (4H, ddd, aminophenyl), 7.09 (2H, d, sal-ald), 7.00 (2H, td, sal-ald). [MoO₂L³]₂: Yield 81%, mp 210–212 °C, Λ_M, 15 (Ω⁻¹ cm² mol⁻¹). Anal. calcd. for Mo₂C₅₂H₃₆N₄O₁₂S₂: C, 53.62; H, 3.11; N, 4.81; Mo, 16.47. Found: C, 53.50; H, 3.01; N, 4.95; Mo, 16.47%. Main IR (KBr, cm⁻¹): 1625 (C=N), 1620 (C=C), 1310 and 1298 (C–O), 928, 898 (Mo=O), 508 (Mo–O), 452 (Mo–N). ¹H NMR (400 MHz, CDCl₃, internal reference TMS): 9.55 (2H, s, CH=N), 7.58–7.49 (4H, m, sal-ald), 7.38 (4H, ddd, aminophenyl), 7.14 (4H, ddd, aminophenyl), 7.11 (2H, d, sal-ald), 6.78 (2H, td, sal-ald).

2.5. Catalytic epoxidations with $[MoO_2L^{1-3}]_2$

Epoxidation of cyclohexene was carried out in a 25 ml round bottom flask equipped with a condenser and a magnetic stirrer. *tert*-Butylhydroperoxide (TBHP, 80% in di-tertiary butyl peroxide) was used as oxidant. In a typical procedure, to a mixture of catalyst (0.025 mmol) and olefin (33.33 mmol) in 1,1,2,2-tetrachloroethane (6 ml) was added TBHP (8.33 mmol) under nitrogen atmosphere. The mixture was refluxed for a given time. Samples were withdrawn periodically and after cooling and dilution with 1,1,2,2-tetrachloroethane were analyzed using a gas chromatograph. The products were quantified using isooctane (1 g, 8.75 mmol) as internal standard.

2.6. Purification of SWNTs

SWNTs (200 mg) were suspended in a 3 M HNO_3 solution (20 ml) and maintained at reflux temperature for 24 h. After this treatment, the product was vacuum-filtered using a Teflon membrane with a pore size of 0.2 μm . The resulting solid was then thoroughly washed with deionized water and THF and dried in vacuum.

2.7. Catalytic epoxidations in the presence of SWNT

In a typical procedure, to a mixture of catalyst (0.025 mmol), olefin (33.33 mmol) and SWNTs (0.833 mmol) in 1,1,2,2-tetrachloroethane (6 ml) was added TBHP (8.33 mmol) under nitrogen atmosphere. The mixture was refluxed for a given time. After filtration and washing with solvent, the filtrate was concentrated and then subjected to gas chromatograph. The concentration of products was determined using isooctane as internal standard.

3. Results and discussion

In order to prepare dioxomolybdenum(VI) complexes having Schiff-base containing aromatic nitrogen–nitrogen linkers, we studied reactions of $[MoO_2(acac)_2]$ with bis-bidentate Schiff-base ligands having nitrogen and oxygen donor atoms groups (Schemes 1 and 2). Molybdenum starting material and ligand precursors were dissolved in dry methanol in 1:1 molar ratio and the reaction mixtures were stirred at room temperature for several days. The reaction temperature proved to be vital for product composition. Syntheses carried out at higher temperatures increased the amount of side products, probably including the formation of dinuclear oxo-bridged Mo(V) species [20]. Compounds produced out from the reaction mixtures in moderate to high yields upon cooling. All compounds formed powder, which was faint pale yellow. On aging they become more yellow and greenish in color. The powders are stable if stored under dry air in the dark. Electrical conductivity measurements of the metal complexes give Λ_M values of 10–15 $\Omega^{-1} cm^2 mol^{-1}$ and confirm that they are non-electrolytes.

All Schiff-base ligands contain two salicyladimine chelating sites separated by the flexible bridging group; $-C_6H_4OC_6H_4-$,

$-C_6H_4CH_2C_6H_4-$, $-C_6H_4SO_2C_6H_4-$. Such ligands are sufficiently flexible to twist around the central bridging groups, but are not flexible enough to bend within themselves in order to coordinate all four donor atoms to the same metal atom. So the treatment of these ligands with $[MoO_2]^{2+}$ gives rise to the formation of dinuclear double-helicates (Scheme 2).

Some additional information was obtained from a comparison of the FT-IR spectra of the complexes and the corresponding ligands. The changes in the IR spectra of the bis-bidentate Schiff-bases induced by complexation are similar to those observed for other tetradentate dioxomolybdenum(VI) Schiff-base complexes [21]. The O–H stretching frequency of the free ligands are expected to be at ca. 3300–3700 cm^{-1} , however this frequency is generally displaced to ca. 2857 cm^{-1} due to the internal hydrogen bond $OH \cdots N=C$. Hydrogen bonds in these Schiff-bases are usually very strong. The ligands are relatively planar with adequate intramolecular distances that favor formation of the hydrogen bond. These bands disappeared in the spectra of complexes, indicating the deprotonation of the O–H group and the formation of the Mo–O bonds. The band at ca. 1249 cm^{-1} in the IR spectrum of the ligand is ascribed to the phenolic C–O stretching vibration. This band is found at ca. 1245–1248 cm^{-1} in the spectra of the complexes. The IR spectra of the complexes show two strong absorption bands at 892–898 and 920–928 cm^{-1} , which are due to asymmetric and symmetric Mo=O stretches, respectively [21]. The $\nu_{C=N}$ side was considerably disturbed by complexation; the absorption bands were split into several components, some of them, in the spectra of complexes, were shifted to higher wave numbers in comparison to those in the spectra of the free ligands. Generally, involvement of the lone pair electrons of the N atom of the imine group in bonding to the metal ion leads to a lowering in the $\nu_{C=N}$ frequencies. The opposite effect was observed in the spectra of complexes of highly hindered configuration [21,22]. Compared with those of the ligands, the spectra of the complexes exhibit additional complexity in the region of ν_{C-O} vibrations (1290–1310 cm^{-1}), as well as below 445–508 cm^{-1} , in which the Mo–N and Mo–O vibrations are expected [21]. The pattern of the IR spectra of the complexes confirms a different arrangement of both imine moieties in the complexes and suggests a deviation of the C=N bond from the planarity of the molecule. The nonplanarity of the chelate ring and distortion around the Mo atom has been reported for dioxomolybdenum(VI) complex of *N,N*-Bis(salicylidene)-1,2-propanediamine [23]. The phenolic C–O stretching vibrations that appeared at $\sim 1290 cm^{-1}$ in the Schiff-bases [24] undergo a shift towards higher frequencies ($\sim 4 cm^{-1}$) in the complexes (Tables 1 and 2). This shift confirms the participation of oxygen in the C–O–M bond [25,26]. Also a strong band appeared at about 1617–1630 cm^{-1} in the free ligands and their complexes. This band is attributed to the C=N stretching vibration [27,28]. The ring skeletal vibrations (C=C) were consistent in all derivatives and unaffected by complexation. In the low frequency region, the band observed in the complexes in the region 504–508 cm^{-1} is attributed to (M-phenolic O) and in the region 445–452 cm^{-1} to (Mo–N). All the IR data suggest that the metal is bonded to the Schiff-bases through the phenolic oxygen and the imino nitrogen [29].

Table 1
Epoxidation of cyclohexene catalyzed by *cis*-dioxomolybdenum(VI) complexes involving bis-*N,O*-bidentate Schiff-base ligands

Entry	Catalyst	Temperature (°C)	Time (min)	Cyclohexene:oxidant ratio	Conversion (%)	Epoxide yield (%)
1	[MoO ₂ L ¹] ₂	80	180	4:1	73	74
2	[MoO ₂ L ²] ₂	80	180	4:1	81	82
3	[MoO ₂ L ³] ₂	80	180	4:1	88	94
4	[MoO ₂ L ³] ₂	70	180	4:1	42	38
5	[MoO ₂ L ³] ₂	60	180	4:1	16	27
6	[MoO ₂ L ³] ₂	50	180	4:1	8	9
7	[MoO ₂ L ³] ₂	40	180	4:1	4	2
8	[MoO ₂ L ³] ₂	30	180	4:1	–	–
9	[MoO ₂ L ³] ₂	80	20	4:1	6	9
10	[MoO ₂ L ³] ₂	80	40	4:1	19	20
11	[MoO ₂ L ³] ₂	80	60	4:1	31	38
12	[MoO ₂ L ³] ₂	80	80	4:1	42	64
13	[MoO ₂ L ³] ₂	80	100	4:1	59	72
14	[MoO ₂ L ³] ₂	80	120	4:1	68	84
15	[MoO ₂ L ³] ₂	80	140	4:1	73	88
16	[MoO ₂ L ³] ₂	80	160	4:1	80	90
17	[MoO ₂ L ³] ₂	80	200	4:1	87	95
18	[MoO ₂ L ³] ₂	80	180	3:1	74	83
19	[MoO ₂ L ³] ₂	80	180	2:1	51	71
20	[MoO ₂ L ³] ₂	80	180	3:2	38	55
21 ^a	[MoO ₂ L ³] ₂	80	180	4:1	66	42
22 ^b	[MoO ₂ L ³] ₂	80	180	4:1	11	16

Reaction conditions: 0.025 mmol of catalyst; 6 ml of 1,1,2,2-tetrachloroethane as solvent; 8.33 mmol TBHP and 33.33 mmol cyclohexene (cyclohexene:oxidant ratio = 4:1).

^a Epoxidation of cyclohexene without the solvent.

^b Epoxidation of 1-octene without the solvent.

The ¹H NMR spectra of the ligands showed a chemical shift of about ~13.30 ppm characteristic for aromatic O–H group [30]. The ¹H NMR spectra of the complexes are indicative of binding of the ligands through a phenoxo and imine group, leaving any additional groups unbound. The resonances were assigned based on the splitting of resonance signal and spin coupling constants. Furthermore, a singlet at ~8.55 ppm observed in the spectra for the ligand showed down field shift by 0.70 ppm to appear at 9.25 ppm upon complexation. This is attributed to proton on the azomethine carbon. The range of chemical shifts observed for aromatic protons did not show any appreciable change upon complexation. The chemical shift observed for the OH protons in the ligands was not observed in any of the complexes; this confirms the bonding of oxygen to the metal ions (C–O–M). The same result was confirmed by the IR spectra.

The electronic spectra of the Schiff-bases and their complexes are investigated. The spectra of the ligands exhibit three main peaks: at about 270, 333 and 372 nm. The first and the second

peaks are attributed to benzene $\pi \rightarrow \pi^*$ and imino $\pi \rightarrow \pi^*$ transitions, respectively. These bands were not significantly affected by chelation. The third band in the spectra of the ligand (372 nm) is assigned to $n \rightarrow \pi^*$ transition. This band is shifted to a longer wavelength (28 nm) along with increasing in its intensity. This shift may be attributed to the donation of the lone pairs of the nitrogen atoms of the Schiff-base to the metal ion ($N \rightarrow M$) [31]. The absorption maxima at 398–410 nm could be assigned to ligand-to-metal Mo ($d\pi$) \leftarrow O(π) charge transfer (LMCT) transition. This is in the range usually observed for MoO complexes [32]. The LMCT transition showed a slight dependence on the solvent coordination power. This appears about 10 nm more in the visible region in the solvents of low coordination power.

The catalytic performances of complexes; [MoO₂L¹]₂, [MoO₂L²]₂ and [MoO₂L³]₂; for epoxidation reactions were investigated using cyclohexene as a model substrate and TBHP as the oxygen donor. In a control experiment, carried out without catalyst, no reaction occurred, whereas in the presence of *cis*-dioxomolybdenum(VI) complexes involving bis-bidentate Schiff-base ligands epoxy cyclohexane was obtained almost quantitatively within 180 min and 80 °C reaction, indicating that these compounds act as catalysts and exhibit excellent product selectivity (Table 1, Figs. 1–3).

The percentage conversion for the cyclohexene oxide in the presence of the various molybdenum complexes as catalysts at 80 °C are shown in Table 1, Fig. 1. The order of catalytic activities is [MoO₂L³]₂ > [MoO₂L²]₂ > [MoO₂L¹]₂. This result indicates that introduction of the electron-withdrawing group to the aromatic bridge ring strongly increases the effectiveness of a catalyst, while the electron-donating one decreases the activities.

Table 2
Epoxidation of olefin catalyzed by *cis*-dioxomolybdenum(VI) complexes involving bis-*N,O*-bidentate Schiff-base ligands

Catalyst	Olefin	Conversion (%)	Epoxide yield (%)
[MoO ₂ L ³] ₂	Cyclooctene	97	98
[MoO ₂ L ³] ₂	Cyclohexene	88	94
[MoO ₂ L ³] ₂	1-Hexene	38	100
[MoO ₂ L ³] ₂	1-Octene	24	100

Reaction conditions: Catalyst, 0.025 mmol; solvent, 1,1,2,2-tetrachloroethane (6 ml); TBHP, 8.33 mmol; olefin, 33.33 mmol (olefin:oxidant ratio = 4:1); time = 180 min; temperature = 80 °C.

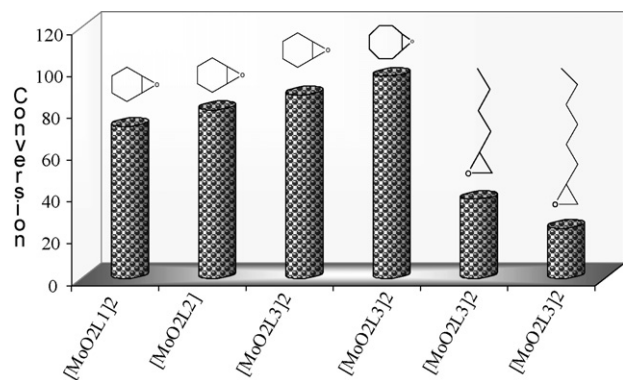


Fig. 1. Epoxy yield in the reaction of epoxidation catalyzed by cis-dioxomolybdenum(VI) complexes of bis-*N,O*-bidentate Schiff-base containing aromatic nitrogen–nitrogen linkers (reaction conditions: 0.025 mmol of catalyst; 6 ml of 1,1,2,2-tetrachloroethane as solvent; 8.33 mmol TBHP and 33.33 mmol olefin; time, 180 min; temperature, 80 °C).

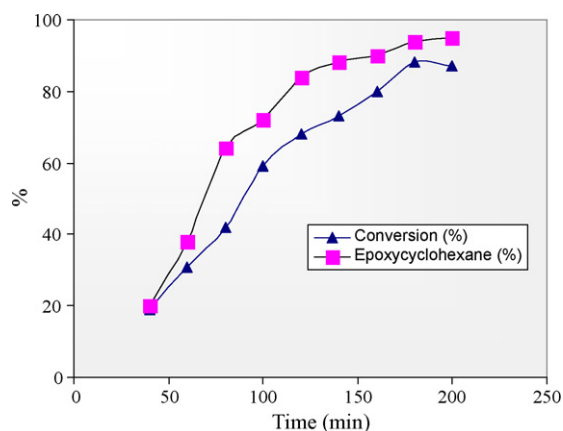


Fig. 2. Effect of time on substrate conversions in the epoxidation of cyclohexene with TBHP in the presence of $[\text{MoO}_2\text{L}_3]_2$ as catalyst.

The reason may be that the electron-withdrawing group could increase the Lewis acidity, and therefore the catalytic activities of epoxidation [33]. Complex $[\text{MoO}_2\text{L}^3]_2$ may be considered as the best catalyst in this reaction among these complexes.

In order to gain a better insight into the catalytic activity of $[\text{MoO}_2\text{L}^3]_2$ in epoxidation of cyclohexene, the effect of the reaction temperature, time, solvent and the olefin:oxidant ratio

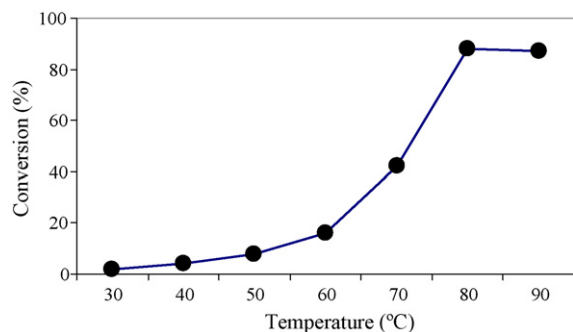


Fig. 3. Effect of temperature on substrate conversions in the epoxidation of cyclohexene with TBHP in the presence of $[\text{MoO}_2\text{L}_3]_2$ as catalyst (reaction conditions: catalyst, 0.025 mmol; solvent, 1,1,2,2-tetrachloroethane (6 ml); TBHP, 8.33 mmol; cyclohexene, 33.33 mmol; time, 180 min).

Table 3
Epoxidation of cyclohexene catalyzed by $[\text{MoO}_2\text{L}^{1-3}]_2/\text{SWNT}$

Catalyst	Olefin	Conversion (%)	Epoxide yield (%)
$[\text{MoO}_2\text{L}^1]_2/\text{SWNT}$	Cyclohexene	86	85
$[\text{MoO}_2\text{L}^2]_2/\text{SWNT}$	Cyclohexene	96	98
$[\text{MoO}_2\text{L}^3]_2/\text{SWNT}$	Cyclohexene	100	100
$[\text{MoO}_2\text{L}^3]_2/\text{SWNT}^a$	Cyclohexene	99	100
$[\text{MoO}_2\text{L}^3]_2/\text{SWNT}^b$	Cyclohexene	98	98
$[\text{MoO}_2\text{L}^3]_2/\text{SWNT}^c$	Cyclohexene	100	100
$[\text{MoO}_2\text{L}^3]_2/\text{SWNT}^d$	Cyclohexene	94	97
SWNT	Cyclohexene	–	–
$[\text{MoO}_2\text{L}^3]_2/\text{SWNT}$	Cyclooctene	100	100
$[\text{MoO}_2\text{L}^3]_2/\text{SWNT}$	1-Hexene	52	100
$[\text{MoO}_2\text{L}^3]_2/\text{SWNT}$	1-Octene	46	100

Reaction conditions: Catalyst, 0.025 mmol; solvent, 1,1,2,2-tetrachloroethane (6 ml); TBHP, 8.33 mmol; olefin, 33.33 mmol (olefin:oxidant ratio = 4:1); SWNTs (0.833 mmol); time = 180 min; temperature = 80 °C.

^a First reuse.

^b Second reuse.

^c Third reuse.

^d Fourth reuse.

was investigated and the results were summarized in Table 1 and Figs. 2 and 3. Comparing entry 3 with 21, it was found that the absence of solvent (1,2-dichloroethane) during the epoxidation of cyclohexene at 80 °C led to a decrease in the epoxycyclohexane yield from 94% with the solvent to 42% without it. The reaction was performed in 1,1,2,2-tetrachloroethane, because it is known that chlorinated solvents facilitate epoxidation [34] and the complexes studied are stable in this solvent. Another advantage of this solvent is its boiling point, so that we were able to increase the temperature of the reaction up to 100 °C. The reaction of epoxidation of 1-octene without the solvent gave only trace amounts of 1,2-epoxyoctane, while with the use of 1,1,2,2-tetrachloroethane we obtained a 16% epoxide yield (entry 22).

The temperature dependence of cyclohexene epoxidation by $[\text{MoO}_2\text{L}^3]_2$ was investigated and the reaction yields are given in Table 1. It can be seen that the epoxycyclohexane yield strongly depends on the reaction temperature. At 30 °C, we observed no epoxy-compounds. As we obtained 2% epoxide yield at 40 °C it may be presumed that the reaction starts at about 40 °C; at 80 °C the yield increased up to 94% (Fig. 3).

From entry 3 and 18–20, the influence of the olefin:oxidant ratio on the epoxycyclohexane yield was investigated. The epoxycyclohexane yield was shown to be strongly dependent on the cyclohexene:TBHP molar ratio. The cyclohexene:TBHP ratio of 3:1 gave a 83% yield of epoxide, while a significant decrease in the epoxycyclohexane yield was observed for the decrease in ratio of 3:2 (Table 1).

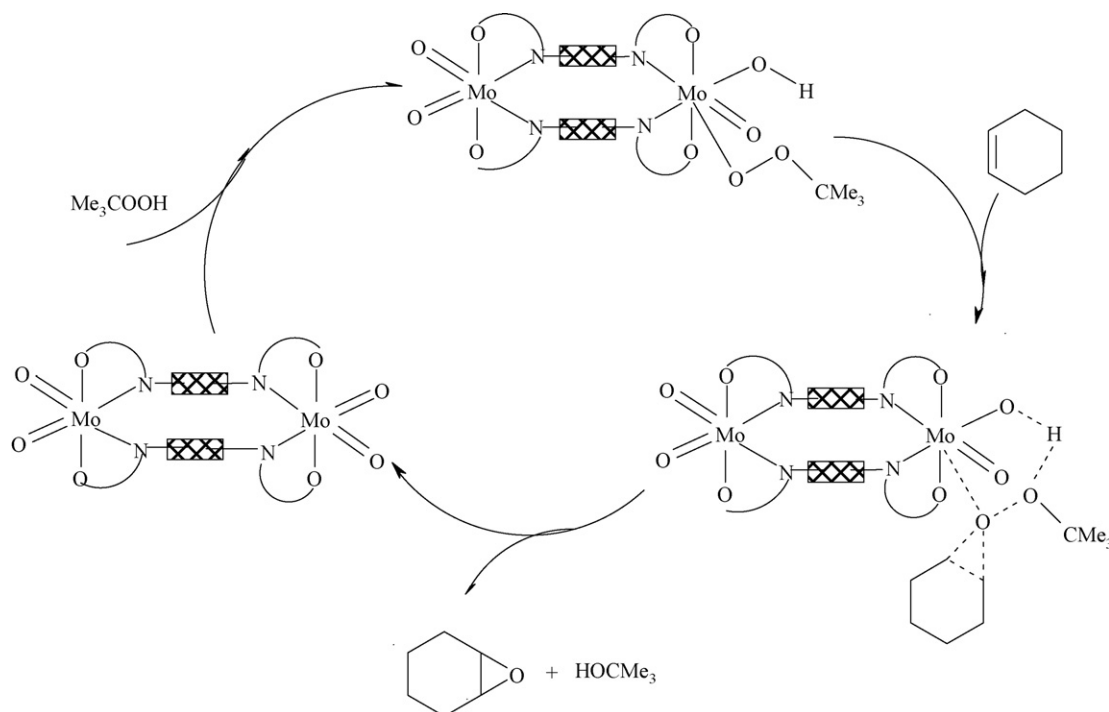
From Table 3 we can see that SWNTs alone have no activity. It demonstrated that SWNTs have not been doped by some Fe and Cu, which might be active for oxidation, after washing by HNO_3 and that SWNTs had no oxidation activity itself. It can increase the conversion and selectivity to epoxy while used together with the Mo complex. This might be due to the electronic property and the carboxyl on the coping of carbon nanotubes. Lei reported that the organic acid had similar function in the oxidation of

cyclohexene at 70 °C catalyzed by PS-bipy-Ru-bipy [35], but the catalytic activity decreased very much. Differently from that result, while the SWNTs were added to the reaction system the cyclohexene conversion increased obviously in our system. The addition of SWNTs also facilitates the recycling of the catalyst. Table 3 shows the performance of the repeatedly used catalyst. The reactions were performed using the catalyst which have been used in the previous reaction and separated from the products by filtration without supplement of any Mo complex and SWNTs. The catalyst still has high activity after four times of reuse. The increase in the conversion of cyclohexene in the second and third time reactions hints that there is an induction period. From the fourth times on, the conversion of cyclohexene maintains a level of about 95% of the original one while keeping the selectivity unchanged. The results of fourth times using show that the leaching of Mo should be less (Table 3). The four times using also demonstrated that SWNTs loaded homogeneous catalyst had enough stability under mild oxidation conditions.

After filtration, Mo content of the SWNTs-supported catalysts was estimated by dissolving the known amounts of the heterogeneous catalyst in concentrated HCl and from these solutions, Mo contents were estimated by atomic absorption spectrometer. The Mo content of the different catalysts synthesized was almost the same in all the supported system and was 0.065 mol g^{-1} . The chemical composition confirmed the purity and stoichiometry of the neat and SWNTs-supported complexes. The chemical analysis of the samples reveals the presence of organic matter with a N/Mo ratio (~ 0.29) roughly similar to neat complexes. Thus, the SWNTs-supported Mo complex is found to increase the life of the catalyst by reducing dimerization due to the site isolation and restriction of internal framework

structure. IR spectrum of the recycled sample is quite similar to that of fresh sample indicating little changes in the coordination of Schiff-base after the oxidation reactions.

In general, the mechanisms proposed for *t*-BuOOH-based epoxidation of olefins with Mo(VI) complexes are heterolytic in nature, involving coordination of the oxidant to the metal centre, which acts as a Lewis acid thereby increasing the oxidizing power of the peroxy group, and subsequently the olefin is epoxidized by nucleophilic attack on an electrophilic oxygen atom of the oxidizing species [36]. Spectroscopic and computational methods applied to molybdenum dioxo and oxodiperoxo complexes bearing bipyridine and pyrazolylpyridine ligands, respectively, support a reaction mechanism involving an activation state formed between the complex, oxidant and olefin [37,38]. The proposed mechanism is shown in Scheme 3, involves the initial coordination of $-\text{OO}-t\text{-Bu}$ to the molybdenum centre, followed by attack of the olefin on the electrophilic Mo(VI)-coordinated alkyl hydroperoxide [39]. Therefore stronger electron-withdrawing ability of the sulfone ($[\text{MoO}_2\text{L}^3]_2$) should give higher reaction conversion. The weaker electron-withdrawing ability of methylene compared with sulfone leads to a lower electron density on the active centre in $[\text{MoO}_2\text{L}^3]_2$ and is responsible for the more favorable nucleophilic attack of olefin on the electrophilic active centre compared with that in $[\text{MoO}_2\text{L}^1]_2$. The by-product of the epoxidation reaction, *tert*-butanol, is a competitor to TBHP for coordination to the metal centre, leading to the formation of inactive species and a consequent rapid decrease in the olefin conversion [37]. Our results also support the proposed mechanism for this type of catalytic epoxidation. Most importantly, they can guide us in the search for a better choice of catalyst for this type of reaction.



Scheme 3. Proposed mechanism for epoxidation of cyclohexene.

Investigation of the results reveals that both olefin and catalyst structures affect the catalyst activity. Based on the epoxidation mechanism, higher electron-donating ability of olefin double bond is expected to facilitate the reaction rate. As seen in Table 2, the order of increasing reactivities based on either conversions are as cyclooctene > cyclohexene > 1-hexene > 1-octene. To explain this trend, two determining parameters of electronic and steric effects should be taken into consideration. One of reasons that confirmed this trend is solubility of the complexes in bellow substrates on the other hand cyclic olefins are soluble better than linear olefins. The higher electronic density of the double bond is expected to show more epoxidation reactivity. Therefore, cyclooctene and cyclohexene with double bonds driven from secondary carbons should exhibit more activities in comparison with 1-hexene and 1-octene which contain double bonds between secondary and primary carbons. On the other hand, cyclooctene is more reactive than cyclohexene due to the presence of more electron-donating (CH₂)₆ cyclic bridge connected to the double bond. That 1-octene is epoxidized slower than 1-hexene can be inferred since larger hexyl group connected to double bond sterically hinders it in approaching to the catalyst metal centre with respect to 1-hexene which its double bond carries a smaller butyl group.

4. Conclusions

This set of dioxomolybdenum(VI) complexes with bis-bidentate Schiff-base ligands derived from aromatic nitrogen–nitrogen linkers (4,4'-diaminodiphenylmethane; 4,4'-diaminodiphenylether; 4,4'-diaminodiphenylsulfone) exhibit good catalytic activities and selectivity in the epoxidation of cyclohexene with *t*-butylhydroperoxide. The electron-withdrawing group on the aromatic nitrogen–nitrogen linkers of complex is advantageous over electron-donating one on the effectiveness of a catalyst but disadvantageous on the redox stability of a complex. The addition of SWNTs to the Mo complex can enhance the conversion of olefin and the selectivity to epoxy. SWNTs can also take up the Mo catalysts by adsorption and thereby facilitate the reusability at a quite high conversion level.

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