

New dioxomolybdenum(VI) complexes of tetradentate Schiff base as catalysts for epoxidation of olefins

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Received 11 May 2003; accepted 18 September 2003

Abstract

Six dioxomolybdenum(VI) complexes of Schiff-bases derivatives of *trans*-1,2-diaminocyclohexane and *R*-salicylaldehyde as well as 2-hydroxynaphthaldehyde have been synthesised and characterized by IR, UV-Vis and NMR-spectroscopic methods. The catalytic activities of the complexes in the reaction of epoxidation of cyclohexene and 1-octene with *tert*-butyl hydroperoxide (TBHP) as oxidant have been studied.

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Keywords: Epoxidation; Dioxomolybdenum(VI) complexes of tetradentate Schiff bases; *tert*-Butyl hydroperoxide

1. Introduction

Epoxidation is a one of the fundamental reactions in industrial organic synthesis, as epoxides are intermediates that may be converted in various products of great importance. Catalysis by metal complexes plays a central role in these processes [1–4]. Molybdenum compounds are considered to be very effective catalysts for epoxidation with alkyl hydroperoxides as oxidants [1–7]. Synthesis of a new efficient, selective Mo(VI) catalyst is still a subject of practical and theoretical interest [5–7]. To the best of our knowledge, there are no reports on catalytic properties of Mo(VI) Schiff-base complexes in epoxidation of alkenes.

In this study, we synthesised several Mo(VI) complexes containing Schiff-bases derivatives of *trans*-1,2-diaminocyclohexane and salicylaldehyde with different substituents **1–5** and 2-hydroxynaphthaldehyde, **6** (Scheme 1). We studied their catalytic activity in the epoxidation of cyclohexene and 1-octene by *tert*-butyl hydroperoxide (TBHP).

2. Experimental

2.1. Materials

All the *R*-salicylaldehydes, 2-hydroxynaphthaldehyde, *trans*-1,2-diaminocyclohexane, cyclohexene, 1-octene and *tert*-butyl hydroperoxide in decane (~5.5 mol/dm³) were purchased from Aldrich. Absolute ethanol and 1,1,2,2-tetrachloroethane were purchased from POCh (Gliwice, Poland) and were used as received.

Exact concentration of TBHP in decane (5.2 mol/dm³) was found by the iodometric method [8].

2.2. Preparation of Schiff bases

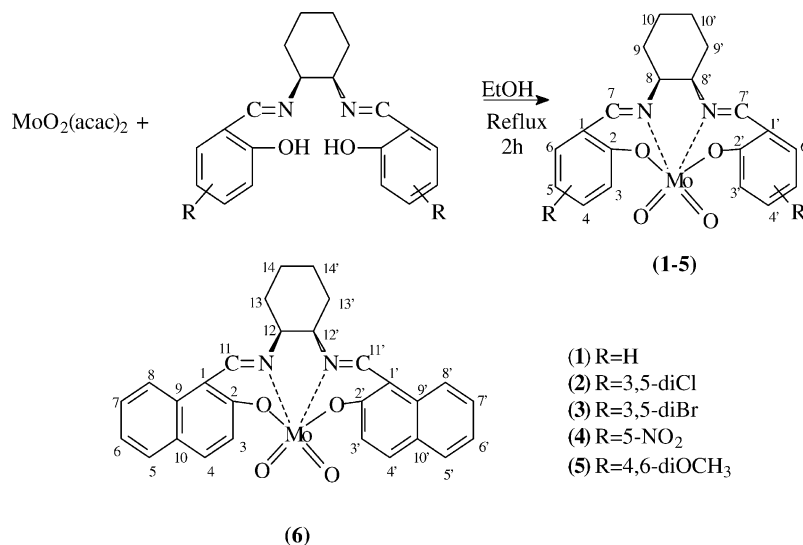
Schiff bases were obtained as described previously [9] by condensation of *trans*-1,2-diaminocyclohexane with respective salicylaldehyde or 2-hydroxynaphthaldehyde in absolute ethanol solution.

2.3. Preparation of MoO₂(*acac*)₂

bis(Acetyloacetato) dioxomolybdenum(VI) was prepared according to the procedure reported by Chen et al. [10].

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Scheme 1. Synthesis of the studied dioxomolybdenum(VI) Schiff-base complexes.

2.4. Preparation of dioxomolybdenum(VI) Schiff-base complexes

Appropriate amount of the Schiff base (0.001 mol) dissolved in 100 ml absolute ethanol was allowed to reflux with Mo(acac)₂ (0.001 mol) for 2–6 h. After 30 min all Mo(acac)₂ was dissolved, the solution became clear and after next 30–60 min a solid started to precipitate. Then at the end of the reaction, the precipitated solid was filtered off and washed with absolute ethanol.

2.4.1. [*trans-N,N'*-bis-(Salicylidene)-1,2-cyclohexanediaminato] dioxomolybdenum(VI) MoO₂[bis-(Sal)] (1)

Calcd. for C₂₀H₂₀N₂O₄Mo: C, 53.58; H, 4.50; N, 6.25; Mo, 21.40. Found: C, 53.49; H, 4.51; N, 6.07; Mo, 20.61.

IR(KBr) (cm⁻¹): 1635, 1612 ν(C=N)/ν(C=C); 1532 ν(N=C=C=O); 1302, 1278 ν(CO); 914, 886 ν(MoO₂); ν(MoO)/ν(MoN) 576, 532, 452.

UV-Vis (CH₂Cl₂) λ_{max} (cm⁻¹): 31720, 24078.

¹H NMR: 8.77 (1H, s, H-7); 8.75 (1H, s, H-7'); 7.76 (1H, d, H-6); 7.63 (1H, overlapped, H-4); 7.61 (1H, overlapped, H-6'); 7.42 (1H, t, H-4'); 7.14 (1H, t, H-5); 7.09 (1H, d, H-3); 6.75 (1H, t, H-5'); 6.70 (1H, d, H-3'); 4.06 (1H, t, H-8), 3.00 (1H, t, H-8'); 2.65 (1H, d, H-9); 2.33 (1H, d, H-9'); 1.95–1.84 (3H, m, H-10', H-10, H-9'); 1.52–1.36 (3H, m, H-9, H-10', H-10).

2.4.2. [*trans-N,N'*-bis-(3,5-Dichlorosalicylidene)-1,2-cyclohexanediaminato] dioxomolybdenum(VI) MoO₂[bis-(3,5-diClSal)] (2)

Calcd. for C₂₀H₁₆Cl₄N₂O₄Mo: C, 40.98; H, 2.75; N, 4.78. Found: C, 39.02; H, 2.44; N, 4.68.

IR(KBr) (cm⁻¹): 1640, 1610 ν(C=N)/ν(C=C); 1544, 1516 ν(N=C=C=O); 1316, 1302 ν(CO); 924, 896 ν(MoO₂); 586, 528, 502, 480 ν(MoO)/ν(MoN).

UV-Vis (CH₂Cl₂) λ_{max} (cm⁻¹): 32120, 23120.

¹H NMR: 8.87 (1H, s, H-7); 8.84 (1H, s, H-7'); 7.98 (1H, s, H-4); 7.92 (1H, s, H-4'); 7.78 (1H, s, H-6); 7.76 (1H, s, H-6'); 4.06 (1H, t, H-8), 3.17 (1H, t, H-8'); ~2.59 (1H, overlapped, H-9); 2.31 (1H, d, H-9'); 1.92–1.85 (3H, m, H-10', H-10, H-9'); 1.57–1.37 (3H, m, H-9, H-10', H-10).

2.4.3. [*trans-N,N'*-bis-(3,5-Dibromosalicylidene)-1,2-cyclohexanediaminato] dioxomolybdenum(VI) MoO₂[bis-(3,5-diBrSal)] (3)

Calcd. for C₂₀H₁₆Br₄N₂O₄Mo: C, 31.45; H, 2.11; N, 3.67. Found: C, 31.35; H, 1.88; N, 3.86.

IR(KBr) (cm⁻¹): 1632, 1602 ν(C=N)/ν(C=C); 1528, 1504 ν(N=C=C=O); 1299, 1316 ν(CO); 924, 894 ν(MoO₂); 580, 524, 474 ν(MoO)/ν(MoN).

UV-Vis (CH₂Cl₂) λ_{max} (cm⁻¹): 31640, 23078.

¹H NMR: 8.85 (1H, s, H-7); 8.81 (1H, s, H-7'); 8.17 (1H, s, H-4); 8.05 (1H, s, H-4'); 7.96 (1H, s, H-6); 7.93 (1H, s, H-6'); 4.09 (1H, t, H-8), 3.17 (1H, t, H-8'); ~2.50 (1H, overlapped, H-9); 2.29 (1H, d, H-9'); 1.92–1.84 (3H, m, H-10', H-10, H-9'); 1.53–1.38 (3H, m, H-9, H-10', H-10).

2.4.4. [*trans-N,N'*-bis-(5-Nitrosalicylidene)-1,2-cyclohexanediaminato] dioxomolybdenum(VI) MoO₂[bis-(5-NO₂Sal)] (4)

Calcd. for C₂₀H₁₈N₄O₃Mo: C, 44.62; H, 3.37; N, 10.41. Found: C, 44.79; H, 3.32; N, 10.77.

IR(KBr) (cm⁻¹): 1638, 1619 ν(C=N)/ν(C=C); 1508 ν(N=C=C=O); 1314, 1300 ν(CO); 928, 898 ν(MoO₂); 508, 450 ν(MoO)/ν(MoN).

UV-Vis (CH₂Cl₂) λ_{max} (cm⁻¹): 30030, 2500sh.

¹H NMR: 9.08 (1H, s, H-7); 9.05 (1H, s, H-7'); 8.87 (1H, s, H-6); 8.80 (1H, s, H-6'); 8.45 (1H, d, H-4); 8.24 (1H, d, H-4'); 7.33 (1H, d, H-3); 6.88 (1H, d, H-3') 4.09 (1H, t, H-8), 3.22 (1H, t, H-8'); 2.50 (1H, d, H-9); 2.34 (1H, d, H-9'); 1.94–1.89 (3H, m, H-10', H-10, H-9'); 1.59–1.37 (3H, m, H-9, H-10', H-10).

2.4.5. [*trans*-*N,N'*-bis-(4,6-Dimethoxysalicylidene)-1,2-cyklohexanediaminato] dioxomolybdenum(VI)

*MoO*₂[*bis*-(4,6-diOCH₃Sal)] (**5**)

Calcd. for C₂₄H₂₈N₂O₈Mo: C, 50.71; H, 4.96; N, 4.93; Mo, 16.88. Found: C, 50.03; H, 4.86; N, 4.78; Mo, 16.29.

IR(KBr) (cm⁻¹): 1610, 1590 ν(C=N)/ν(C=C); 1538 ν(NCCO); 1308 ν(CO); 914, 884 ν(MoO₂); 566, 552, 432 ν(MoO)/ν(MoN).

UV-Vis (CH₂Cl₂) λ_{max} (cm⁻¹): 29316, 25000.

¹H NMR: 8.81 (1H, s, H-7); 8.42 (1H, s, H-7'); 6.28 (1H, s, H-3); 6.27 (1H, s, H-3'); 5.89 (1H, s, H-5); 5.81 (1H, s, H-5'); 3.92 (1H, t, H-8), 3.87 (3H, s, H-OMe); 3.84 (3H, s, H-OMe'); 3.83 (3H, s, H-OMe); 3.74 (3H, s, H-OMe'); 3.17 (1H, t, H-8'); ~2.59 (1H, overlapped, H-9); 2.31 (1H, d, H-9'); 1.92–1.85 (3H, m, H-10', H-10, H-9'); 1.57–1.37 (3H, m, H-9, H-10', H-10).

2.4.6. [*trans*-*N,N'*-bis-(2-Hydroxynaphthylidene)-1,2-cyklohexanediaminato] dioxomolybdenum(VI)

*MoO*₂[*bis*-(Naph)] (**6**)

Calcd. for C₂₈H₂₄N₂O₄Mo: C, 61.32; H, 4.41; N, 5.11; Mo, 17.49. Found: C, 61.28; H, 4.35; N, 5.09; Mo, 16.31.

IR(KBr) (cm⁻¹): 1616, 1600 ν(C=N)/ν(C=C); 1552, 1536 ν(NCCO); 1290 ν(CO); 908, 886, 872 ν(MoO₂); 590, 540, 500, 456 ν(MoO)/ν(MoN).

UV-Vis (CH₂Cl₂) λ_{max} (cm⁻¹): 30998, 23041.

¹H NMR: 9.66 (1H, s, H-11); 8.96 (1H, s, H-11'); 8.59 (1H, d, H-8); 8.21 (1H, d, H-8'); 8.09 (1H, d, H-4); ~8.00 (1H, overlapped, H-4^a); ~7.98 (1H, overlapped, H-5^a); 7.83 (1H, d, H-5'); 7.67 (1H, t, H-7); 7.60 (1H, t, H-6^b); 7.52 (1H, t, H-7^b); ~7.39 (1H, overlapped, H-6'); ~7.36 (1H, overlapped, H-3); 6.87 (1H, d, H-3'); 4.13 (1H, t, H-12), 3.05 (1H, t, H-12'); 2.89 (1H, d, H-13); 2.62 (1H, d, H-13'); 1.96–1.92 (3H, m, H-13', H-14', H-14); 1.65–1.42 (3H, m, H-13, H-14, H-14'); s: singlet, d: doublet, t: triplet, m: multiplet; a and b: possible reverse assignment.

2.5. Epoxidation of non-functionalised alkenes by catalysts **1–6**

Epoxidation of cyclohexene and 1-octene catalyzed by dioxomolybdenum(VI) Schiff-base complexes with TBHP was carried out according to the following general procedure: a mixture of 0.025 mmol catalyst, 4 ml solvent (1,1,2,2-tetrachloroethane) and 25 mmol alkene was stirred in a round bottom flask equipped with a condenser and a dropping funnel at an appropriately chosen temperature for 5 min. Then 8.33 mmol of TBHP (solution 5.2 mol/dm³ in *n*-decane) was added. The molar ratio of the catalyst to TBHP was 3 × 10⁻³:1. The resulting mixture was then stirred for 2 h at an appropriately chosen temperature. Then, the mixture was subjected to GC analysis. The concentrations of products were determined using *n*-hexane as an internal standard.

2.6. Physical measurements

Elemental analyses of the complexes were performed on an Euro EA Elemental Analyzer. The molybdenum content in the complexes (**1**, **5** and **6**) was evaluated by thermal gravimetric analysis (TGA) using STA 449C Netzsch instrument by burning the sample to MoO₃ at 963–1003 K.

IR spectra were acquired by the use of a Perkin-Elmer SPECTRUM ONE spectrometer in KBr pellets. UV-Vis spectra were recorded on a Specord M-Carl Zeiss Jena spectrometer in CH₂Cl₂. ¹H NMR and ¹³C NMR spectra were measured on a Bruker DPX-400 in DMSO with TMS as internal standard.

GC analysis of the product was made on a Fisons GC 8000^{Top} using 30 m long J&W DB1, 0.53 mm Megabore, film 1.5 μm—100% polydimethylsiloxan capillary column with FID detector. Column temperature programmed between 308 and 453 K, injection temperature 453 K, detector temperature 473 K and helium carrier gas flow 6 ml/min.

3. Result and discussion

Numerous dioxomolybdenum(VI) complexes with Schiff-base ligands are known [11–21], but only one derivative of *trans*-1,2-diaminocyclohexane **1** has been obtained and characterized by the spectroscopic method so far [14]. We have obtained [*trans*-*N,N'*-bis-(*R*-salicylidene)-1,2-cyclohexanediaminato] dioxomolybdenum(VI) **1–5** and [*trans*-*N,N'*-bis-(2-hydroxynaphthylidene)-1,2-cyclohexanediaminato] dioxomolybdenum(VI) (**6**), following the method of Yamanouchi et al. [12] by the reaction of bis-(acetylacetonato) dioxomolybdenum(VI) with a respective Schiff base (Scheme 1).

The synthesis of complexes of dioxomolybdenum(VI) salicylaldehydes with *trans*-1,2-diaminocyclohexane was not successful. Complexes **2–4** were slightly soluble in organic solvents, while **1** and **5** were soluble in 1,1,2,2-tetrachloroethane and dimethylsulphoxide. All the complexes were stable in the solid state and 1,1,2,2-tetrachloroethane but not stable in dimethylsulphoxide, (except **5**), methylene chloride and chloroform.

The purity of the complexes **1–6** were determined by elemental analysis. Molybdenum content was evaluated only for complexes **1**, **5** and **6**. For complexes **2–4** containing halogens and nitro-substituents in the salicylidene ring, the TGA was unsuccessful because burning the samples did not led to MoO₃.

In order to obtain more details on the structure of complexes **1–6**, the IR, UV-Vis spectra of complexes have been measured and compared with the spectra of the respective ligands. Since many of the complexes decompose fairly fast in solution, the spectral measurements were carried out as quickly as possible. The measurements of ¹H NMR spectra of complexes in dimethylsulphoxide were repeated to check for any spectral change due to decomposition.

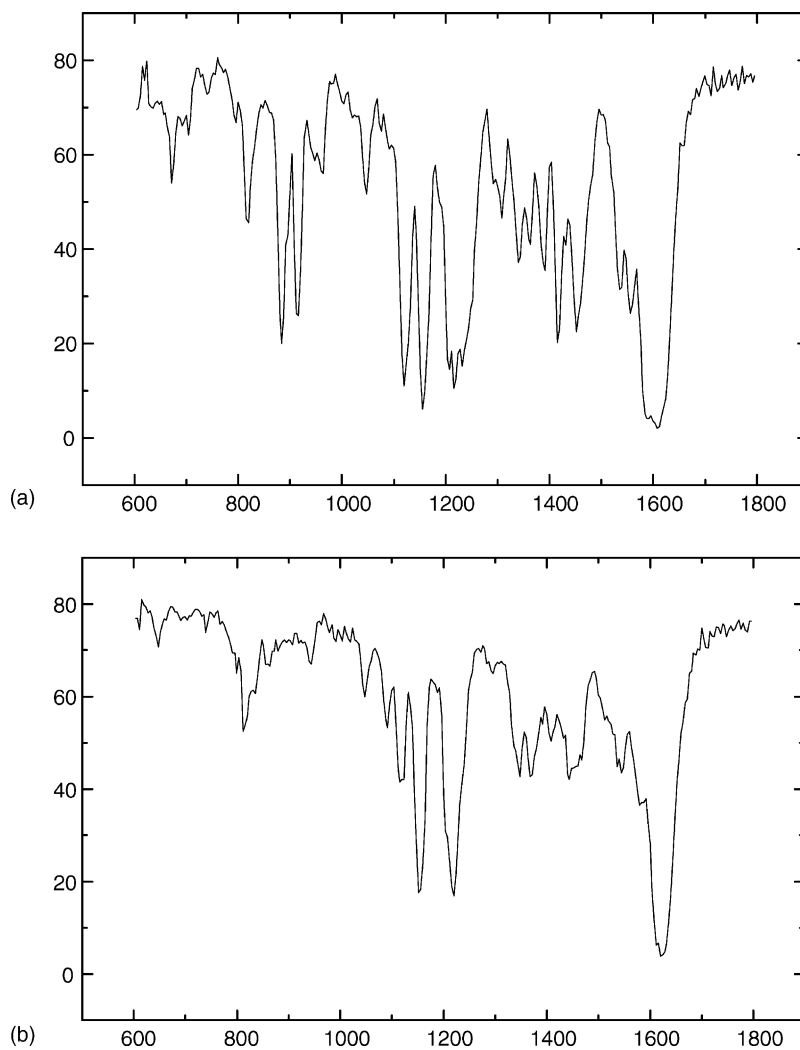


Fig. 1. The IR spectra of (a) $\text{MoO}_2[\text{bis}-(4,6\text{-diOCH}_3\text{Sal})]$ (**5**) (b) and its Schiff-base ligand.

The IR spectra of all complexes in the solid state show two absorption bands in the region between 872 and 928 cm^{-1} , which is a characteristic of *cis*- MoO_2 group [11–16]. The exemplary IR spectrum of complex (**5**) and its ligand are presented in Fig. 1. The absorption band of MoO/MoN was observed below 550 cm^{-1} [15]. Disappearance of the broad $\nu(\text{O-H})$ absorption on complexation indicated a coordination of the phenolic oxygen to the metal. The characteristic imine bands in the region $1610\text{--}1640\text{ cm}^{-1}$ are split and shifted to the lower and higher wave numbers in comparison to the spectra of the ligands. The coordination of the metal to the imine nitrogen is expected to shift the $\nu\text{C=N}$ band to lower wave numbers [13]. The pattern of the $\nu\text{C=N}$ absorption suggests the non-equivalence of both imine groups and a possible deviation of the C=N group from the aromatic ring plane. Such a structure has been found by the X-ray method for the MoO_2 complex of Schiff bases derived from 2-methyl-1,3-diaminopropane [14,17].

The electronic spectra of the complexes revealed a high intensity charge transfer band near $31,000\text{ cm}^{-1}$, while the

LMCT band was near $23,000\text{--}25,000\text{ cm}^{-1}$, similar to the spectra of the other Mo(VI) complexes of Schiff bases [11–14,16].

The splitting of the signals in the ^1H NMR spectra of all the complexes confirms the non-equivalence of both the chelate rings. A particularly large difference in the positions of the methine (C-7 for **1–5**; C-11 for **6**) signals is observed for complexes **5** and **6**. The region of the imine and aromatic signals for complex **1** and its ligand is shown in Fig. 2 [12,14].

The spectroscopic study shows that both the chelate rings in the complexes are not coplanar, similarly as it is in the other sterically hindered complexes [12,14,17]. This lack of coplanarity may result from the presence of the chelate rings with the bulky groups and the steric requirement of the *cis*- MoO_2 . These effects may be responsible for a relatively low stability of the complexes studied. The presence of the electrodonor substituent in the salicylidene ring of **5** may account for strengthening the Mo-N bond and increasing the stability of the complex. The decreasing electron density

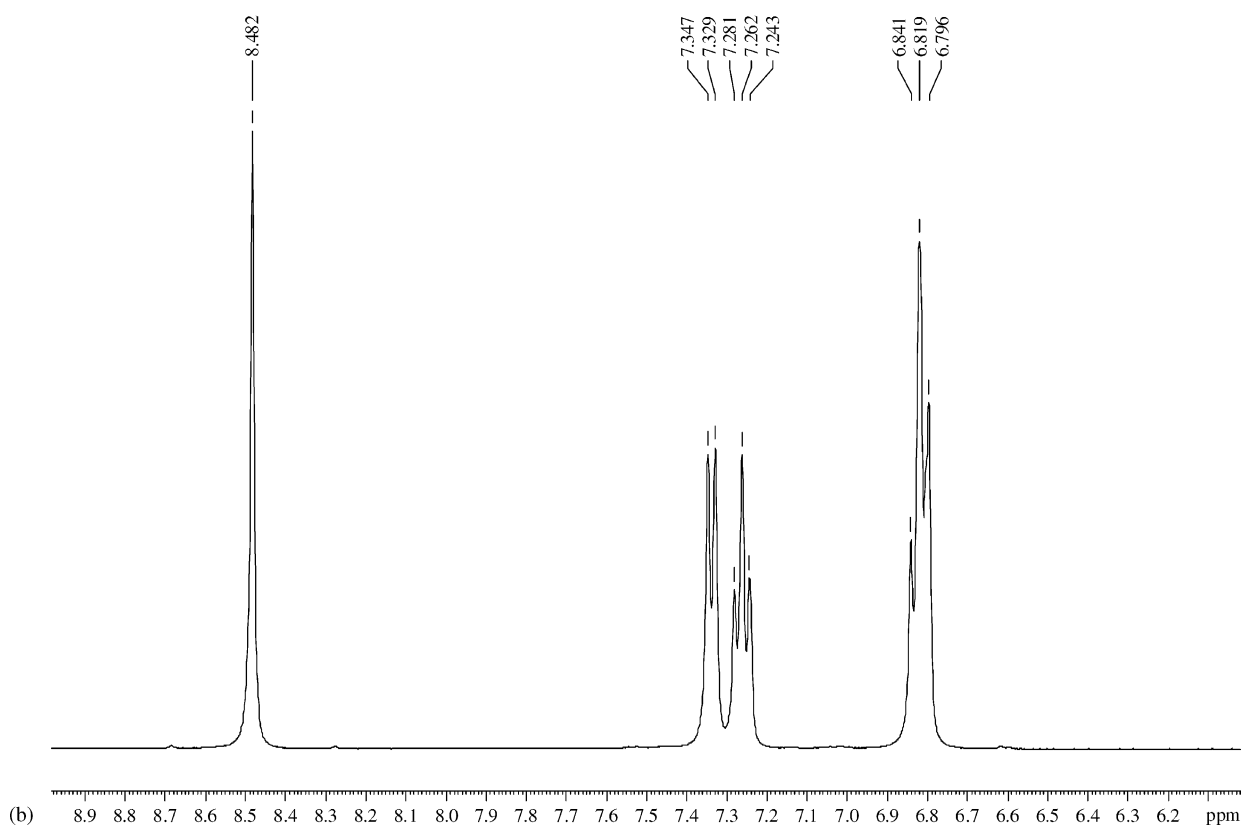
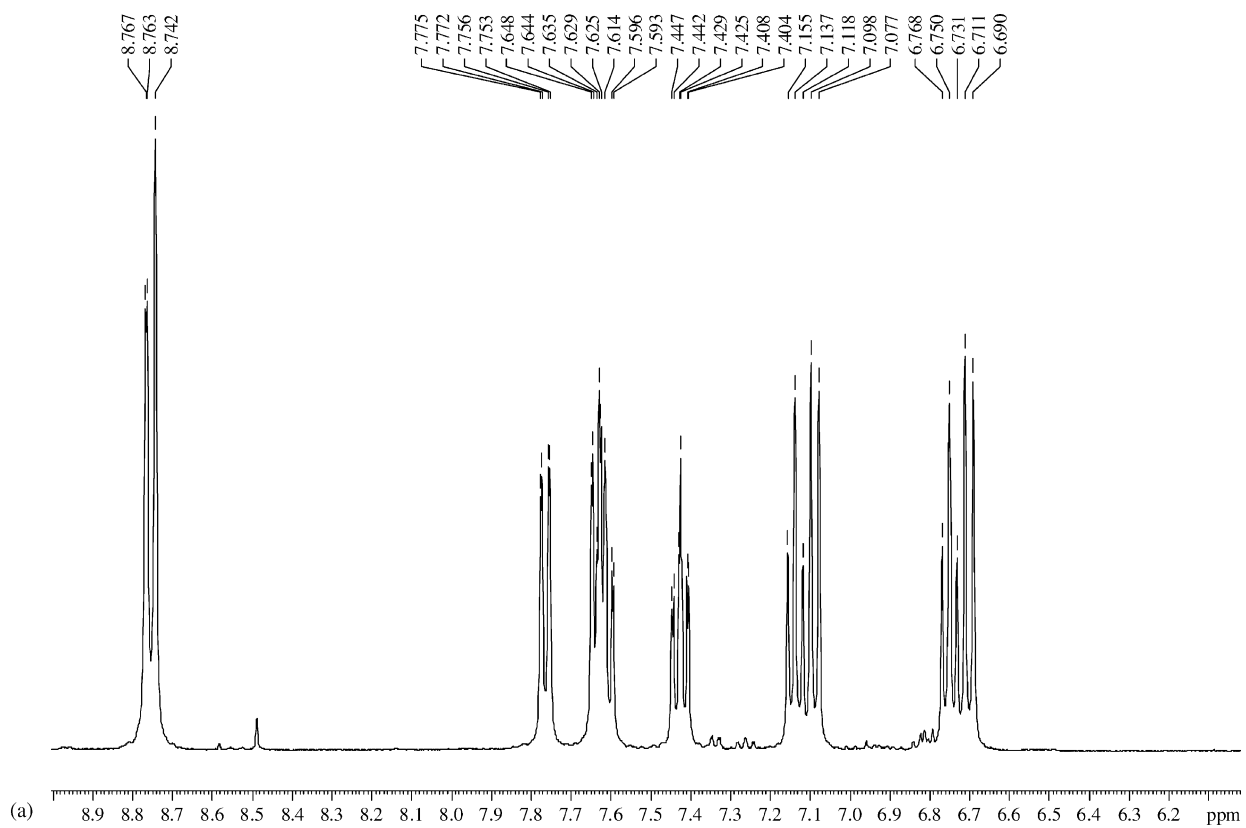
Fig. 2. ^1H NMR spectra of (a) $\text{MoO}_2[\text{bis-Sal}]$ (**1**) and (b) its ligand.

Table 1
Epoxidation of cyclohexene and 1-octene catalyzed by dioxomolybdenum(VI) Schiff-base complexes^a

Entry	Catalyst	Epoxide yield (%)	
		Epoxycyclohexane	1,2-Epoxyoctane
1	MoO ₂ [bis-Sal] (1)	92	23
2	MoO ₂ [bis(3,5-diClSal)] (2)	98	40
3	MoO ₂ [bis-(3,5-diBrSal)] (3)	98	29
4	MoO ₂ [bis-(5-NO ₂ Sal)] (4)	94	15
5	MoO ₂ [bis-(4,6-diOCH ₃ Sal)] (5)	100	45
6	MoO ₂ [bis-(Naph)] (6)	93	74
7	MoO ₂ [bis-(Naph)](6) ^b	74	~2
8	MoO ₂ [bis-(Naph)] (6) ^c	100	86

^a Reaction conditions: 25 mmol alkene; 8.33 mmol TBHP (5.2 mol in *n*-decane); 4 ml of 1,1,2,2-tetrachloroethane as solvent; 0.025 mmol of catalyst; 358 K; 2 h.

^b Reaction carried out without solvent.

^c Reaction carried out at 373 K.

on the O atom, following from the presence of electron withdrawing NO₂, seems to explain the lowest stability of this complex.

The catalytic activities of dioxomolybdenum(VI) complexes **1–6** were determined by the yield at epoxidation of cyclohexene and 1-octene using *tert*-butyl hydroperoxide as oxidant. The yield of the reaction was expressed as $Y = (C_{\text{epox}}/C_{\text{TBHP}}) \times 100\%$, where C_{epox} and C_{TBHP} are the molar concentration of the epoxide and the initial concentration of TBHP, respectively. The epoxycyclohexane and 1,2-epoxyoctane yields are given in Table 1. The selectivity of the epoxidation was found to be close to 100% either for epoxycyclohexane or for 1,2-epoxyoctane. The epoxide yield was higher for cyclohexene than that for 1-octene, in accordance with the known higher reactivity of cyclic alkenes in these reactions [6]. The high yield of epoxide in the reaction of cyclohexene epoxidation catalyzed by all complexes **1–6** made it difficult to compare their catalytic activities; the differences in the yield were within the measure-

ment error range. However, MoO₂[bis-(4,6-diOCH₃Sal)] (**5**) may be considered to be the best catalyst in this reaction, as only for this catalyst no trace of TBHP was found when the reaction was completed (entry 5 in Table 1). Another advantage of MoO₂[bis-(4,6-diOCH₃Sal)] (**5**) complex is its stability in DMSO, which is important from the viewpoint of the spectroscopic studies of this complex in solution. In the reaction of epoxidation of 1-octene the yield changes within the limits from 15% found for MoO₂[bis-(5-NO₂Sal)] (**4**) up to 74% for MoO₂[bis-(Naph)] (**6**), (Table 1 and Fig. 3). This results indicate that introduction the electron-withdrawing NO₂ group to the salicylidene ring strongly decrease the effectiveness of a catalyst.

In order to gain a better insight into the catalytic activity of MoO₂[bis-(4,6-diOCH₃Sal)] (**5**) in epoxidation of cyclohexene, the effect of the olefin:oxidant ratio and the reaction temperature was investigated (Fig. 4).

The epoxy-compound yield was shown to be strongly dependent on the cyclohexene:TBHP molar ratio. The

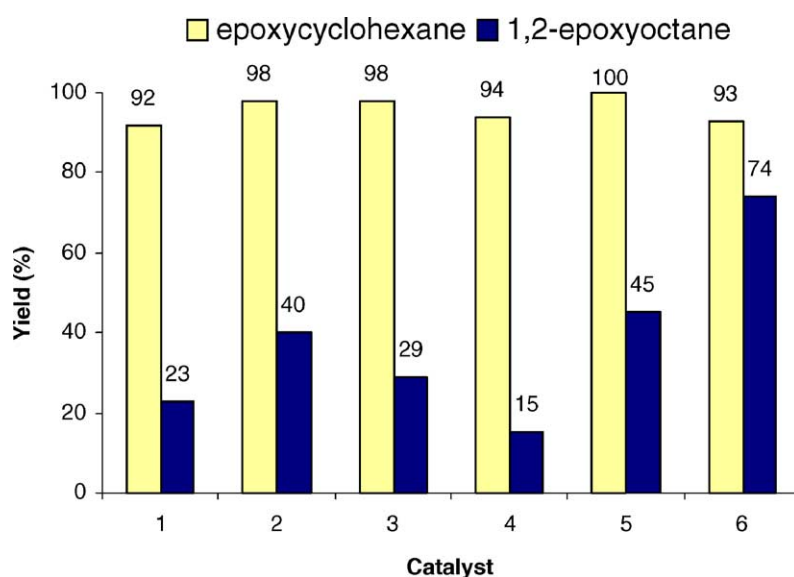


Fig. 3. Epoxycyclohexane and 1,2-epoxyoctane yield in the reaction of epoxidation catalyzed by dioxomolybdenum(VI) Schiff-base complexes.

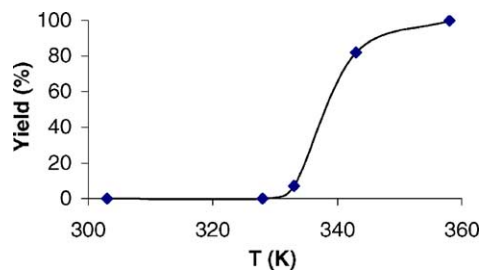


Fig. 4. The effect of temperature on the yield of cyclohexene epoxidation catalyzed by $\text{MoO}_2[\text{bis}-(4,6\text{-diOCH}_3)]$ (**5**).

olefin:TBHP ratio of 3:1 gave a 100% yield of epoxide, whilst a significant decrease in the epoxycyclohexane yield was observed for the decrease in ratio of 3:1.5 and 3:2 (Table 2). It is worth noting that we obtained a 100% epoxide selectivity for all the experiments.

The temperature dependence of cyclohexene epoxidation by **5** was investigated and the reaction yields are given in Fig. 2. It can be seen that the epoxycyclohexane yield strongly depends on the reaction temperature. At 303 and 328 K, we observed no epoxy-compounds. As we obtained 7% epoxide yield at 333 K it may be presumed that the reaction starts at about 333 K; at 358 K the yield increased up to 100%.

We also carried out the epoxidation of 1-octene and cyclohexene at 373 K using $\text{MoO}_2[\text{bis}-(\text{Naph})]$ (**6**) as a catalyst. It can be seen in Table 1 (entry 8) that both the epoxide yields increased with increasing temperature. For the reaction of cyclohexene epoxidation an increase in the epoxide yield to 100% was observed when the temperature was increasing from 358 to 373 K, whilst in the reaction of 1-octene epoxidation, an increase in temperature by 15 K caused an increase in the 1,2-epoxyoctane yield from 74 to 86%.

The reaction was performed in 1,1,2,2-tetrachloroethane, because it is known that chlorinated solvents facilitate epoxidation [22] 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 373 K. In order to show the role of the solvent we also carried out epoxidation of cyclohexene and 1-octene with $\text{MoO}_2[\text{bis}-(\text{Naph})]$ (**6**) catalyst without 1,1,2,2-tetrachloroethane (Table 1, entry 7). The absence of the solvent during the epoxidation of cyclohexene at

358 K led to a decrease in the epoxycyclohexane yield from 93% with the solvent to 74% without it. 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 74% epoxide yield. Insolubility of $\text{MoO}_2[\text{bis}-(\text{Naph})]$ (**6**) in octene accounted for a very low yield of this reaction, which can indicate that the catalytic reaction takes place in the homogenous phase.

The results of our study have revealed that two of the synthesised complexes: **5** and **6**, are effective catalysts for epoxidation of cyclohexene and 1-octene in 1,1,2,2-tetrachloroethane.

4. Conclusions

The synthesised dioxomolybdenum(VI) complexes of tetradentate Schiff-base derivatives of *trans*-1,2-diaminocyclohexane are found to be very selective catalysts for the epoxidation of cyclohexene and 1-octene. High yield (90–100%) of epoxidation was found for the first of the reactions at 358 K; for the epoxidation of 1-octene the yield was in the range 15–74%. The best results were obtained for [*trans*-*N,N'*-bis-(4,6-dimethoxysalicylidene)-1,2-cyclohexanediaminato]-dioxomolybdenum(VI) and [*trans*-*N,N'*-bis-(2-hydroxynaphthylidene)-1,2-cyclohexanediaminato]-dioxomolybdenum. An increase in the reaction temperature may lead to an increase in the yield of the epoxide. The complexes are stable in the solid state, however, they undergo decomposition during the reaction.

Acknowledgements

The authors wish to thank Mrs. Magdalena Janus for TG measurements.

References

- [1] K.A. Jorgensen, Chem. Rev. 89 (1989) 436.
- [2] H. Mimoun, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 6, first ed., Pergamon Press, New York, 1987, p. 317.
- [3] R.H. Holm, Chem. Rev. 87 (1987) 1401.
- [4] V. Schurig, F. Betschinger, Chem. Rev. 92 (1992) 873.
- [5] S.V. Kotov, T.M. Kolev, M.G. Georgieva, J. Mol. Catal. A 195 (2003) 83.
- [6] U. Arnold, R. Serpa da Cruz, D. Mandelli, U. Schuchardt, J. Mol. Catal. A 165 (2001) 149.
- [7] M. Masteri-Parahani, F. Farzaneh, M. Ghandi, J. Mol. Catal. A 192 (2003) 103.
- [8] W.F. Brill, J. Am. Chem. Soc. 85 (1963) 141.
- [9] K. Ambroziak, T. Dziembowska, Z. Rozwadowski, B. Bieg, J. Mol. Struct. 616 (2002) 109.
- [10] G.J.-J. Chen, J.W. McDonald, W.E. Newton, Inorg. Chem. 15 (1976) 2612.
- [11] K. Yamanouchi, S. Yamada, Inorg. Chim. Acta 9 (1974) 83.
- [12] K. Yamanouchi, S. Yamada, Inorg. Chim. Acta 9 (1974) 161.

Table 2

The effect of the olefin:oxidant molar ratio on the $\text{MoO}_2[\text{bis}-(4,6\text{-diOCH}_3\text{Sal})]$ (**5**) catalyzed epoxidation of cyclohexene^a

Entry	Cyclohexene:TBHP ratio	Epoxycyclohexane yield (%)
1	3:1	100
2	3:1.5	88
3	3:2	69

^a Reaction conditions: 25 mmol alkene; 8.33, 12.25, 16.66 mmol TBHP (5.2 mol in *n*-decane); 4 ml of 1,1,2,2-tetrachloroethane as solvent; 0.025 mmol of catalyst; 358 K; 2 h.

- [13] W.E. Hill, N. Attabay, C.A. McAuliffe, F.P. McCullough, S.M. Raz-zoki, *Inorg. Chim. Acta* 35 (1979) 35.
- [14] M. Gullotti, A. Pasini, G.M. Zanderighi, G. Ciani, A. Sironi, *J. Chem. Soc. Dalton* (1981) 902.
- [15] O.A. Rajan, A. Chakravorty, *Inorg. Chem.* 20 (1980) 660.
- [16] U. Sandbhor, S. Padhe, E. Sinn, *Trans. Met. Chem.* 27 (2002) 681.
- [17] A.C. Villa, L. Coghi, A.G. Manfredotti, C. Gaustini, *Cryst. Struct. Commun.* 3 (1974) 551.
- [18] J. Topich, *Inorg. Chem.* 20 (1981) 3704.
- [19] J. Topich, J.T. Lion, *Polyhedron* 3 (1984) 55.
- [20] J. Liimatainen, A. Lehtonen, R. Sillanpaa, *Polyhedron* 19 (2000) 1133.
- [21] M. Kato, K. Nakajima, J. Joshikawa, M. Hirotsu, M. Kojima, *Inorg. Chim. Acta* 311 (2000) 69.
- [22] B.C. Reichardt, *Solvents and Solvent Effect in Organic Chemistry*, VCH, Weinheim, 1988.