

Synthesis, characterization and catalytic property of tetradentate Schiff-base complexes for the epoxidation of styrene

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Abstract

A series of Schiff-base complexes has been synthesized by the condensation of 1,2-diaminocyclohexane with salicylaldehyde, 2-pyridinecarboxaldehyde, and 2-hydroxy-1-naphthaldehyde, followed by the metallation with manganese (**1**, **2**, **3a**), cobalt (**3b**), copper (**3c**) and iron (**3d**) salts. These Schiff-base ligands **L**₁–**L**₃ and complexes **1**, **2**, **3a**–**d** were then characterized by IR, ¹H NMR, ¹³C NMR, UV–vis spectra, and DSC measurement. Schiff-base Mn complex (**3a**) resulting from *N,N'*-bis(2-hydroxy-1-naphthalidene)cyclohexanediamine (**L**₃) ligand was considerably active for the catalytic epoxidation of styrene under mild conditions, in which the highest yield of styrene oxide reached 91.2 mol%, notably higher than those achieved from simple salt catalysts Mn(Ac)₂·4H₂O and MnSO₄·H₂O. However, another two salen–Mn complexes **1** and **2** derived from ligands *N,N'*-bis(salicylidene)cyclohexanediamine (**L**₁) and *N,N'*-bis(2-pyridine carboxalidene)cyclohexanediamine (**L**₂) exhibited relatively poor activity under identical experimental conditions.

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1. Introduction

The catalytic epoxidation of olefins has been a subject of growing interest in the production of chemicals and fine chemicals. Since epoxides are key starting materials for a wide variety of products [1,2], much effort has been made to develop new active and selective epoxidation catalysts for those processes that require an elimination of by-products. Catalytic epoxidation of carbon–carbon double bonds is of pivotal importance in organic chemistry, due to the wide-range applications of highly regio-selective ring openings and other reactions of epoxides in the synthesis of a variety of functionalized products [3–8]. It is well documented that epoxides can be easily transformed into a large variety of compounds by means of regio-selective ring-opening reactions.

Styrene is a major industrial chemical used extensively in the production of plastics, resins and synthetic rubbers. Styrene oxide can be used for producing epoxy resin diluting agent,

ultraviolet absorbent, flavoring agent, and so on, and is also an important intermediate in organic synthesis, pharmacology and perfumery. For example, catalytically-hydrogenated product of styrene oxide is β-phenethyl alcohol, which is a main component in the flower oil of attar, clove and neroli, and extensively used for the preparation of food, tobacco, soap, cosmetics essence etc. In recent years, the growth of domestic and international demand for β-phenethyl alcohol and laevorotary imidazole has resulted in the shortage of styrene oxide supply on the market, which thus brings about vast foreground to the research of styrene epoxidation.

Sharpless epoxidation of allylic alcohols was the first breakthrough in this field [9,10], and this method led to the preparation of a variety of different allylic epoxides, many of which have been used for the synthesis of valuable target molecules with very high selectivity [11]. Amongst various catalysts developed so far for the selective epoxidation, salen–Mn(III) complexes have been demonstrated to be efficient laboratory and industrial homogeneous catalysts in the epoxidation of some unfunctionalized alkenes using iodosylbenzene, sodium hypochlorite and hydroperoxide as oxygen sources [12,13]. However, oxidation reactions with environmentally-benign oxidants such as molecu-

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lar oxygen and hydrogen peroxide have been intensively studied during recent years [14–17]. Both oxidants are highly attractive since they are cheap and produce non-toxic waste products in contrast to many commonly employed oxidants, such as MCPBA, PhIO, NaOCl, etc. The mild activity of hydrogen peroxide can be significantly enhanced by the addition of various metal catalysts [18,19]. Oxidation of hydrocarbons is of immense interest in the area of transition-metal complexes mediated reactions under moderate reaction conditions. Two main oxidation reactions viz. epoxidation and hydroxylation have been reported using hydrogen peroxide as source of oxygen atom and transition-metal complexes as catalysts.

It is generally recognized that manganese and iron complexes are less environmentally damaging than other transition-metal complexes, and that such complexes have received considerable attention as oxidation catalysts [20]. Manganese has been involved in many biological processes as well, for instance as the active site of several enzymes [21]. In order to mimic these enzymes, many manganese complexes consisting of porphyrin, phthalocyanin, triazamacrocyclic and Schiff-base ligands have been synthesized and studied in connection with oxidation state [22–24], coordination number [25] and number of manganese site present in these biological catalysts [26].

In the present study, three different Schiff-base ligands *N,N'*-bis(salicylidene)cyclohexanediamine (**L**₁), *N,N'*-bis(2-pyridine carboxaldehyde)cyclohexanediamine (**L**₂) and *N,N'*-bis(2-hydroxy-1-naphthalidene)cyclohexanediamine (**L**₃) (Scheme 1) were synthesized. Subsequently, they were coordinated with metals Mn, Co, Cu and Fe to achieve six Schiff-base complex catalysts (**1**, **2**, **3a–d**) (Scheme 2). It was observed that

all the catalysts containing Mn metal showed excellent catalytic activity for the epoxidation of styrene with dilute hydrogen peroxide (30%) under mild conditions.

2. Experimental

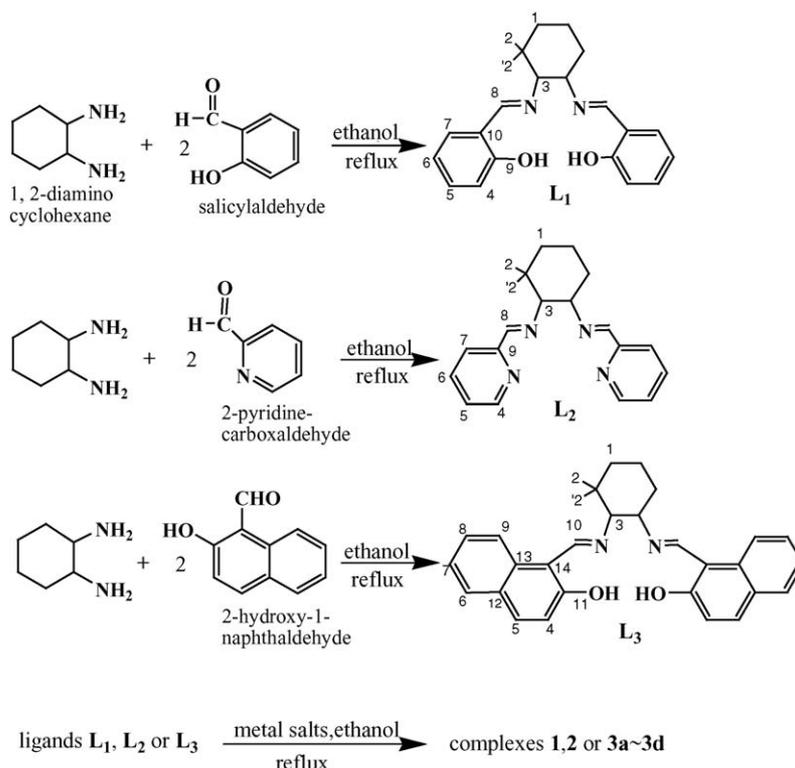
2.1. Materials

The main reagents used in the synthesis of Schiff-base complexes were salicylaldehyde (98%, Tianjin), 2-pyridine-carboxaldehyde (99%, Acros) and 2-hydroxy-1-naphthaldehyde (>98%, Acros), 1,2-diaminocyclohexane (99%, Aldrich), in which salicylaldehyde was redistilled three times prior to use, while others were directly used as received. The freshly distilled solvents were absolute ethanol, chloroform, acetone and dichloromethane. Other reagents included sodium bicarbonate (0.2 M), *N,N'*-dimethylformamide (99.5%), styrene (>99%), manganese(II) acetate tetrahydrate (99%, Mn(Ac)₂·4H₂O), manganese(II) sulfate monohydrate (99%, MnSO₄·H₂O), cobalt(II) acetate tetrahydrate (99.5%, Co(Ac)₂·4H₂O), cupric acetate monohydrate (99%, Cu(Ac)₂·H₂O) and anhydrous ferric trichloride (98%, FeCl₃).

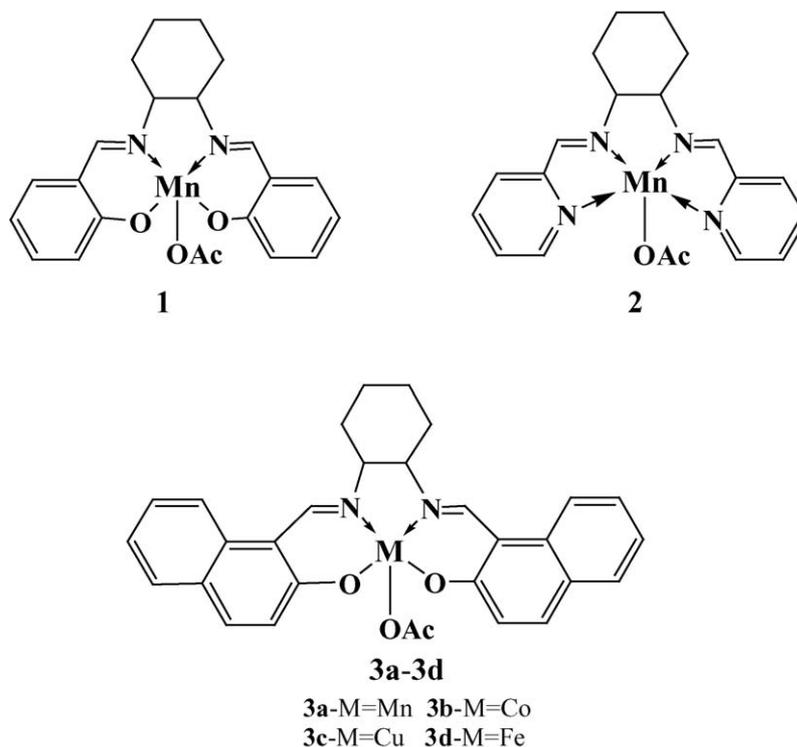
2.2. Synthesis of Schiff-base ligands

2.2.1. *N,N'*-bis(salicylidene)cyclohexanediamine (**L**₁)

A solution of salicylaldehyde (0.877 mmol, 0.214 g) in 10 ml of absolute ethanol was dropwise added over 1.5 h into the solution of 1,2-diaminocyclohexane (0.438 mmol, 0.100 g) in 10 ml of warm absolute ethanol while stirring. Then the resulting mix-



Scheme 1. Synthetic routes of ligands and salen-metal complexes.

Scheme 2. Structure of salen-metal complexes **1**, **2** and **3a-d**.

ture was refluxed at 78 °C for 5 h until the completion of reaction (checked by TLC). Thereafter, the solvent was removed by a rotary evaporator to receive a creamy compound, which was further re-crystallized in chloroform to obtain pure yellowish crystal ligand **L₁** with a yield of 92.0% (Table 1).

M.p.: 90.5 °C; Elemental analysis (C, H, N and O, wt.%) calculated for C₂₀H₂₂N₂O₂ (**L₁**): C, 74.51; H, 6.88; N, 8.69; O, 9.93; Found: C, 75.09; H, 6.92; N, 8.36; O, 9.63; IR (KBr) (cm⁻¹): 3420, ν(OH); 1622, 1614 ν(C=N)/ν(C=C); ¹H NMR (CDCl₃) (600 MHz): δ, 1.754–1.477 (m, 6H, H-1, H-2), ~1.903 (m, 1H, H-2' (*cis*)) ↔ ~1.971 (m, 1H, H-2' (*trans*)), ~3.314 (d, 1H, H-3 (*cis*)) ↔ 3.607 (d, 1H, H-3 (*trans*)), 6.779 (d, 1H, H-4 (*cis*)) ↔ ~6.795 (d, 1H, H-4 (*trans*)), ~6.844 (d, 1H, H-6 (*cis*)) ↔ ~6.879 (d, 1H, H-6 (*trans*)), ~6.916 (t, 1H, H-5 (*cis*)) ↔ ~7.140 (t, 1H, H-5 (*trans*)), ~7.246 (t, 1H, H-7 (*cis*)) ↔ ~7.285 (t, 1H, H-7 (*trans*)), 8.254 (bs, 1H, H-8 (*cis*)) ↔ 8.315 (bs, 1H, H-8 (*trans*)), 13.321 (s, 1H, –OH (*cis*)) ↔ 13.469 (s, 1H, –OH (*trans*)); ¹³C{¹H} NMR (CDCl₃)

(150 MHz): δ, 24.640 (C-1 (*cis*)) ↔ 22.962 (C-1 (*trans*)), 33.562 (C-2 (*cis*)) ↔ 31.148 (C-2 (*trans*)), 73.094 (C-3 (*cis*)) ↔ 69.913 (C-3 (*trans*)), 117.227–117.482 (C-4 (*cis*)) ↔ 118.958 (C-4 (*trans*)), 119.046 (C-6), 119.119–119.294 (C-10), 131.927 (C-7), 132.625 (C-5), 161.706 (C-8 (*cis*)) ↔ 161.432 (C-8 (*trans*)), 165.139–165.193 (C-9 (*cis*)) ↔ 164.605 (C-9 (*trans*)).

2.2.2. *N,N'*-bis(2-pyridinecarboxaldehyde)-cyclohexanediamine (**L₂**)

A solution of 2-pyridinecarboxaldehyde (0.785 mmol, 0.168 g) in 10 ml of absolute ethanol was dropwise added over 1.5 h into the solution of 1,2-diaminocyclohexane (0.392 mmol, 0.089 g) dissolved in 10 ml of warm absolute ethanol while stirring. Subsequently, the resultant mixture was treated for 6 h at 78 °C until the completion of reaction (monitored by TLC). After that, the solvent was evaporated off by a rotary evaporator to yield a creamy compound, which was further purified by re-crystallization in chloroform to obtain a pure yellowish crystal ligand **L₂** with a yield of 73.1% (Table 1).

M.p.: 129.1 °C; Elemental analysis (C, H and N, wt.%) calculated for C₁₈H₂₀N₄ (**L₂**): C, 73.94; H, 6.89; N, 19.16; Found: C, 74.19; H, 7.04; N, 18.67; IR (KBr) (cm⁻¹): 1645 ν(C=N); ¹H NMR (CDCl₃) (600 MHz): δ, 1.528–1.515 (m, 6H, H-1, H-2), 1.846 (m, 1H, H-2' (*cis*)) ↔ ~1.882 (m, 1H, H-2' (*trans*)), 3.544–3.529 (d, 2H, H-3), 7.230–7.210 (d, 2H, H-5), 7.265 (d, 2H, H-6), 7.656–7.631 (d, 2H, H-7), 7.889–7.875 (d, 2H, H-4), 8.311 (bs, 1H, H-8 (*cis*)) ↔ ~8.552 (bs, 1H, H-8 (*trans*)); ¹³C{¹H} NMR (CDCl₃) (150 MHz): δ, 24.801 (C-1), 33.173 (C-2), 73.995 (C-3), 121.781 (C-7), 124.890 (C-5), 136.863 (C-6), 149.672 (C-4), 155.096 (C-9), 161.897 (C-8).

Table 1
Isolated yield of Schiff-base ligands and complexes

Sample	Schiff-base ligand yield (wt.%)	Complex yield (%)
1	92.0	65.0
2	73.1	95.0
3a	97.8	97.0
3b		80.0
3c		93.6
3d		92.0

Samples **3a-d** used the same ligand **L₃**.

2.2.3. *N,N'*-bis(2-hydroxy-1-naphthalidene)-cyclohexanediamine (**L₃**)

A solution of 2-hydroxy-1-naphthaldehyde (0.570 mmol, 0.198 g) in 10 ml of absolute ethanol was added dropwise over 1.5 h into a stirred solution of 1,2-diaminocyclohexane (0.285 mmol, 0.065 g) in 10 ml of warm absolute ethanol. Then, the resulting cloudy mixture was refluxed at 78 °C for 6 h until the completion of reaction (checked by TLC). The precipitate was recovered by filtration. The filtrate was further concentrated to yield a yellowish solid powder. Thereafter, the recovered precipitate and solid powder were combined to undergo a further purification by re-crystallization in chloroform. The pure product was a yellow crystal with a yield of 97.8%, designated as **L₃** (Table 1).

M.p.: 198.4 °C; Elemental analysis (C, H, N and O, wt.%) calculated for C₂₈H₂₆N₂O₂ (**L₃**): C, 79.59; H, 6.20; N, 6.63; O, 7.57; Found: C, 80.07; H, 6.25; N, 6.15; O, 7.53; IR (KBr) (cm⁻¹): 3420, ν(OH); 1622, ν(C=N); 1247, 1311 ν(CO); ¹H NMR (CDCl₃) (600 MHz): δ, 1.786–1.525 (m, 6H, H-1, H-2), ~2.026 (m, 1H, H-2' (*cis*)) ↔ ~2.217 (m, 1H, H-2' (*trans*)), 3.445 (d, 1H, H-3 (*cis*)) ↔ 3.860 (d, 1H, H-3 (*trans*)), 6.856 (d, 1H, H-7 (*cis*)) ↔ ~6.912 (d, 1H, H-7 (*trans*)), ~7.132 (t, 1H, H-4 (*cis*)) ↔ ~7.198 (t, 1H, H-4 (*trans*)), ~7.237 (t, 1H, H-8 (*cis*)) ↔ ~7.293 (t, 1H, H-8 (*trans*)), ~7.353 (d, 1H, H-9 (*cis*)) ↔ ~7.461 (d, 1H, H-9 (*trans*)), ~7.468 (d, 1H, H-6 (*cis*)) ↔ ~7.640 (d, 1H, H-6 (*trans*)), ~7.725 (d, 1H, H-5 (*cis*)) ↔ ~7.822 (d, 1H, H-5 (*trans*)), 8.759 (bs, 1H, H-10 (*cis*)) ↔ 8.879 (bs, 1H, H-10 (*trans*)), 14.659 (s, 1H, -OH (*cis*)) ↔ 14.793 (s, 1H, -OH (*trans*)); ¹³C{¹H} NMR (CDCl₃) (150 MHz): δ, 24.676 (C-1), 33.192 (C-2), 69.587 (C-3 (*cis*)) ↔ 65.464 (C-3 (*trans*)), 107.561 (C-14), 118.857 (C-4), 123.320–123.288 (C-7 (*cis*)) ↔ 123.778 (C-7 (*trans*)), 127.102 (C-9), 127.011 (C-8), 128.273 (C-6), 129.541 (C-12 (*cis*)) ↔ 129.328 (C-12 (*trans*)), 133.844 (C-5 (*cis*)) ↔ 133.659 (C-5 (*trans*)), 137.071 (C-13 (*cis*)) ↔ 136.939 (C-13 (*trans*)), 59.677 (C-11), 172.605 (C-10).

2.3. Preparation of catalysts **1**, **2** and **3a–d**

An appropriate amount of Schiff-base ligands **L₁** (0.253 mmol, 0.081 g) and **L₂** (0.253 mmol, 0.074 g) was separately dissolved in absolute ethanol in nitrogen atmosphere under vigorous stirring. Then was added Mn(Ac)₂·4H₂O (0.253 mmol, 0.062 g), and the resulting mixture was refluxed for 7 h in nitrogen atmosphere until the complete reaction of ligand compound (checked by TLC). Finally, the precipitate complexes (**1** and **2**) were recovered by filtration, and washed several times with absolute ethanol and dichloromethane, dried in vacuum at 65 °C for 5 h, and again purified by re-crystallization in acetone. Syntheses of the catalysts **3a–d** with Schiff-base ligand **L₃** and various metallic salts were similar to the procedure performed in the preparation of complexes **1** and **2**. The yields of various complexes are listed in Table 1.

Analytical data for all the complexes are as follows:

Catalyst 1: {[bis(salicylidene)-1,2-cyclohexanediaminato]-dioxomanganese}. IR (KBr) (cm⁻¹): 1622 ν(C=N), 1614

ν(C=C); 1255, 1311 ν(CO); 570 ν(Mn–O), 426 ν(Mn–N). UV–vis (toluene) λ_{max} (nm): 261, 275, 283, 298.

Catalyst 2: {[bis(2-pyridinecarboxylidene)-1,2-cyclohexanediaminato]dioxo-manganese}. IR (KBr) (cm⁻¹): 1645 ν(C=N); 480 ν(Mn–N). UV–vis (toluene) λ_{max} (nm): 259, 266, 282, 326.

Catalysts 3a–d: {[bis(2-hydroxynaphthylidene)-1, 2-cyclohexanediaminato]dioxo-M (M = Mn, Co, Cu, Fe)} (designated as **3a**, **3b**, **3c** and **3d**). IR (KBr) (cm⁻¹): **3a**—1622, ν(C=N); 1247, 1311 ν(C–O); 567 ν(Mn–O), 420 ν(Mn–N); **3b**—1618, ν(C=N); 1247, 1311 ν(C–O); 570 ν(Co–O), 451 ν(Co–N); **3c**—1618, ν(C=N); 1247, 1311 ν(C–O); 555 ν(Cu–O), 408 νCu–N; **3d**—1616, ν(C=N); 1247, 1311 ν(C–O); 553 ν(Fe–O), 410 ν(Fe–N). UV–vis (toluene) λ_{max} (nm): **3a**—260, 263, 275, 281, 284, 299; **3b**—263, 276, 280, 304, 322, 365, 381, 424; **3c**—264, 282, 305, 319, 384, 402; **3d**—276, 282, 306, 378.

2.4. Structural characterization of ligands and complexes

The differential scanning calorimetric analysis of *N,N'*-bis(salicylidene)cyclohexanediamine (**L₁**), *N,N'*-bis(2-pyridinecarboxalidene)cyclohexanediamine (**L₂**) and *N,N'*-bis(2-hydroxy-1-naphthalidene)cyclohexanediamine (**L₃**) was performed by a Shimadzu DSC-60 instrument (differential scanning calorimeter) in the range of room temperature –400 °C. Elemental analyses (C, H, N and O) of the Schiff-base ligands were conducted on an Elementar VarioEL-III instrument. IR spectra (KBr pellets) were recorded on a Shimadzu IR Prestige-21 Fourier Transform Infrared Spectrometer. UV–vis spectra of samples in toluene were determined with a Shimadzu UV-2550 spectrometer. ¹H NMR spectra (600 MHz) and ¹³C NMR spectra (150 MHz) of samples dissolved in CDCl₃ were measured on a Varian Inova-600 (600 MHz) NMR instrument using TMS ((CH₃)₄Si) as an internal standard of chemical shifts (ppm).

2.5. Epoxidation of styrene

2.5.1. Blank reactions without any catalyst

Reactions were run in a round-bottom flask at 0 °C by mixing styrene (0.384 mmol), 1.53 ml of 0.2 M NaHCO₃ solution (pH 8) and 2.0 ml of solvent, and then adding dropwise 1.68 mmol 30% H₂O₂ under stirring. The solvent was chosen from various solvents DMF, CH₃CN, CH₂Cl₂ and Bu'OH. Each reaction was sustained for 3, 10, 17, 20, and 30 h before conducting GC analysis.

2.5.2. Epoxidation with metal salts catalysts

The epoxidation of styrene with H₂O₂ catalyzed by metal salts was carried out according to the procedure: 0.634 mmol of MnSO₄·H₂O catalyst (or 0.896 mmol of Mn(Ac)₂·4H₂O), 1.53 ml of 0.2 M NaHCO₃ solution (pH 8), 2.0 ml DMF and 0.384 mmol of styrene were mixed in a round-bottom flask at 0 °C while stirring; subsequently, 1.68 mmol of aqueous 30% H₂O₂ was added within 1.5 h by a dropping funnel. Each reaction was sustained for 3, 4.5, 6, 9, and 24 h prior to GC determination.

2.5.3. Epoxidation with catalysts **1**, **2**, and **3a–d**

A mixture of 0.02 mmol catalyst, 1.53 ml of 0.2 M NaHCO₃ solution (pH 8), 2.0 ml DMF and 0.384 mmol of styrene was stirred in a round-bottom flask at 0 °C for 10 min while stirring before 1.68 mmol of aqueous 30% H₂O₂ was dripped within 1.5 h. Similarly, each reaction was sustained for 3.5, 6, 9, 20 and 30 h prior to GC determination.

2.5.4. GC analysis of products

The quantitative GC analysis of the epoxidized products was carried out by a GC-900A equipped with an FID detector and a SUPELCO BETA-DEXTM 120 capillary column (30 m × 0.25 mm × 0.25 μm). Hydrogen was used as carrier gas. GC error for the determination was within ±3%.

3. Results and discussion

As shown in Section 2, the elemental contents (C, H, N and O) of all the ligands synthesized are relatively close to those calculated based on molecular formulae proposed, which indicates the correctness of molecular compositions proposed. IR spectra of synthesized ligands (**L**₁ and **L**₃) and complexes (**1** and **3a**) are presented in Figs. 1 and 3. The strong band emerging at 3440 cm⁻¹ in the IR spectra of Schiff-base ligands **L**₃ can be assigned to the vibration of ν(O–H). Upon complexation, the broad ν(O–H) band will disappear, indicating the occurrence of coordination of naphtholic oxygen to metal. In the spectra of ligands **L**₁ and **L**₃, the complexation leads to the splitting of the characteristic imido (C=N) bands in the region of 1610–1640 cm⁻¹ and the occurrence of more or less shifting of these bands, as has been reported in the literature [27].

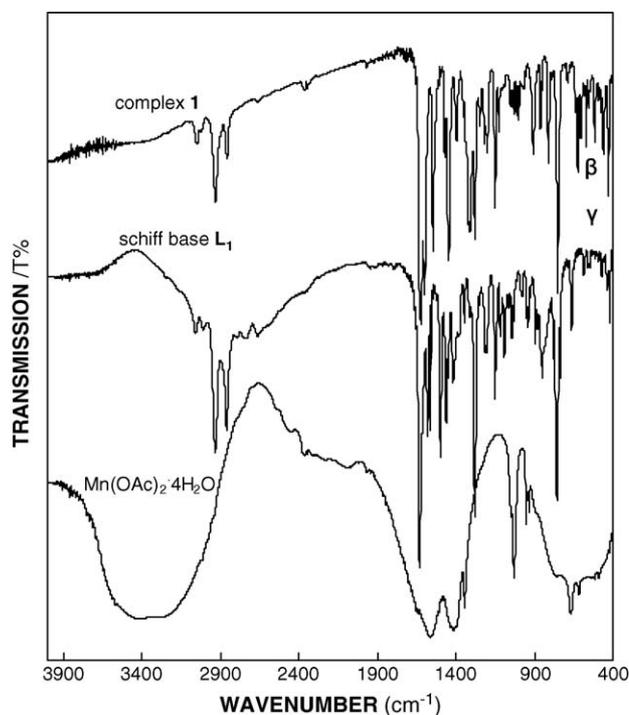


Fig. 1. IR spectra of Schiff-base ligand **L**₁, complex **1** and Mn(OAc)₂·4H₂O (peak β: 569 cm⁻¹ Mn–O; peak γ: 426 cm⁻¹ Mn–N).

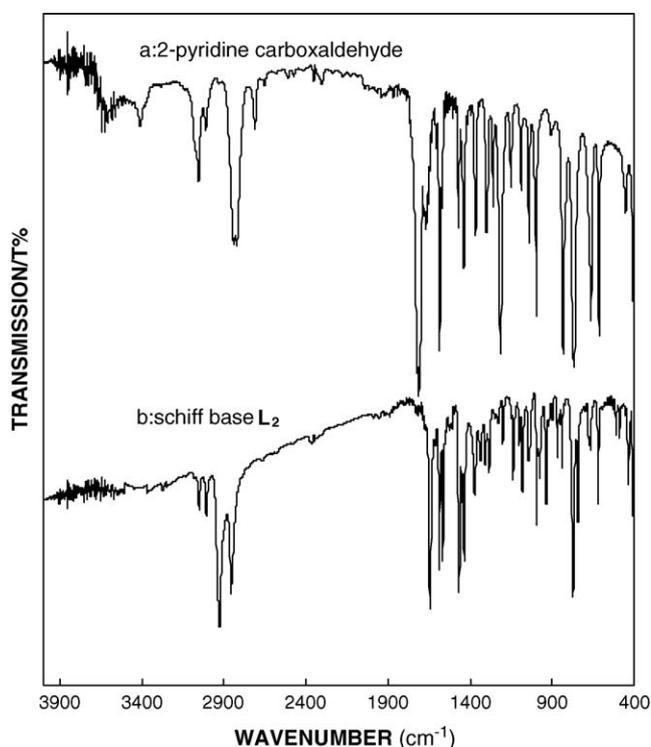


Fig. 2. IR spectra of 2-pyridinecarboxaldehyde and Schiff-base ligand **L**₂.

The pattern of νC=N absorbance suggests non-equivalence of two imido groups and possible deviation of C=N group from the aromatic ring plane. Upon coordination with metals, the absorption bands near 567 and 420 cm⁻¹ are observed from the spectra of complexes **1** and **3a**, ascribable to Mn–O and Mn–N bands [28,29].

Fig. 2 shows IR spectra of 2-pyridinecarboxaldehyde and Schiff-base ligand **L**₂. Prior to coordination, the ligand **L**₂ shows two characteristic C=O bands at about 1400 and 1700 cm⁻¹, and two C–H bands of the aldehyde group near 2700 and 2840 cm⁻¹; however, upon condensation with diamine these peaks disappear totally. Instead, a characteristic C=N band emerges at 1640 cm⁻¹ for ligand **L**₂ and its complexes, distinctly different from the cases of ligands **L**₁ and **L**₃. Note that this peak cannot be observed in the IR spectra of 2-pyridinecarboxaldehyde.

¹H NMR spectra of synthesized **L**₁–**L**₃ were measured in CDCl₃. For Schiff-base ligand **L**₁, twin H NMR peaks at 13.321 (*cis*) and 13.469 (*trans*) ppm are assigned to phenolic OH protons. The H NMR peak at 9.906 ppm resulting from CH=O proton of salicylaldehyde, disappears completely for ligand **L**₁, due to the condensation between salicylaldehyde and 1,2-diaminocyclohexane. The peaks at 6.779–7.285 ppm are attributed to aromatic protons (=C–H), and those at 1.477–1.754 ppm, 1.903 (*cis*) and 1.971 ppm (*trans*) to the protons of CH₂ in the ring of cyclohexane. Two proton peaks at 8.254 (*cis*) and 8.315 (*trans*) ppm can be assigned to CH=N protons, consistent with the observations made by Belokon et al. [30], who had assigned H NMR peaks of 2H at 8.2–8.4 ppm in the salen compounds to CH=N protons. In a similar manner to Schiff-base ligand **L**₁, the H NMR peak at 10.102 ppm

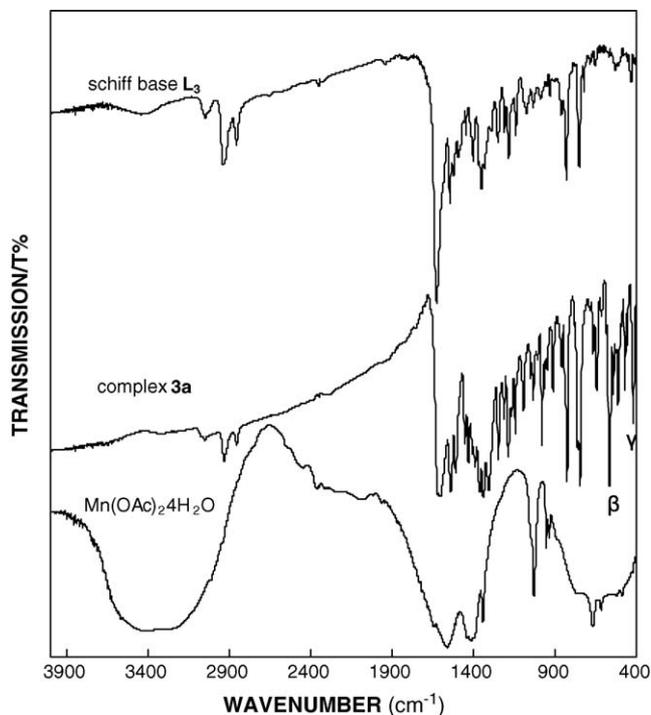


Fig. 3. IR spectra of Schiff-base ligand **L₃**, complex **3a** and $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (peak β : 567 cm^{-1} Mn–O; peak γ : 420 cm^{-1} Mn–N).

resulting from CH=O proton of 2-pyridinecarboxaldehyde, disappears totally for ligand **L₂**. The peaks at 7.210–7.889 ppm are attributed to =C–H of the pyridyl group, and those at 1.528–1.515 ppm, 1.846 (*cis*) ppm and 1.882 (*trans*) ppm to the protons of CH₂ in the ring of cyclohexane. The bands at 8.311 (bs, 2H, H-8 (*cis*)) and 8.552 (bs, 2H, H-8 (*trans*)) ppm in the H NMR spectra are due to CH=N protons.

For Schiff-base ligand **L₃**, twin H NMR peaks at 14.659 (*cis*) ppm and 14.793 (*trans*) ppm can be attributed to naphtholic OH protons. The disappearance of the H NMR peak at 10.797 ppm resulting from CH=O proton of 2-hydroxy-1-naphthaldehyde, and the emergence of two new proton peaks at 8.759 (*cis*) ppm and 8.879 (*trans*) ppm assigned to CH=N protons proves the condensation reaction between 2-hydroxy-1-naphthaldehyde and 1,2-diaminocyclohexane. The peaks at 6.856–7.822 ppm are attributable to aromatic protons (=C–H), and those at 1.525–1.786 ppm, 2.026 (*cis*) ppm, and 2.217 (*trans*) ppm to the protons of CH₂ in the ring of cyclohexane (Scheme 1).

UV–vis spectra of salen–Mn complexes (**1**, **2** and **3a**) show absorbance bands at 261, 275, 283, 298 nm for complex **1**, at 259, 266, 282, 326 nm for complex **2**, and at 260, 263, 275, 281, 284, 299 nm for complex **3a**, respectively, slightly different from those at 259, 263, 282, 305, 313 nm of the corresponding metal salt $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ [31], which shows the complexation between ligands and metal Mn ions. Fig. 4 compares UV–vis spectra of salen complexes (**3a–d**) coordinated with different metals Mn, Co, Cu, and Fe. Evidently, these complexes coordinated with various metal ions possess considerably different ultraviolet absorbance characteristics. For example, there are six recognizable bands at 260, 263, 275, 281, 284, 299 nm for complex **3a**, eight bands at 263, 276, 280, 304, 322, 365, 381, 424 nm

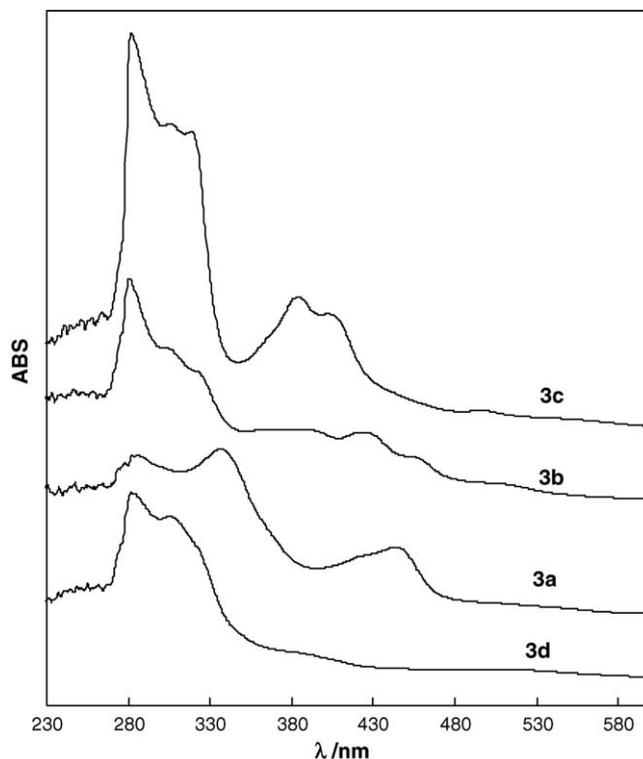


Fig. 4. UV–vis spectra of salen complexes coordinated with different metals (**3a–d**).

for complex **3b**, six bands at 264, 282, 305, 319, 384, 402 nm for complex **3c**, and four bands at 276, 282, 306, 378 nm for complex **3d**.

The effect of various solvents such as DMF, CH₃CN, CH₂Cl₂ and Bu^tOH on the epoxidation of styrene with 30% aqueous hydrogen peroxide was investigated. When no catalyst was added, the blank reaction with solvent DMF exhibited extremely low reactivity towards the yield of styrene oxide from styrene substrate; within 10 h almost no conversion occurred. When the reaction time was prolonged to 17 h, the yield of styrene oxide increased to 42.3 mol%. Along with increasing time to 20 h, the yield of styrene oxide was rapidly elevated to 70 mol%. However, in the same reaction time span (20 h) using CH₃CN as the solvent only 0.55 mol% of styrene oxide was yielded, and in the presence of CH₂Cl₂ and Bu^tOH there was no epoxide detectable from the reaction mixture. The results propose that DMF was a preferred solvent for the epoxidation of styrene under our experimental conditions. Thus, in unspecified cases DMF was chosen as the solvent to test the catalytic activity of various catalysts.

Fig. 5 shows the relationship between the yield of styrene oxide and the reaction time, where the reaction temperature was fixed at 0 °C. It is evident that for blank reaction, the yield of 70 mol% was achieved within 20 h, and further increasing the reaction time to 30 h merely exhibited an extremely small increment to 70.2 mol%. Very notably, both catalysts $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ showed relatively high activity for this reaction with almost the same conversion tendency, considerably similar to the results reported by Burgess et al. [32–34]. At 3 h, the yield of 28.3–32.2 mol% was achieved; thereafter, it lin-

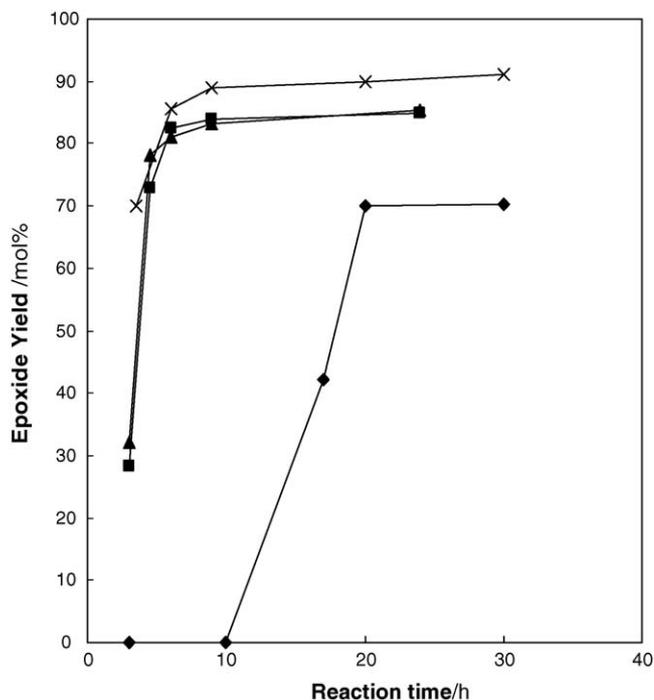


Fig. 5. The relationship between epoxide yield and reaction time with or without catalysts (◆: blank reaction; ▲: Mn(OAc)₂·4H₂O; ■: MnSO₄·H₂O; ×: salen-Mn complex **3a**).

early increased to 73.0–78.2 mol% within only 1 h. When the reaction time was prolonged to 6 h, the yield of styrene oxide continuously increased to 81.2–82.5 mol%. Further increasing the reaction time to 9 h slightly increased the yield of styrene oxide to 83.2–83.9 mol%. Then, when the reaction time was prolonged to 24 h, the yield of epoxide slowly reached about 85.3 mol%. As expected, the salen-Mn complex **3a** exhibited an excellent activity for the conversion of styrene-to-styrene oxide. Within 3.5 h, the yield of styrene oxide was reached 70.0 mol%. When the reaction time was increased to 6 h, the yield linearly increased to 85.6 mol%. The epoxidation of styrene with H₂O₂ catalyzed by complex **3a** approached conversion equilibrium at about 9 h to achieve 89.9 mol% of the yield. After that, even when the reaction time was prolonged to 30 h, the yield of styrene oxide was merely elevated to 91.2 mol%.

It was observed that the efficiency of catalysts was strongly dependent on the structure of Schiff-base ligands. When *N,N'*-bis(salicylidene)cyclohexanediamine ligand **L**₁ and *N,N'*-bis(2-pyridinecarboxalidene)cyclohexanediamine ligand **L**₂ were coordinated with manganese, the resulting complex catalysts **1** and **2** reached the epoxide yield of 71.7 and 53.9 mol% within 6 h, notably lower than 85.6 mol% of the catalyst **3a** and even much lower than 81.2–82.5 mol% of inorganic precursors Mn(Ac)₂·4H₂O and MnSO₄·H₂O. This could be due to the poor coordination stability of complex catalysts **1** and **2**, which easily underwent decomposition in the reaction environment, similar to the observations made by Ambroziak et al. [35].

The complex catalysts **3a–d** coordinated with metals Mn, Co, Cu, and Fe exhibit obviously different activities, as shown in Table 2. It is evident that salen-Co catalyst (**3b**) is less active for the epoxidation reaction of styrene than salen-Mn catalyst (**3a**).

Table 2
Catalytic activity of different metal centers

Metal	Epoxide yield (mol%)				
	3.5 h	6 h	9 h	20 h	30 h
Mn	69.9	85.6	88.9	89.9	91.2
Co	34.8	45.4	46.0	46.2	46.2
Cu	–	–	–	–	–
Fe	–	–	–	–	–

–: Not detectable. Epoxide yield (mol%) was determined by GC.

The yield of epoxide on salen-Co complex catalyst **3b** is about half of that on salen-Mn catalyst **3a**. In 3.5 h, the catalyst **3b** yielded 34.8 mol% of styrene oxide, while at this time the yield of styrene oxide reached 70 mol% on the catalyst **3a**. Similarly, conversion equilibrium could be reached at about 9 h for both catalysts; however, the highest yield on the catalyst **3b** was only 46.2 mol%, but that on the catalyst **3a** was 91.2 mol%. Regardless of the reaction time, Fe-complex and Cu-complex did not show any catalytic activity for the epoxidation of styrene with H₂O₂ under identical conditions. These results could be due to several factors, such as the nature of metals, the ability of coordination with reactants, the solubility of complexes in solvent, etc.

4. Conclusions

Several Schiff-base complexes have been synthesized by the condensation of 1,2-diaminocyclohexane with salicylaldehyde, 2-pyridinecarboxaldehyde, and 2-hydroxy-1-naphthaldehyde, followed by the metallation with manganese (**1**, **2**, **3a**), cobalt (**3b**), copper (**3c**) and iron (**3d**) salts. The structure of ligands **L**₁–**L**₃ and complexes **1**, **2**, **3a–d** were confirmed by means of DSC, FTIR, elemental analysis, ¹H NMR, ¹³C NMR and UV–vis spectroscopy. The selective epoxidation of styrene with dilute hydrogen peroxide (30%) was performed in the presence of Schiff-base complex catalysts (**1**, **2**, **3a–d**). Under our experimental conditions, Schiff-base Mn complex (**3a**) resulting from *N,N'*-bis(2-hydroxy-1-naphthalidene)cyclohexanediamine ligand (**L**₃) showed effectiveness on the catalytic epoxidation of styrene, leading to the highest yield of styrene oxide of 91.2 mol%. However, the catalytic efficiency of other salen-Mn complexes **1** and **2** derived from ligands *N,N'*-bis(salicylidene)cyclohexanediamine (**L**₁) and *N,N'*-bis(2-pyridinecarboxalidene)cyclohexanediamine (**L**₂) was poor, even notably lower than that of simple inorganic salt catalysts Mn(Ac)₂·4H₂O and MnSO₄·H₂O.

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