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Chiral Ni(II) Schiff base complex-catalysed enantioselective epoxidation of prochiral non-functionalised alkenes

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Abstract

The synthesis, characterisation and single crystal X-ray structures of square planar Ni(II) chiral Schiff base complexes with N_2O_2-type ligands have been described. These catalysts were used for enantioselective epoxidation of non-functionalised alkenes viz. 1-hexene, 1-octene, styrene, 4-chloro-, 4-nitrostyrene and 1,2-dihydronaphthalene using NaOCl as oxidant, giving excellent conversions with long chain alkenes while *ee*'s were moderate to good. A mechanism for the Ni(II)-catalysed epoxidation with NaOCl is proposed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The design of catalysts that ensures high enantioselectivity in the epoxidation of non-functionalised alkenes constitutes one of the most significant challenges in asymmetric synthesis [1–3]. In principle, it may be attainable with systems that can exert high asymmetric induction without requiring any specific functionality on the substrate for catalyst precoordination [4,5]. The major advances in this field have been achieved with chiral porphyrins [6,7] and Jacobsen et al. [5,8] with the system of Katsuki et al. [9, 10] based on chiral Mn(III) Schiff base complexes using NaOCl as oxidant. Several other oxidants, such as iodosyl benzene [10], molecular oxygen [11], H_2O_2 [12], Bu_4NIO_4 [13], dimethyldioxirane [14] and *m*-chloroperbenzoicacid [15] with related complexes, were also explored. Mononuclear, as well as dinuclear metal centers, are commonly found in the active site of various oxygenase [16–18] and the information on key structural features and factors governing oxygenase activity is rapidly increasing [19,20]. The first example of olefin epoxidation by nickel(II) catalysts with iodosylbenzene was shown by Koola and Kochi [21]. Later, Burrows et al. [22–24] also reported the synthesis, crystal structure of nickel(II) complexes and has used them as catalysts in the presence of iodosylbenzene, as well as hypochlorite for epoxidation of a wide variety of olefins. Dinuclear nickel(II) complexes have

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also been synthesised and used for epoxidation reactions by Gelling et al. [25].

We have been involved in the evaluation of the epoxidation capacity of prochiral non-functionalised alkenes using Ru(III), Ru(II), Mn(III), Co(II) and Ni(II) chiral Schiff base complexes [26–30]. As part of this pursuit, we are reporting here the synthesis, characterization and X-ray single crystal determination of mononuclear chiral Ni(II) Schiff base complexes with a view to use them as active catalysts for enantioselective epoxidation of representative non-functionalised alkenes viz. styrene, 4-chlorostyrene, 4-nitrostyrene, 1-octene, 1-hexene and 1,2-dihydronaphthalene using NaOCl as oxidant.

2. Experimental

Nickel acetate (Sisco), 3-acetyl-4-hydroxy-6-methyl-2-pyrone (National), 1*S*,2*S*-(+)-1,2-cyclohexane diamine, 1*R*,2*R*-(−)-cyclohexane diamine, 1*S*,2*S*-(+)-diphenyldiaminoethane, 1*R*,2*R*-(−)-diphenyldiaminoethane, styrene, 4-chlorostyrene, 4-nitrostyrene, 1-hexene, 1-octene and 1,2-dihydronaphthalene (Aldrich) were either used as such or passed through a short column of alumina neutral if it contains stabilizer. Solvents methanol, ethanol, dichloromethane and acetonitrile were dried and distilled by commonly used procedures. *S*-(+)-1,2-diaminopropane was resolved from its dl form by the reported procedure [31].

2.1. Synthesis of chiral Schiff bases

The chiral Schiff bases 1*S*,2*S*-(+)-DPHS and 1*R*,2*R*-(−)-CyLS were synthesised by the following method.

Methanolic solution of 1*R*,2*R*-(−)-1,2-cyclohexane diamine and 1*S*,2*S*-(+)-1,2-diphenyl ethylene diamine a (0.01 mol) was added to the hot methanolic solution of 3-acetyl 4-hydroxy 6-methyl 2-pyrone (0.02 mol) and the resulting solution was refluxed for 7 9 h (TLC checked). After the completion of reaction, the solvent was concentrated on rotaevaporator and the desired ligand were precipitated by 40–60 petroleum ether.

The chiral Schiff bases 1*S*,2*S*-(+)-DPHS and 1*R*,2*R*-(−)-CyLS were characterised by micro-analysis, IR-, ^{1}H NMR spectroscopy, while 1*S*,2*S*-(+)-*N*,*N*′-bis{(4-hydroxy-6-methyl-2-pyrone)3-acetylidine} 1′,2′-cyclohexane diamine (CyLS), 1*R*,2*R*-(−)-*N*,*N*′-bis{(4-hydroxy-6-methyl-2-pyrone)3-acetylidine} 1′,2′-diphenyl diaminoethane, (DPHS) and *1′S*-(+)-*N*,*N*′-bis {(4-hydroxy-6-methyl-2-pyrone)3-acetylidine} 1′,2′-diaminopropane (PROS) were synthesised and characterized according to our previous communication [30].

1. *1S,2S-(+)-N,N′-bis{(4-hydroxy-6-methyl-2-pyrone)3-acetylidine} 1′,2′-diamino diphenyl ethylene diamine (DHPS).* Yield 70%, m.p. 205°C. ^{1}H NMR ($CDCl_3$): δ, 2.12 (s, 6H, CH_3, H_7), 2.85 (s, 6H, CH_3, H_9), 5.57 (s, 2H, 5H), 7.29–7.53 (m, aromatic phenyl) and 15.26 (bs, 2H, OH keto/enol). Calcd. for $C_{30}H_{28}N_2O_6$: C, 70.30; H, 5.50; N, 5.46. Found: C, 70.27; H, 5.48; N, 5.45. IR(KBr) : ν(C=N) = 1625 cm^{-1}.
2. *1R,2R-(−)-N,N′-bis{(4-hydroxy-6-methyl-2-pyrone)3-acetylidine} 1′,2′-cyclohexane diamine (CyLS).* Yield 65%, m.p. d. 220°C. ^{1}H NMR ($CDCl_3$): δ, 1.4–1.8 (m, 8H, $(CH_2)_4$, H'_3 to H'_6), 2.14 (s, 6H, CH_3, H_7), 2.65 (s, 6H, CH_3, H_9), 3.39 (m, 2H, H'_1 and H'_2), 5.68 (s, 2H, phenyl, H_5), and 14.79 (bs, 2H, OH keto/enol). Calcd. for $C_{22}H_{26}N_2O_6$: C, 63.75; H, 6.3; N, 6.7. Found: C, 63.72; H, 6.1; N, 6.58. IR(KBr): ν(C=N) = 1625 cm^{-1}.

2.2. Preparation of Ni(II) chiral Schiff base complexes

Appropriate amount of the chiral Schiff bases (0.001 mol) dissolved in ethanol was allowed to reflux in inert atmosphere with $Ni(CH_3COO)_2$

(0.001 mol) in the presence of triethylamine tetrahydrate (0.001 mol) for 10–13 h. Progress of the reaction was checked on TLC. The solution was filtered and concentrated on rotaevaporator till dryness. The resulting residue was washed in ethanol and dried in vacuum. The overall yield for all the complexes were in the range of 65–70%. All the complexes were tried on to get suitable crystal for X-ray but only complexes *S*-(+)-PROS Ni(II), 1*S*,2*S*-(+)-DPHS Ni(II) and 1*R*,2*R*-(−)-DPHS Ni(II) crystallized out in the proper way.

2.3. The analytical data for the Ni(II) complex 1S,2S-(+)-DPHS Ni(II)

Calcd. for $C_{30}H_{26}N_2O_6Ni$: C, 63.37; H, 4.61; N, 4.93. Found: C, 63.38; H, 4.59; N, 4.91; ^{1}H NMR ($CDCl_3$): δ, 2.11 (s, 6H, CH_3, H_7), 2.16 (s, 6H, CH_3, H_9), 4.62 (s, 2H, CH, H'_1 and H'_2), 5.93 (s, 2H, CH, H_5), 7.49–7.56 (m, 10H, aromatic Phenyl). IR(KBr) cm^{-1} 1585 ν(H–C=N), 1265 ν(C–O) UV–VIS (nm) (MeOH) λ_{max} (ε) : 238 (5598), 264 (5868), 300 (6158), 314 (6293), 366 (5380); CD λ_{max} ($\Delta\varepsilon$) (MeOH) 332 (+1.1), 365 (+1.1), 440 (+2.1), 505(+5.7); $[\alpha]_D^t = +28.7$ Configuration (*S*); Λ_M (MeOH) 5 mho cm^{-1} mol^{-1}; $\Delta E_{pa} = +0.82$ V.

2.4. Analytical data for the Ni(II) complex 1R,2R-(−)-CyLs Ni(II)

Calcd. for $C_{22}H_{24}N_2O_6Ni$: C, 56.16 : H, 5.15 : N, 5.96. Found: C, 56.15: H, 5.14: N, 5.94. ^{1}H NMR ($CDCl_3$): δ, 1.65–1.83 (m, 8H, $(CH_2)_4$, H'_3 to H'_6), 2.28 (s, 6H, CH_3, H_7), 2.85 (s, 6H, CH_3, H_9), 3.85 (bs, 2H, H'_1 and H'_2), 5.60 (s, 2H, CH, H_5). IR (KBr) cm^{-1} 1585 ν(H–C=N), 1260 ν(C–O). UV–VIS (nm) MeOH λ_{max} (ε), 234 (5422), 302 (5369); CD λ_{max} ($\Delta\varepsilon$) (MeOH) 346 (−4.5), 365 (−3), 510 (−1); $[\alpha]_D^t = -28.73$; Configuration (*R*); Λ_M (MeOH), 5 mho cm^{-1} mol^{-1}:Δ $E_{pa} = +0.78$ V.

Analytical data for the complexes *S*-(+)-PROS Ni(II), 1*R*,2*R*-(−)-DPHS Ni(II) and 1*S*,2*S*-(+)-CyLS Ni(II) are reported earlier [30].

3. X-ray crystallography

Cell parameters and reflection intensities for all the three compounds were measured at room temperature on an Enraf-Nonius CAD-4 X-ray diffractometer using graphite monochromatised MoK_α radiation (0.7107 Å) in the range $\theta = 2$–25° in the case of **1** and **3** and upto $\theta = 22.5°$ for **2**. Crystals of **1** were stable outside the mother liquor, whereas those of **2** and **3** had to be sealed in Lyndman glass capillary for the X-ray intensity measurements. Twenty-five high angle reflections ($\theta = 9$–12°) were used for getting the accurate cell dimensions. Three standard reflections were monitored after every 100 reflections during the entire period of data collection, which showed no significant variation, indicating the stability of the crystal. The crystal orientation, refinement of the cell parameters and intensity measurements were carried out using the program CAD-4 PC [32]. The raw intensity data were corrected for Lorentz polarization effects but not for absorption. The Lorentz polarization corrections and data reduction were carried out using NRCVAX program [33]. The structure was solved by direct method for **1** and by Patterson for **2** and **3** using the program SHELX-97 [34]. Since the number of observed reflections to parameter ratio was rather low, each molecules in the asymmetric units was refined in blocks using the program SHELX-97 [34] in all the three complexes. The full matrix least squares refinement of all non-hydrogen atoms with isotropic temperature factors was carried out till the convergence reached in all the three cases. The full matrix least squares refinement with anisotropic thermal parameters was carried out in blocks, keeping each molecule in the asymmetric unit and solvent acetonitrile molecule in separate blocks till

Table 1
Summary of crystallographic data and parameters for complexes **1**, **2** and **4**

Formula	Complex **1** $C_{38}H_{40}N_4O_{12}Ni_2$	Complex **2** $C_{66}H_{61}N_7O_{12}Ni_2$	Complex **4** $C_{66}H_{61}N_7O_{12}Ni_2$
M	862.16	1261.64	1261.64
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1	C 2	C 2
Crystal dimensions (mm)	$0.20 \times 0.16 \times 0.08$	$0.18 \times 0.14 \times 0.06$	$0.20 \times 0.12 \times 0.10$
a (Å)	7.267 (9)	24.73 (2)	24.748 (17)
b (Å)	13.508 (7)	18.642 (15)	18.764 (5)
c (Å)	18.891 (6)	19.239 (19)	17.469 (9)
α (°)	90.0	90.0	90.0
β (°)	95.17 (5)	135.42 (9)	128.92 (4)
γ (°)	90.0	90.0	90.0
U (Å^3)	1847 (3)	6226 (9)	6311 (6)
Z	2	4	4
D_c (g cm^{-3})	1.550	1.346	1.328
$F(000)$	896	2632	2632
Total reflections	3402	4065	5552
Observed reflections [$I \geq 2\sigma(I)$]	1841	2704	4054
Parameters refined	514	739	739
Final ($R1$) (on F)	0.078	0.097	0.052
Final ($wR2$) (on F^2)	0.185	0.235	0.146

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

convergence is reached. The H-atoms were fixed stereochemically using riding model using Shelex-97 or located from the difference Fourier map. The final cycles of least-squares refinements, in blocked fashion described earlier, yielded the R-value of $R1 = 0.078$ ($wR2 = 0.185$) for **1**, $R1 = 0.097$($wR2 = 0.235$) for **2** and $R1 = 0.052$ ($wR = 0.15$) for **3**, respectively. Crystallographic data for the compound is summarized in Table 1.

*3.1. Epoxidation of non-functionalised alkenes by catalysts **1–5***

Enantioselective epoxidation of styrene, 4-chlorostyrene, 4-nitrostyrene, 1-hexene, 1-octene and 1,2-dihydronaphthalene catalysed by chiral Ni(II) Schiff base complexes with NaOCl at pH = 11.3 was carried out by the following procedure: The chiral catalyst (0.02 mmol), styrene, 4-chlorostyrene, 4-nitrostyrene, 1-hexene, 1-octene, and 1,2-dihydronaphthalene (1 mmol), dissolved in 1 ml dichloromethane was stirred with NaOCl at the pH = 11.3 as oxidant at room temperature. After each interval of 1 h, an aliquot was taken from the reaction and analyzed by GLC. After completion of reaction, the reaction mixture was washed with water and dried over sodium sulfate. After 1 h, solvent was removed and product was separated by short column of silica gel using hexane : dichloromethane (9:1) as eluent. Evaluation of enantiomeric excess was done by GC on chiraldex BDA/BPH capillary column.

4. Methods

Microanalysis of the complexes was done on Perkin-Elmer model 1106. Molar conductance was measured at room temperature on a Digisun Electronic Conductivity Bridge DI-909. The IR spectra were recorded on Biorad FTS-40 spectrophotometer in KBr/nujol mull. Electronic spectra were recorded on Hewlett-Packard Diode Array spectrophotometer Model 8452A. ^{1}H NMR 200 was recorded on Bruker FX-200 NMR spectrophotometer in CD_3OD. Cyclic

voltammetry, differential pulse voltammogram were recorded with a Princeton Applied Research (PAR) instrument using tetrabutyl ammonium perchlorate as supporting electrolyte in dichloromethane. The optical rotation of the complexes in methanol was measured by polarimeter Atago, Japan. The CD spectra were recorded in methanol by Jasco Machine Model J-20 Japan. The purity of the solvents, substrates and analysis of the product was determined by GLC using Shimadzu GC 14B coupled with PC using 2-m-long, 3-mm-I.D., 4-mm-O.D. stainless steel column packed with SE 30, 5% mesh size 60–80 with FID detector. Column temperature programmed between 70°C to 150°C and injection temperature 200°C with nitrogen carrier gas flow 30 ml/min. Synthetic standards of the product were used to determine yields by comparison of peak height and area. The optical yield (*ee*'s) of the product was determined by the integration of peak area of both enantiomers on chiraldex BPH and BDA chiral capillary GC-Column.

5. Results and discussion

The synthetic strategy for **1–5** neutral square planar chiral Ni(II) Schiff base complexes involve the condensation of *S*-(+)-1,2-diaminopropane, 1*R*,2*R*-(−)-diphenyldiamino ethane, 1*S*,2*S*-(+)-diphenyldiaminoethane, 1*R*,2*R*-(−)-diaminocyclohexane, 1*S*,2*S*-(+)-diaminocyclohexane with 3-acetyl 4-hydroxy 6-methyl 2-pyrone in methanol followed by insertion of Ni(II) center Fig. 1.

The analytical data of the complexes along with their molar conductance are given in the Experimental section and are consistent with the formation of neutral square planer Ni(II) complexes.

The IR spectra of the Schiff base ligands showed a broad band near 3380 cm^{-1} due to ν(O–H). This band disappeared on complexation showing the coordination of phenolic oxygen to metal. The intense band near 1585–1590 cm^{-1} in the complexes is due to coordinated azomethine nitrogen and this band lie at higher wave number in free ligands.

The electronic spectra of the complexes recorded in methanol show high intensity charge transfer band near 300 ($\varepsilon = 6158$) nm, while the MLCT band lie near 366 ($\varepsilon = 5380$) nm.

CD spectra of the complexes **2** *1S,2S-(+)-DPHS Ni(II)* and **4** *1R,2R-(−)-CyLS Ni(II)* were recorded in methanol (Fig. 2). As both the complexes have opposite absolute configuration, hence, the complex **2** is stereospecifically coordinated to metal such that the gauche chelate ring is exclusively in λ form while the complex **4** is totally in δ form. This conformational and configurational behavior is already reported earlier [26–30].

In the ligand field region, the bands of opposite cotton effect lie near 505 (+5.7) nm and 510 (−1) nm and are assigned to d–d bands

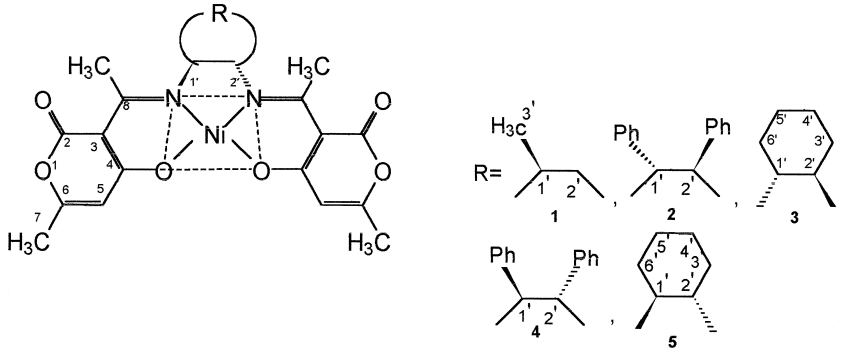


Fig. 1. Representative structures of the catalysts.

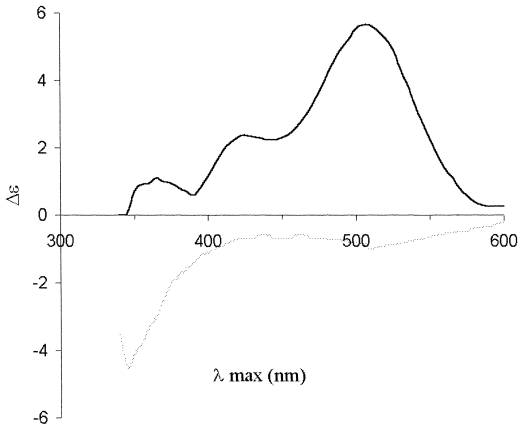


Fig. 2. CD spectra of (—) complex **2** and (- - -) complex **4** recorded in methanol.

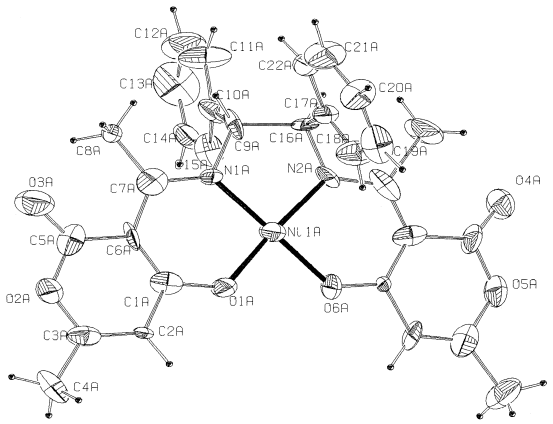


Fig. 4. Structure of complex **2** (ORTEP) with adopted numbering scheme.

and are spin-forbidden ligand bands, while the $d \rightarrow \pi^*$ band lies near 365 (−3) nm and 440 (+2.1) nm. The ligand $\pi \rightarrow \pi^*$ transition lies in higher energy region at 332 (+1.1) nm to 346 (−4.5) nm.

The cyclic voltammetry of the complexes in CH_2Cl_2 shows reversible oxidation in the range +0.78 to +0.82 V vs. SCE using 0.1 M tetra butyl ammonium perchlorate as supporting electrolyte. The values are consistent with those reported earlier [35,36].

*5.1. Structure of complexes **1**, **2** and **4***

The complexes **1**, **2** and **4** crystallized with two molecules in an asymmetric unit, which is designated as molecule A and molecule B, respectively, in each case. However, ORTEP [37] view of only one molecule with atom numbering scheme is depicted in Figs. 3–5 for the complexes **1**, **2** and **4**, respectively. The molecular geometry and conformation of molecules A and B are almost same in all cases. The absolute configuration is assigned on the basis of known chirality of the diamine used. Irrespective of the substituents on ethylenediamine collar, the geometry around Ni(II) center is slightly distorted square planar with metal ion contained well within the coordination plane having maximum

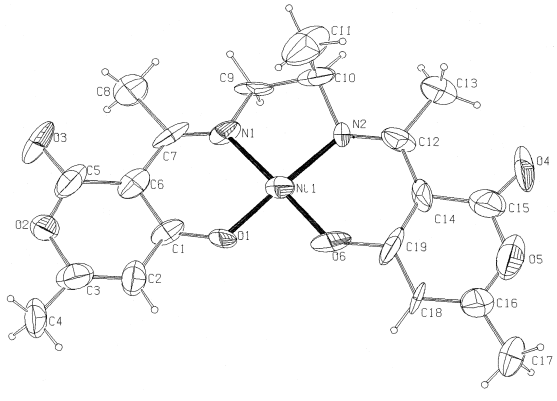


Fig. 3. Structure of complex **1** (ORTEP) with adopted numbering scheme.

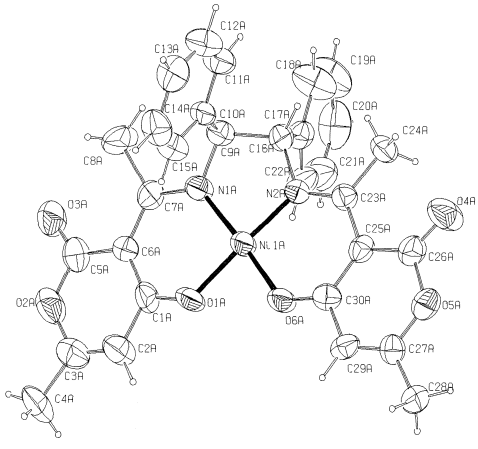


Fig. 5. Sructure of complex **4** (ORTEP) with adopted numbering scheme.

deviation of atoms ranging from ± 0.040 to 0.096 Å.

All the complexes have a "stepped" conformation with a slight twist in the ligand moiety. The twist, as indicated by the angle between the planes defined by atoms N1, Ni, N2 and O1, Ni, O6, is slightly more in the case of complex **1** (7.02–8.21°) than complex **2** and **4** (3.74–4.66°). Complexes **2** and **4** are isostructural with minor variations in the degree of non-planarity of the ligand and are not very different from complex **1**. This is evident from the dihedral angles between the mean planes defined by atoms N1, C7, C8, C6, C1, O1 and N2, C12, C13, C14, C19, O6 with respect to the plane defined by atoms N1, N2, O1 and O6 in the case of complex **1** (4.72–7.43°). While in the case of **2** and **4**, it is defined by atoms N1, C6, C7, C8, C1, O1 and by N2, C23, C24, C25, C30, O6 with respect to the plane N1, N2, O1, O6 (3.40–9.99°).

In complex **1**, "pyrone 1" and "pyrone 2" planes are bent symmetrically, making angles 8.69°, 5.03° (in molecule A) and 8.51°, 6.44° (in molecule B) with respect to the N_2O_2 plane. The twist angles between pyrone units are 12.89° and 9.24° with respect to one another in structures A and B. The substituted ethylenediamine

Table 2
Data for enantioselective epoxidation of prochiral non-functionalised olefins catalyzed by symmetrical chiral Ni(II) complexes[a]

Catalyst	Substrate	Time (h)	% Conversion[b]	*ee*[c]	Configuration
1	1-octene	24	79	34	*R*
	1-hexene	24	82	39	*R*
	styrene	24	83	37	*R*
	4-Cl styrene	24	72	42	*R*
	4-NO_2 styrene	24	49	46	*R*
	1,2 dihydronaphthalene	24	58	47	1*S*, 2*R*
2	1-octene	24	72	39	*S*
	1-hexene	24	74	44	*S*
	styrene	24	42	42	*S*
	4-Cl styrene	24	45	37	*S*
	4-NO_2 styrene	24	48	44	*S*
	1,2 dihydronaphthalene	24	45	49	1*R*, 2*S*
3	1-octene	24	70	37	*R*
	1-hexene	24	72	42	*R*
	styrene	24	40	45	*R*
	4-Cl styrene	24	45	42	*R*
	4-NO_2 styrene	24	40	47	*R*
	1,2 dihydronaphthalene	24	63	58	1*S*, 2*R*
4	1-octene	24	71	39	*R*
	1-hexene	24	73	44	*R*
	styrene	24	42	42	*R*
	4-Cl styrene	24	50	37	*R*
	4-NO_2 styrene	24	53	44	*R*
	1,2 dihydronaphthalene	24	45	50	1*S*, 2*R*
5	1-octene	24	69	39	*S*
	1-hexene	24	72	44	*S*
	styrene	24	40	42	*S*
	4-Cl styrene	24	45	37	*S*
	4-NO_2 styrene	24	43	44	*S*
	1,2 dihydronaphthalene	24	61	48	1*S*, 2*R*

[a] Reaction conditions : Substrate (1 mmol), catalyst (0.02 mmol), solvent 1.0 ml dichloromethane at pH = 11.3, NaOCl (4 ml) at room temperature.
[b] Determined by GC analysis.
[c] Determined by chiraldex BPH and BDA.

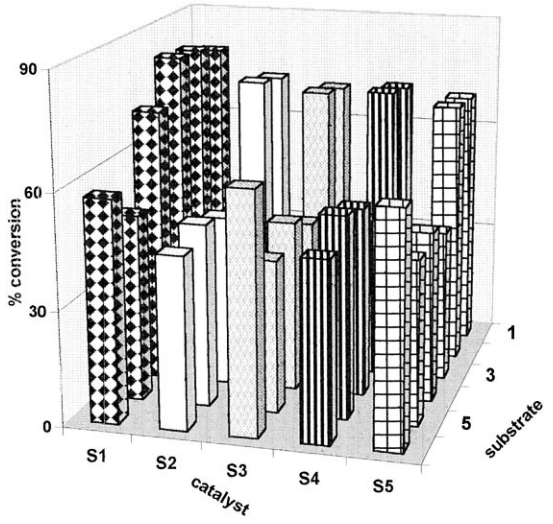


Fig. 6. 3D view of % conversion to epoxide vs. catalyst **1–5** and substrate S1–S6; S1 = 1-octene, S2 = 1-hexene, S3 = styrene, S4 = 4-chlorostyrene, S5 = 4-nitrostyrene, S6 = 1, 2 dihydronaphthalene.

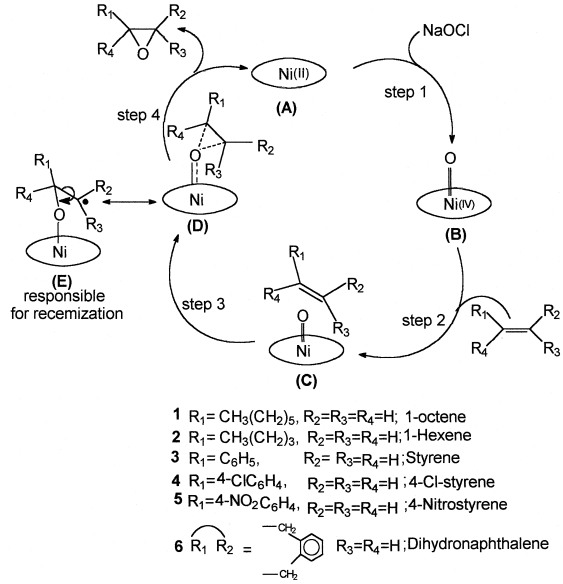
moiety is also buckled in opposite direction from the NiN1N2 plane with the displacement of C9 being −0.407 Å and C10 being 0.232 Å in A and the corresponding displacements in molecule B, which are 0.318 and −0.313 Å. This is further confirmed by the torsion angles of the substituted ethylenediamine collar moiety, which is in gauche conformation [torsion angles in A N1–C9–C10–N2 = 44.66(1)° in molecule B N1′–C9′–C10′–N2′ = 43.43(1)°], making the five-membered chelate ring in half-chair conformation. The methyl group of the substituted ethylenediamine moiety is almost perpendicular to the coordination sphere. The molecules are stabilized in the crystal lattice by strong C–H . . . O hydrogen bonding.

In the case of complexes **2** and **4**, the five-membered chelate ring, including the imino nitrogen, adopts "half chair" conformation in which phenyl rings are almost perpendicular to the coordination plane and are oriented in the opposite direction (the angle between plane Ni, O1, N1, N2 with C10–C15 = 84.92 for **2** and 87.81(2)° for **4**, and plane Ni, O1, N1, N2 with C17–C22 = 86.84 for **2** and 83.50(2)° for **4**). The low stability of the crystals in open air for **2** and **4** may be due to the loosely bound acetonitrile molecules present as solvent of crystallization in the lattice.

6. Enantioselective epoxidation of non-functionalised alkenes.

The catalysts **1–5** were screened by GLC for enantioselective epoxidation of styrene, 4-chlorostyrene, 4-nitrostyrene, 1-hexene, 1-octene, and 1,2-dihydronaphthalene using NaOCl, to give corresponding epoxide at pH = 11.3. Data regarding the enantioselectivities are given in Table 2. The catalysts **1–5** gave excellent conversion with 1-octene and 1-hexene (70–82%), while in the case of styrene and 4-chlorostyrene, this could be achieved with the catalyst **1**. Moderate to low conversion was obtained in the case of 1,2-dihydronaphthalene with all the catalysts (Fig. 6).

The enantiomeric excess for the resulting epoxide separated by short column of silica gel was evaluated by chiral capillary column (chiraldex BPH and BDA). In absence of the catalyst under similar reaction conditions, there is no reaction between oxidant and olefins, indi-



Scheme 1. A probable mechanism for catalytic reaction.

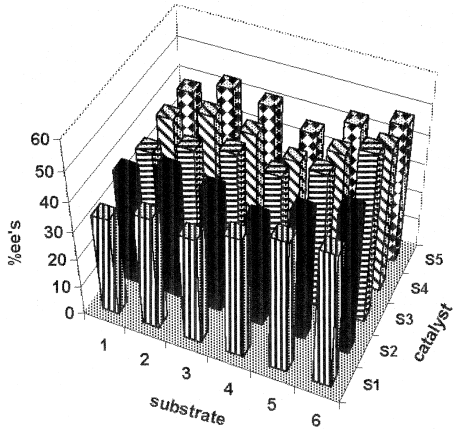


Fig. 7. 3D view of % *ee*'s to epoxide vs. catalyst **1–5** and substrate S1–S6; S1 = 1-octene, S2 = 1-hexene, S3 = styrene, S4 = 4-chlorostyrene, S5 = 4-nitrostyrene, S6 = 1,2 dihydronaphthalene.

cating indirectly the involvement of catalyst during our catalytic runs. During the catalytic reaction, the square planar Ni(II) complexes seem to extend their coordination number up to six at an intermediate stage to accommodate oxygen atom and substrate (Scheme 1). Therefore, the most plausible mechanism for the reaction would involve the formation of Ni(II) oxo intermediate at first step. Highly reactive oxo intermediate (B) reacts with the substrate to form an intermediate (C), which on rearrangement gives oxametallocyclic intermediate (D). If the intermediate (D) is to produce epoxide directly and the catalyst back, one would expect 100% enantioinduction. However, experimentally, this is not the case (enantiomeric excess 34–58%). These results can be explained on the basis of formation of another intermediate of free radical nature (E), where fast rotation of C–C bond on alkene and Ni–O bond between metal complex and olefin get precedence over collapse step responsible for the formation of product epoxide.

Further, it is interesting to point out that for all catalysts, the better enantioinduction was in the case of 1,2-dihydronaphthalene (Fig. 7), though the chemical conversions were low in comparison to the long chain alkenes. The steric consideration, rather than electronic, therefore, seems to be more dominating at intermediate stages responsible for oxygen atom transfer.

Furthermore, in order to understand the mechanism of metal-salen catalysed asymmetric epoxidation, Jacobsen et al. proposed approaches **a** and **b** (Fig. 8) on the basis of repulsive steric interactions among the substituents on the salen ligand and alkenes. While Katsuki et al. suggested pathway **c** along nitrogen–manganese bond axis based on the repulsive π-electron interactions between ligand and substrate π-electrons. However, recently, Houk et al. gave a powerful unified hypothesis and suggested pathway **e** with twisted salen geome-

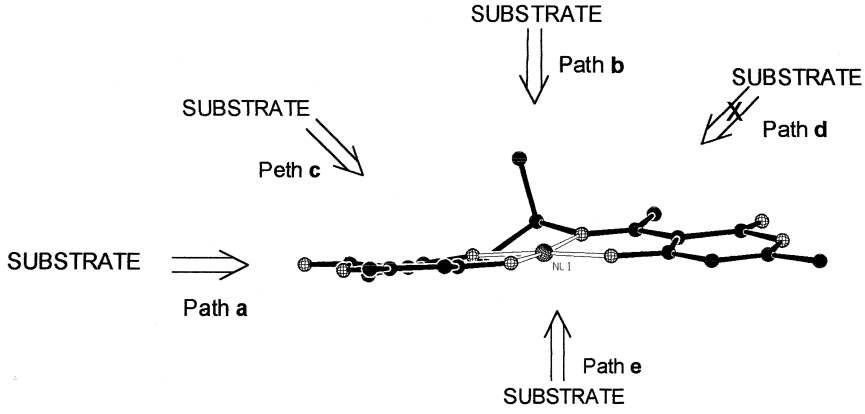


Fig. 8. Different mode of approach of the substrate towards the catalyst-**1**.

try, where the enantioselection is provided by the chiral environment set up by transmission through Salen ligand of the effect of the stereogenic carbon [38].

In the present case, the Ni(II) salen complex is conformationally very similar to that of Mn(III) salen complex, although the steric requirements are not sufficient in order to define the specific pathway except for the methyl group on azomethine carbon offering some resistance on path **d** (Fig. 8). This can be one of the reasons for these complexes not showing desirable enantioselection besides the factors explained in Scheme 1.

7. Conclusions

Square planar chiral Ni(II) Schiff base complexes derived from *S*-(+)-1,2-diaminopropane, 1*R*,2*R*-(−)-diphenyldiamino ethane, 1*S*,2*S*-(+)-diphenyldiamino ethane, 1*R*,2*R*-(−)-diamino cyclohexane, 1*S*,2*S*-(+)-diamino cyclohexane, with 3-acetyl 4-hydroxy 6-methyl 2-pyrone were investigated as catalysts for the enantioselective epoxidation of 1-hexene, 1-octene, styrene, 4-chloro-, 4-nitrostyrene and 1,2-dihydronaphthalene in the present study in the presence of NaOCl as oxidant. Excellent conversions were obtained with long chain alkenes than other non-functionalised alkene. Enantiomeric excess of the epoxide formed was better in the case of 1,2-dihydronaphthalene, which infers that the steric consideration rather than electronic; therefore, it seems to be more dominating at intermediate stage responsible for oxygen atom transfer. Hence, it would be desirable to introduce more steric constrains on the pyrone rings in order to achieve better enantioselection.

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