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Crystal structures and catalytic performance of three new methoxy substituted salen type nickel(II) Schiff base complexes derived from *meso*-1,2-diphenyl-1,2-ethylenediamine



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HIGHLIGHTS

- Three new Ni(II) Schiff base complexes were synthesized.
- Crystal structures of these complexes were determined.
- Physico-chemical properties were correlated with position of substituents.
- Epoxidation of cyclooctene with these catalysts was studied.
- Solvent free conditions gave enhanced catalytic activity and epoxide selectivity.

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1. Introduction

The steric and electronic properties of salen type Schiff base ligands could be fine tuned by the introduction of appropriate substituents on the phenyl rings of their salicylaldehyde moieties [1-10] and many metal complexes of such ligands have been synthesized. These metal complexes have found versatile applications in a wide range of areas such as catalysis, biochemistry,

G R A P H I C A L A B S T R A C T

Catalytic epoxidation of cyclooctene was studied with three new structurally characterized salen type Ni(II) Schiff base complexes and enhanced catalytic activity and epoxide selectivity was achieved in solvent free conditions.



ABSTRACT

Three new nickel(II) complexes of a series of methoxy substituted salen type Schiff base ligands were synthesized and characterized by IR, UV–Vis and ¹H NMR spectroscopy and elemental analysis. The ligands were synthesized from the condensation of *meso*-1,2-diphenyl-1,2-ethylenediamine with *n*-methoxysalicylaldehyde (n = 3, 4 and 5). Crystal structures of these complexes were determined. Electrochemical behavior of the complexes was studied by means of cyclic voltammetry in DMSO solutions. Catalytic performance of the complexes was studied in the epoxidation of cyclooctene using *tert*-butyl-hydroperoxide (TBHP) as oxidant under various conditions to find the optimum operating parameters. Low catalytic activity with moderate epoxide selectivity was observed in in-solvent conditions but in the solvent-free conditions, enhanced catalytic activity with high epoxide selectivity was achieved.

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electrochemistry, and spectroscopy [11–19]. In the case of catalysis, knowledge of the role played by such structural and electronic effects to control the electrochemistry of such complexes has been proven to be critical [20]. Schiff base complexes have been used as catalysts in different industrially and laboratory important reactions such as oxidation, reduction and polymerization [21–27]. Epoxidation of olefins is among the most important reactions in organic chemistry since it provides an expedient and effective way to produce several invaluable new compounds. Various metal complexes of salen type Schiff base ligands have been studied in such reactions [28]. Nickel(II) complexes have also been used as catalyst for epoxidation of olefins [23]. In continuation of our previous

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studies on the preparation of Schiff base ligands with different electronic and/or steric properties and metal complexes, and the study of their potential application in epoxidation of alkenes, herein we report the synthesis and characterization of three new salen type Schiff base complexes of Ni(II). The ligands were synthesized from the condensation of meso-1,2-diphenyl-1,2-ethylenediamine with *n*-methoxysalicylaldehyde (n = 3, 4 and 5). The nickel central atom was chosen to compare the effect of different central metal atoms in epoxidation studies since we have previously reported the results of the epoxidation of cyclooctene with similar ligands but different metal ions, namely VO(IV) and Cu(II) [2,13,29]. The methoxy substituent is interesting in the field of Schiff base complexes since different isomers of methoxysalicylaldehyde are commercially available and hence, it readily provides the opportunity of studying the positional effects of a single substituent. The new complexes were characterized by different spectroscopic and analytical methods. The positional effects of the methoxy substituents were studied and discussed. Crystal structures of these three complexes have also been determined. Electrochemical properties of these complexes were studied by cyclic voltammetry. Catalytic performance of these complexes was examined in the epoxidation of cyclooctene under various conditions. Several factors such as solvent type and amount, reaction temperature, time, catalyst amount and oxidant to substrate ratio were optimized. Solventfree epoxidation of cyclooctene with these complexes has also been studied. It was found that under optimized in-solvent conditions, these complexes showed low catalytic performance with moderate epoxide selectivity which was similar to previously reported analogous [23,25] but under solvent-free conditions, enhanced catalytic activity and high epoxide selectivity was achieved.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from commercial sources and were used as received. Meso-1,2-diphenyl-1,2-ethylenediamine [30] and the H_2L^x (x = 1-3) ligands were synthesized as described elsewhere [2]. Melting points were obtained on a thermoscientific 9100 apparatus. Elemental analyses were performed using a Perkin-Elmer 2400II CHNS-O elemental analyzer. ¹H NMR spectra were recorded on a 500 MHz Bruker FT-NMR spectrometer using $CDCl_3$ as solvent; chemical shifts (δ) are given in ppm. IR spectra were obtained as KBr plates using a Bruker FT-IR instrument. UV-Vis spectra were obtained on a Shimadzu UV-1650PC spectrophotometer in DMSO solutions. A Metrohm 757 VA computerace instrument was employed to obtain cyclic voltammograms. X-ray data were collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using Mo/Ka radiation $(\lambda = 0.71073 \text{ Å})$. Gas chromatography (GC) analyses were carried out on a GC-17A Shimadzu instrument.

2.2. Synthesis of the complexes

2.2.1. Synthesis of NiL¹·CH₃CN

The complexes were synthesized following a similar procedure as described elsewhere for the un-substituted parent complex (Scheme 1) [31]. In a typical experiment, a solution of 0.48 g (1 mmol) of H₂L in 30 mL of ethanol was placed in a round bottom two-necked flask equipped with a magnetic stirrer, a dropping funnel and a condenser. This solution was heated to about 60 °C while being vigorously stirred and then a solution of 0.25 g Ni(OAc)₂·4H₂. O (1 mmol) in 30 mL of ethanol was added drop-wise from the dropping funnel. The color of the solution gradually turned red. The reaction mixture was heated for 3 h and then it was left undisturbed overnight. The resulting precipitate was filtered off, washed with 10 mL of ethanol and air dried. Recrystallization from acetonitrile yielded single crystals of the target compound suitable for X-ray crystallography. Yield: 0.46 g, 80%. ¹H NMR (δ , ppm): 7.26 (2H, s, **HC=N**); 7.41–6.23 (m, 16H, **H**_{Ar}); 4.98 (s, 2H, C**H**Ph); 3.77 (s, 6H, OC**H**₃). Selected IR (KBr, cm⁻¹); 1604 (v_{C=N}); 432 (v_{Ni-N}); 543 (v_{Ni-O}). UV–Vis in DMSO, λ nm; (ε M⁻¹ cm⁻¹): 261 (53,100), 345 (7500), 414 (4800), 562 (140). Anal. Calcd. for C₃₂H₂₉N₃NiO₄; C: 66.40, H: 5.01, N: 7.26, found; C: 66.32, H: 5.05, N: 7.33.

2.2.2. Synthesis of NiL^2

This complex was prepared following a similar procedure as described for NiL¹ except H_2L^2 was used instead of H_2L^1 . Recrystallization from acetonitrile yielded single crystals of the target compound suitable for X-ray crystallography. Yield: 0.48 g, 85%. ¹H NMR (δ , ppm): 7.29 (2H, s, **H**C=N); 7.38–6.08 (m, 16H, **H**_{Ar}); 4.83 (s, 2H, **CH**Ph); 3.73 (s, 6H, OC**H**₃). Selected IR (KBr, cm⁻¹); 1605 ($v_{C=N}$); 455 (v_{Ni-N}); 532 (v_{Ni-O}). UV–Vis in DMSO, λ nm; (ε M⁻¹ cm⁻¹): 268 (52,200), 313 (13,300), 400 (7500), 543 (440). Anal. Calcd. for C₃₀H₂₆N₂NiO₄; C: 67.01, H: 4.84, N: 5.21, found; C: 67.12, H: 4.75, N: 5.20.

2.2.3. Synthesis of NiL³·CH₃CN

This complex was prepared following a similar procedure as described for NiL¹ except H₂L³ was used instead of H₂L¹. Recrystallization from acetonitrile yielded single crystals of the target compound suitable for X-ray crystallography. Yield: 0.49 g, 87%. ¹H NMR (δ , ppm): 7.27 (2H, s, **H**C=N); 7.43–6.04 (m, 16H, **H**_{Ar}); 5.06 (s, 2H, **CH**Ph); 3.58 (s, 6H, OC**H**₃). Selected IR (KBr, cm⁻¹); 1605 (v_C=N); 462 (v_{Ni}–N); 547 (v_{Ni}–O). UV–Vis in DMSO, λ nm; (ε M⁻¹ cm⁻¹): 261 (51,800), 336 (9300), 440 (8700), 563 (280). Anal. Calcd. for C₃₂H₂₉N₃NiO₄; C: 66.40, H: 5.01, N: 7.26, found; C: 66.44, H: 5.07, N: 7.21.

2.3. X-ray crystallography

Diffraction data were collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using Mo/K α radiation (λ = 0.71073 Å). Data collections, cell refinements, data reductions and absorption corrections were performed using multi-scan methods with Bruker software [32]. The structures were solved by direct methods using SIR2004 [33]. The non-hydrogen atoms were refined anisotropically by the full matrix least squares method on F^2 using SHELXL [34]. All the hydrogen (H) atoms were placed at the calculated positions and constrained to ride on their parent atoms. Details concerning collections and analyses are reported in Table 1.

2.4. Cyclic voltammetry

A Metrohm 757 VA computerace instrument was employed to obtain cyclic voltammograms in DMSO solutions at room temperature (25 °C) under nitrogen atmosphere using 0.1 M tetra-noctylammonium bromide (TOAB) as supporting electrolyte. A platinum working electrode, a platinum auxiliary electrode and an Ag/AgCl reference electrode was used to obtain cyclic voltammograms.

2.5. General oxidation reactions

2.5.1. In-solvent oxidation of cyclooctene

These nickel(II) Schiff-base complexes were used as catalysts for oxidation of cyclooctene using TBHP as oxidant in different solvents and various reaction conditions. The progress of the reaction was monitored by GC in 30 min intervals. The retention



Scheme 1. Synthetic procedure for the ligands and complexes.

times for the starting materials and the products were determined by comparison with authentic samples. In the absence of the complexes, no or very little oxidation products were observed. Oxidation of cyclooctene gave cycloocteneoxide as the major product of the reaction. The conversion percentages (%) and the TONs were calculated by Eqs. (1) and (2), in which C_i and C_f are initial and final concentration of the substrate, respectively, and [Q] is the concentration of the catalyst. In a typical experiment, 10 µmol of NiL¹ catalyst was dissolved in 10 mL of freshly distilled acetonitrile and then 15 mmol of cyclooctene

Table 1

Crystal data, data collection and structure refinement parameters for NiL¹⁻³.

Compound	NiL ¹	NiL ²	NiL ³
Empirical formula	$C_{32}H_{29}N_3NiO_4$	$C_{30}H_{26}N_2NiO_4$	$C_{32}H_{29}N_3NiO_4$
Formula weight	578.29	537.24	578.29
T (K)	298(2)	298(2)	298(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	P-1	P2 ₁ /n
Unit cell dimensions (Å, °)			
a (Å)	15.5622(5)	10.8302(2)	11.8708(2)
b (Å)	10.7402(4)	10.8986(2)	18.7418(4)
<i>c</i> (Å)	17.3074(6)	12.5082(3)	12.6293(3)
α _. °	90.00	109.6430(10)	90.00
$\beta^{\circ}_{.}$	105.009(2)	100.1540(10)	98.9600(10)
γ°.	90.00	110.2130(10)	90.00
Volume (Å ³), Z	2794.09(17), 4	1231.34(4)	2775.48(10)
Calculated density (g cm ⁻³)	1.375	1.449	1.384
Absorption coefficient (mm ⁻¹)	0.730	0.828	0.741
F(000)	1208	560	1208
θ Range for data collection (°)	2.25-26.00	2.30-28.00	2.19-28.00
Limiting indices	$-19 \leqslant h \leqslant 19$	$-14 \leqslant h \leqslant 14$	$-15 \leqslant h \leqslant 15$
	$-13 \leqslant k \leqslant 13$	$-14 \leqslant k \leqslant 14$	$-24 \leqslant k \leqslant 24$
	$-21 \leqslant l \leqslant 21$	$-16 \leqslant l \leqslant 16$	$-16 \leqslant l \leqslant 16$
Data/restraints /parameters	5480/0/362	5945/0/336	6686/0/364
Total reflections	89,468	140,952	50,821
Unique reflections (R_{int})	$5480 [R_{(int)} = 0.0548]$	5945 $[R_{(int)} = 0.0260]$	6686 $[R_{(int)} = 0.0806]$
Completeness	99.9% (θ = 26.00)	99.8% (<i>θ</i> = 28.00)	99.7% (θ = 28.00)
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F ²	Full-matrix least squares on F^2
Goodness-of-fit on F^2	1.040	1.089	1.064
Final <i>R</i> index $[I > 2\sigma(I)]$	$R_1 = 0.0457, WR_2 = 0.1434$	$R_1 = 0.0251, WR_2 = 0.0768$	$R_1 = 0.0350, wR_2 = 0.0962$
K index [all data]	$K_1 = 0.0622, WR_2 = 0.1663$	$R_1 = 0.0277, WR_2 = 0.0811$	$R_1 = 0.0479, WR_2 = 0.1048$
Largest difference peak and hole ($e A^{-3}$)	0.549 and -0.349	0.281 and -0.348	0.536 and -0.336

and 30 mmol of TBHP were added. The reaction mixture was refluxed while being stirred and the reaction progress was monitored at 30 min intervals.

$$Conversion (\%) = [(C_i - C_f) \times 100]/C_i$$
(1)

Turn over number (TON) = $[(\% \text{ Conversion}) \times C_i]/[Q]$ (2)

2.5.2. Solvent free oxidations

Typically, a mixture of $15 \,\mu$ mol of the catalysts, $15 \,\mu$ mol of cyclooctene, and $45 \,\mu$ mol of TBHP were refluxed and the progress of the reaction was monitored every 30 min by GC.

3. Results and discussions

3.1. Spectroscopic characterization of the complexes

In the IR spectra of the Schiff base ligands [2] the presence of an intense band at around 1620 cm⁻¹ has been assigned to the stretching vibrations of the azomethine groups. This band is present in the IR spectra of the complexes and has shifted to lower wave numbers upon coordination. This shift is indicative of the coordination of the ligands through their iminic nitrogen atoms. Another important observation for the complexes is the omission of the bands at around 3400 cm⁻¹ which were present in the ligands. These bands were assigned to the stretching vibrations of the O-H groups in the ligands which are absent in the IR spectra of the complexes. This confirms that the ligands have acted as dianionic L^{2-} ligands. Indeed, the ligands have provided an N_2O_2 coordination sphere around the Ni(II) central atoms and the complexes are therefore neutral. Another conclusive evidence for the formation of Ni-N and Ni-O bonds is also shown by the appearance of new bands at around 450 and 550 nm which could be assigned to the Ni-N and Ni-O stretching vibrations, respectively [35]. In the ¹H NMR spectra of the ligands, the presence of signals at above 10 ppm has been assigned to the phenolic protons of the salicylaldehyde moieties [2]. These signals are absent in the 1 H NMR spectra of the diamagnetic Ni(II) complexes and this observation further confirms the L^{2-} character of the ligands in complexes. The ¹H NMR spectra of the ligands have shown sharp singlet signals (s) at around 8 ppm due to the azomethine protons. These signals are present in the ¹H NMR spectra of the complexes but have shifted up-field to about 7.25 ppm which is indicative of the incorporation of the azomethine nitrogen atoms in coordination. Other signals which have appeared as multiplets (m) in the aromatic region at around 7.5–6.0 ppm are assignable to the aromatic protons. Aliphatic protons of the diamine part of the Schiff base ligands have also been observed at around 5 ppm. The OCH₃ protons are also observed at around 3.7 ppm with appropriate signal intensity. The electronic absorption spectra of the complexes have shown very similar features which are representative of the UV-Vis spectra of Ni(II) complexes in a square planar pocket of a tetradentate Schiff base ligand. In the UV-Vis spectra of their parent ligands, two intense bands at around 260 and 300 nm had been assigned to the $\pi \to \pi^*$ transitions in the phenyl rings and azomethine groups, respectively [31]. These peaks are present in the electronic absorption spectra of the complexes. The former peaks are observed without any significant shift but the latter ones are considerably red shifted. The red shift of the latter bands $(\pi \rightarrow \pi^*)$ transitions of the C=N groups) is also indicative of the coordination of the nitrogen atoms of the azomethine groups to the metal center. The electronic absorption spectra of the complexes showed bands at around 420 ± 20 nm with a shoulder at higher wavelengths which could be assigned to the MLCT comprised of a transition between the metal centered HOMO to the ligand centered LUMO ($C=N(\pi^*)$) [36]. The weak bands at about 545 nm are also assignable to the *d*-*d* transitions. Fig. 1 shows the UV–Vis spectra of the three complexes. An interesting feature which is evident from this figure and the comparison of the UV–Vis data is the blue shift of the data for NiL² compared to both NiL¹ and NiL³. In the NiL², the methoxy substituents are in the para positions of the iminic groups and hence, are able to denote the electron density to the π^* of the C=N. This increased electron density has caused the energy of the MLCT transition shift to higher energies (i.e. lower wave lengths). The π to π^* transition of the azomethine groups and the *d*-*d* transition are also affected by this electron donation and show similar features.

3.2. Description of the crystal structures

ORTEP drawings of NiL¹, NiL² and NiL³ are shown in Figs. 2–4, respectively with common atom numbering schemes. A summary of the crystallographic data for the three complexes is collected in Table 1 and the selected bond lengths and bond angles are listed in Table 2. The neutral species of NiL^{1-3} contain one Ni(II) ion ligated to one L²⁻ ligand and have similar structures. As it could be seen from Table 2, in the crystal structures of NiL complexes, both of the N(1)-Ni-N(2) and O(1)-Ni-O(2) bond angels deviate from and are smaller than the ideal 90° whereas the cisoid N-Ni-O angels are both larger than 90°. The transoid N—Ni—O angels are also both smaller than 180° causing a slightly distorted square planar geometry around the metal centers which are similar to previously reported analogous [25,37,38]. The angle between the two NCCCO chelating ring system for NiL¹, NiL² and NiL³ complexes are $18.39(3)^\circ$, $14.18(4)^\circ$ and $6.45(3)^\circ$, respectively which indicates a tetrahedral distortion from square planar geometry. The metal atoms are well located at the centers of the N₂O₂ coordination spheres with the average Ni–N bond distance of 1.839 Å compared to the average Ni-O bond distance of 1.834 Å for NiL¹, 1.849 Å compared to 1.841 Å for NiL² and 1.851 Å compared to 1.841 Å for NiL³. All the bond distances and bond angels are similar to previously reported analogous [37,38].

3.3. Electrochemistry

Cyclic voltammetric electrochemical studies of the complexes were performed in the potential range of 0 to -2 volts. The cyclic voltammograms were obtained in DMSO solutions at room temperature (298 K) under nitrogen atmosphere using 0.1 M tetra-n-octylammonium bromide (TOAB) as supporting electrolyte. A platinum working electrode, a platinum auxiliary electrode and



Fig. 1. UV–Vis spectra of the 10^{-5} M DMSO solutions of the complexes. The inset shows the *d*–*d* transition region with 10^{-3} M solutions.



Fig. 2. ORTEP representation of NiL¹. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Solvent of crystallization (CH₃CN) is omitted for clarity.



Fig. 3. ORTEP representation of NiL². Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.



Fig. 4. ORTEP representation of NiL³. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Solvent of crystallization (CH₃CN) is omitted for clarity.

an Ag/AgCl reference electrode was used to obtain cyclic voltammograms. The electrochemical data for the complexes are

Table 2								
Selected	bond	lengths	and	angels	for	NiL ¹⁻³	comple	exes.

Complex	Selected bond lengths (Å)		Selected bond angels (°)		
NiL ¹	Ni(1)-O(1) Ni(1)-O(2) Ni(1)-N(1) Ni(1)-N(2)	1.835(2) 1.832(2) 1.832(2) 1.846(2)	$\begin{array}{c} O(1)-Ni(1)-O(2)\\ O(1)-Ni(1)-N(1)\\ O(2)-Ni(1)-N(1)\\ O(1)-Ni(1)-N(2)\\ O(2)-Ni(1)-N(2)\\ N(1)-Ni(1)-N(2) \end{array}$	84.23(9) 94.73(10) 175.30(10) 175.73(10) 94.76(10) 86.61(11)	
NiL ²	Ni(1)-O(1) Ni(1)-O(2) Ni(1)-N(1) Ni(1)-N(2)	1.8373(9) 1.8460(9) 1.8549(10) 1.8443(11)	$\begin{array}{c} 0(1)-Ni(1)-O(2)\\ 0(1)-Ni(1)-N(1)\\ 0(2)-Ni(1)-N(1)\\ 0(1)-Ni(1)-N(2)\\ 0(2)-Ni(1)-N(2)\\ N(1)-Ni(1)-N(2) \end{array}$	84.36(4) 95.41(4) 172.78(4) 172.51(4) 94.89(4) 86.27(5)	
NiL ³	Ni(1)-O(1) Ni(1)-O(2) Ni(1)-N(1) Ni(1)-N(2)	1.8393(11) 1.8430(11) 1.8574(12) 1.8468(13)	$\begin{array}{c} 0(1)-Ni(1)-O(2)\\ 0(1)-Ni(1)-N(1)\\ 0(2)-Ni(1)-N(1)\\ 0(1)-Ni(1)-N(2)\\ 0(2)-Ni(1)-N(2)\\ N(1)-Ni(1)-N(2) \end{array}$	84.80(5) 95.02(5) 176.39(5) 175.98(6) 94.36(5) 86.06(6)	

Table 3
Redox potential data for 10^{-3} mol L ⁻¹ solutions of NiL ^x (x = 1-3) complexes in DMSO
solutions containing 0.1 mol L ⁻¹ TOAB and scan rate 100 mV s ⁻¹ . Data are in Volts.

Complex	E _{pa}	Epc	E ⁰	ΔE
NiL ¹	-1.44	-1.52	-1.48	0.08
NiL ²	-1.54	-1.60	-1.57	0.06
NiL ³	-1.55	-1.51	-1.53	0.04

collected in Table 3 and the cyclic voltammograms are shown in Fig. 5. The ligands were electro-inactive in the studied potential range but the blank solution containing TOAB in DMSO showed a reversible wave at -735 mV. In the cyclic voltammogram of the NiL^x complexes, a quasi-reversible (for NiL¹) or a reversible (for NiL² and NiL³) reduction wave was observed which were easily assigned to the metal centered Ni^{II}/Ni^I reduction processes. These observations are in good agreement with previously reported analogous [39,40]. The proposed potential of the methoxy substituents in the para position of the C=N groups, which was developed in the description of the UV-Vis spectra, could also help discuss the positional effects of the substituents on the redox properties of the complexes. As it could be seen from Fig. 5 and Table 3, the E^0 value for NiL² is the most negative one. Actually, the increased electron density on the metal center has resulted in the more difficult Ni^{II}/ Ni¹ reduction and more negative E⁰ values.

3.4. Catalysis

3.4.1. In-solvent catalytic oxidation of cyclooctene

The catalytic oxidation of cyclooctene with these new catalysts gave three products which were identified by comparison of their retention times with those of the authentic samples (Scheme 2). Various conditions were optimized including reaction temperature and time, solvent type and amount, catalyst type, amount of the catalyst and oxidant to substrate ratio. All the reactions were performed in triplicates to check the reproducibility of the data. Reported results are given as the average. In a typical experiment, 10 µmol of NiL² were dissolved in 10 mL of freshly distilled acetonitrile and then 15 mmol of cyclooctene and 30 mmol of TBHP were added. The reaction mixture was refluxed while being stirred and the reaction progress was monitored at 30 min intervals up to 30 h. After 24 h no considerable change was observed in the conversion percentages and 24 h was chosen as the optimized reaction time. The catalytic reaction was performed in five different solvents namely dichloromethane, chloroform, methanol, ethanol



Fig. 5. Cyclic voltammograms of NiL^x complexes in DMSO at 298 K and 100 mV s⁻¹ scan rate.



Scheme 2. Products of the catalytic oxidation of cyclooctene with the NiL^x catalysts.

Table 4 The results of the oxidation of cyclooctene with TBHP in the presence of NiL^x complexes in the optimized reaction conditions.

Complex	Conversion (%)	Turn over number (TON)	Selectivity		
				OH	°
NiL ¹	14	140	51	15	34
NiL ²	22	220	54	19	27
NiL ³	18	180	56	29	15

Table 5

The results of the solvent-free oxidation of cyclooctene with TBHP in the presence of NiL^x complexes.

Complex	Conversion (%)	Turn over number (TON)	Selectivity		
				ОН	O
NiL ¹ NiL ² NiL ³	33 52 43	330 520 430	74 73 77	14 12 10	12 15 13

and acetonitrile with NiL² to find the optimized solvent. It was found that acetonitrile was the optimized solvent with conversion percent of about 20% while the other solvents gave less than 10% of the products and then, acetonitrile was chosen as the reaction solvent to study the effect of other parameters. The substrate to oxidant ratio (1:2), catalyst amounts (10 µmol) and the reaction temperature (80 °C) were also optimized. Then the effect of the catalyst type was studied using the above mentioned reaction conditions. Table 4 shows the results of the optimization of the catalyst type and as it could be seen, NiL² was the most efficient catalyst in this process with the highest conversion.

As it could be seen from Table 4, NiL² (4-OMe derivative) was the most effective catalyst with the highest conversion percent. Comparison of these data with the electrochemical data in Table 3 shows another insight into the observed trend, i.e. a good correlation could be found with the E^0 values of the Ni^{II/I} reduction potential with the catalytic performance of the complexes. Indeed, NiL² with the most negative E^0 value was the most efficient oxidation

Table 6

Epoxidation of cyclooctene catalyzed by a variety of nickel based catalysts.

Catalyst	Oxidant	Conversion (%)	% Yield of epoxide	Ref.
NiL ² (in acetonitrile)	TBHP	22	54	This work
NiL ² (solvent free)	TBHP	52	73	This work
bis(Salicylaldimine)nickel(II)	TBHP	33	33	[25]
$Ni(NO_3)_2 \cdot 6H_2O$	TBHP	13	13	[25]
Nickel(III)-salen	H_2O_2	25	36	[41]
Ni(salen)·Y	NaOCl	10	10	[40]
Ni(salen)·Y	KHSO ₅	8.5	8.5	[40]

catalyst while NiL¹ with the least negative E^0 is the least active one. The results of cyclooctene epoxidation with these catalysts are comparable to previously reported analogous [23,39].

3.4.2. Solvent-free catalytic oxidation of cyclooctene

Our in-solvent catalytic studies showed that as the amount of the solvent was decreased, the catalytic performance of these Ni complexes was increased. This observation led us to study the solvent free epoxidation of the substrate and similar catalytic experiments were performed with NiL^x catalysts in the solvent-free conditions. To compare the results, we used the optimized catalytic conditions mentioned for in-solvent oxidation reactions. Similar trend was observed and NiL² was found again to be the most efficient oxidation catalyst with highest conversion percentage and NiL¹ was the least active one. Considering the epoxide selectivity, NiL³ was again the most selective catalyst. Besides, increased catalytic activity and higher epoxide selectivity was observed for all of the complexes in our solvent-free studies compared to in-solvent conditions (Table 5). Table 6 also compares the results of the epoxidation of cyclooctene with different nickel based catalysts. As it could be seen from this table, our in-solvent results are similar to previously reported complexes but we were able to achieve higher conversion percentages and epoxide selectivity in solvent free conditions.

4. Conclusion

Three new Ni(II) complexes of methoxy substituted salen type Schiff base ligands derived from meso-1,2-diphenyl-1,2-ethylenediamine were synthesized and characterized. Crystal structures of these complexes were obtained. Catalytic performance of the new complexes was studies in the epoxidation of cyclooctene with TBHP both in in-solvent and solvent-free conditions under various conditions to find the optimized epoxidation conditions. The central metal atom is one of the most important factors in catalytic reactions. A literature survey showed that usually high-valent metal complexes of e.g. VO(IV), Mo(IV), W(IV), etc. [14,42], are highly active in epoxidation of olefins but some lower valent metal complexes are also reported to show high epoxidation conversions [43]. Hence and in continuation of our previous studies, we decided to prepare Schiff base complexes of similar ligands with different metal ions to study the effect of central atom. Indeed, the oxidation number is not the only factor and more studies are necessary to find all important parameters. Our finding showed that the Ni(II) complexes were less active than VO(IV) and Cu(II). In this study, our complexes showed low catalytic performance in the epoxidation of cyclooctene in studied solvents but in the solvent-free conditions, we were able to achieve higher catalytic activities with high epoxide selectivity.

Appendix A. Supplementary material

CCDC 941407, 941406 and 941408 contains the supplementary crystallographic data for NiL¹⁻³, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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