

Olefin epoxidation catalyzed by novel nickel(II)-complexes containing tridentate Schiff-base ligands

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Novel Schiff base complexes of nickel(II), $[\text{NiL}_1(\text{H}_2\text{O})]$ (**1**) [$\text{H}_2\text{L}_1 = \text{N}$ -(2-hydroxyphenyl)salicylaldehyde imine], $[\text{NiL}_2(\text{H}_2\text{O})]$ (**2**) [$\text{Happ} = \text{N}$ -(2-hydroxyphenyl)pyridine-2-carboxaldimine], $[\text{NiL}_3(\text{H}_2\text{O})]$ (**3**) [N -(2-carboxyphenyl)salicylaldehyde imine] and $[\text{NiL}_4(\text{H}_2\text{O})]$ (**4**) [N -(2-carboxyphenyl)pyridine-2-carboxaldimine] have been prepared and characterized by physico-chemical analysis. Complexes **1-4** are found to be active in catalyzing hydrocarbon oxidation in the presence of single oxygen atom donors. Efficiency of NiL complex towards catalysing epoxidation of olefins in the presence of various oxidants viz., NaOCl, KHSO₅, H₂O₂, pyridine N-oxide (PyO), *t*-BuOOH, etc., has been examined and it is found that the complexes **1-4** can effectively catalyze the epoxidation of olefins in the presence of NaOCl and KHSO₅.

The present work stems from our continued interests in developing homogeneous catalytic systems using non-porphyrinic transition metal complexes for selective oxo-functionalization of organic substrates¹⁻⁷ with cheap and easy-to-handle oxidants. Nickel(II)-schiff base/macrocyelic complexes are of interest with regard to their easy synthesis and ability to catalyze hydrocarbon oxidation using various single oxygen atom donors⁸⁻¹⁰. However, there exists no liaison of catalytic efficiency of nickel complexes with the nature of coordinating ligands versus terminal oxidants. For example, $[\text{Ni}(\text{salen})]$ (a square planer complex) catalyses of olefin epoxidation exclusively in the presence of NaOCl⁷, while square planer $[\text{Ni}(\text{cyclam})]^{2+}$ found active in this regard only in the presence of PhIO⁵. Further, the Ni^{II}(TPP) (TPP = tetraphenylporphyrin) complex is completely inactive towards epoxidation in the presence of either of NaOCl or PhIO. Therefore, it is felt sensible to examine the catalytic efficacy of nickel complexes on the basis of oxo-transfer from various oxidants to olefins. In the present investigation, we have used a new family of Nickel(II)-complexes (**1-4**) containing tridentate Schiff base ligands for examining the efficacy of different oxidants for catalytic epoxidation

of olefins. We report herein, synthesis and characterization of complexes **1-4** and catalysis of olefin epoxidation with various oxidants, viz., NaOCl, KHSO₅, PyO (pyridine N-oxide), H₂O₂, *t*-BuOOH employing complexes **1-4** as catalysts.

Experimental

Syntheses of catalyst complexes

Synthesis of aquo[N-(2-hydroxyphenyl)salicylaldehyde iminato]nickel(II), $[\text{Ni}(\text{amp})(\text{H}_2\text{O})].\text{H}_2\text{O}$ (**1**)

The H_2L_1 (H_2amp) ligand was prepared by interacting 2-aminophenol and salicylaldehyde in a stoichiometric ratio¹¹. The $[\text{NiL}_1(\text{H}_2\text{O})]$ complex (**1**) was prepared by interacting NiCl₂ with Schiff base ligand (H_2L_1) in a stoichiometric ratio⁴. To a methanolic solution (30 ml) of H_2L_1 (0.01 mol, 2.13 g) containing KOH (0.02 mol, 1.12 g) was added NiCl₂.6H₂O (0.01 mol, 2.377 g). The orange-red colour of the resultant mixture changed to yellow. The reaction mixture was stirred at room temperature in air for 1 h and the yellow solid precipitated was filtered, washed thoroughly with methanol and water, and dried over fused CaCl₂ (yield: 80%). [Anal: Found C, 54.13; H, 3.94; N, 4.73%; NiC₁₁H₁₀NO₃ requires C, 54.22; H, 3.82; N, 4.86%]; UV-vis in H₂O: 407 nm ($\epsilon_{\text{max}} = 2380$), 287 nm ($\epsilon_{\text{max}} = 1919$) and 249 nm ($\epsilon_{\text{max}} = 4100$), IR (KBr): 3360 cm⁻¹ (broad), 1620 cm⁻¹ (s), 1435 cm⁻¹ (s), Λ_{M} in CH₃OH, 16.0 Ω⁻¹ mol⁻¹ cm² at 25°C.

Synthesis of aquo [N-(2-hydroxyphenyl)pyridine-2-carboxaldiminato]nickel(II),

$[\text{Ni}(\text{app})(\text{H}_2\text{O})].\text{Cl}.\text{H}_2\text{O}$ (**2**)

The $[\text{NiL}_2(\text{H}_2\text{O})]$ complex (**2**) was synthesized following the same procedure as adopted for complex-**1**. Salicylaldehyde was replaced by 2-pyridine carboxaldehyde in this case. To a methanolic solution (10 ml) of NiCl₂.6H₂O (0.01 mol, 2.377 g) was added methanolic solution (15 ml) of 2-aminophenol (0.01 mol, 1.09 g) and 2-pyridine carboxaldehyde (0.01 mol, 1.07 g) and stirred for 1 h at 40°C. The yellow solution, which upon evaporation to dryness yielded a solid, which was washed thoroughly with water-methanol (8:2) mixture, and finally dried in desiccator over CaCl₂. Yield (70%). [Anal: Found C, 51.69; H, 3.38; N, 9.21%; NiC₁₂H₉N₂O₂Cl requires C, 49.56; H, 3.09; N,

9.63%]; UV-vis in H₂O: 480 nm (ϵ_{\max} = 9812), 322 nm (ϵ_{\max} = 11,562) and 233 (ϵ_{\max} = 17,208), IR (KBr): 3405 cm⁻¹ (broad), 1639 cm⁻¹ (s), 1536 cm⁻¹, 1455 cm⁻¹. Λ_M in CH₃OH, 83 Ω^{-1} mol⁻¹ cm² at 25°C.

Synthesis of aquo[N-(2-carboxyphenyl)salicylaldiminato]nickel(II), [NiL₃(H₂O)] [Ni(ats)(H₂O)].H₂O (3)

To a methanolic solution (10 ml) of NiCl₂·6H₂O (0.01 mol, 2.377 g) was added methanolic solution (15 ml) of 2-anthranilic acid (0.01 mol, 1.37 g) and salicylaldehyde (0.01 mol, 1.22 g) and stirred for 1 h at room temperature. The yellow solution upon evaporation to dryness yielded a solid, which was washed thoroughly with water-methanol (8:2) mixture, and finally dried in desiccator over CaCl₂. Yield (70%). [Anal; Found C, 49.28; H, 3.74; N, 6.05%; NiC₁₄H₁₃NO₅ requires C, 50.45; H, 3.90; N, 4.20%]; UV-vis in H₂O: 411 nm (ϵ_{\max} = 5413), 304 nm (ϵ_{\max} = 7000) and 242 (ϵ_{\max} = 12,331), IR (KBr): 3340 cm⁻¹ (broad), 1610 cm⁻¹ (s), 1585 cm⁻¹ (s), 1444 cm⁻¹ (s). Λ_M in CH₃OH, 10 Ω^{-1} mol⁻¹ cm² at 25°C.

Synthesis of aquo[N-(2-carboxyphenyl)pyridine-2-carboxaldiminato]nickel(II), [Ni(atp)(H₂O)]Cl·H₂O (4)

To a methanolic solution (10 ml) of NiCl₂·6H₂O (0.01 mol, 2.377 g) was added methanolic solution (15 ml) of 2-anthranilic acid (0.01 mol, 1.37 g) and 2-pyridine carboxaldehyde (0.01 mol, 1.07 g) and stirred for 1 h at 40°C. The yellow solution upon evaporation to dryness yielded a solid, which was washed thoroughly with water-methanol (8:2) mixture, and finally dried in desiccator over CaCl₂. Yield (70%). [Anal; Found C, 40.18; H, 3.94; N, 7.16%; NiC₁₃H₁₅N₂O₅Cl requires C, 41.87; H, 4.02; N, 7.51%]; UV-vis in H₂O: 345 nm (ϵ_{\max} = 12015), 247 nm (ϵ_{\max} = 10,230), IR (KBr): 3345 cm⁻¹ (broad), 1604 cm⁻¹ (s), 1565 cm⁻¹ (s), 1484 cm⁻¹ (s). Λ_M in CH₃OH, 104 Ω^{-1} mol⁻¹ cm² at 25°C.

All reagents were of AR grade and were used without further purification. Doubly distilled water was used throughout the experiments. Absorption spectra were recorded on a GBC Cintra 10 spectrophotometer. IR spectra were taken as KBr pellet using a Perkin-Elmer spectrophotometer (Model 783). Electrochemical studies were carried out by using a PAR 174A Electrochemical equipment. Gas chromatographic analysis was performed with a Carlo Erba GC 8000^{Top} series and a Tennex column operating at FID detector was used for this purpose.

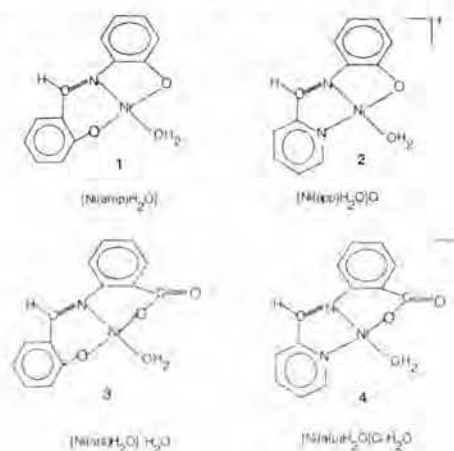
Catalytic epoxidation of olefins

In a typical experiment, 0.1 mmol of complex (1), 5.0 mmol of olefin, and 0.1 mmol of benzyltributylammonium chloride (phase transfer catalyst, PTC) were magnetically stirred with oxidants (5 mmol) at room temperature. Aliquots of CH₂Cl₂ layer were withdrawn at chosen intervals of time and subjected to gas chromatographic (GC) analysis for product(s). GC parameters were quantified by the authentic product samples prior to the analysis.

Results and discussion

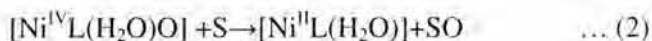
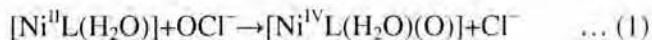
In complexes 1-4 coordinated Schiff base ligands derived from condensation of 2-aminophenol/2-aminobenzoic acid and salicylaldehyde/2-pyridine-carboxaldehyde act as tridentate ligands, while fourth coordination site is occupied by water molecule (Structure I). Spectral properties displayed by complexes 1-4 are somewhat similar to those reported previously with square planar nickel(II)-complexes containing tetradentate Schiff base ligands with N, O coordinating atoms¹²⁻¹⁵. IR spectra of the complexes exhibited typical ligational bands (viz. 1620-1640 cm⁻¹ for C=N stretch) expected for coordinated Schiff-base ligands. Complexes 1 and 3 are non-electrolytic whereas, complexes 2 and 4 behave as 1:1 electrolyte in solution. The cyclic voltammetric studies revealed that complexes 1-4 undergo reductive degradation followed by the electrode pollution in CH₃CN as indicated by a large anodic current observed on the reverse scan. This was further confirmed by electrode deposition.

Epoxidation of olefins was performed in a biphasic medium (CH₂Cl₂/H₂O) in the presence of a phase transfer catalyst (PTC) benzyl tributylammonium chloride. The results of complexes 1-4 catalyzed



Structure I—Schematic representation of complexes 1-4

olefin epoxidation using NaOCl are summarized in Table 1. A series of controlled experiments revealed the fact that each component is necessary for an efficient catalytic conversion and the fundamental system is relatively unaltered by changing the order of mixing. Examination of the greyish-brown suspension appeared in the reaction mixture upon addition of NaOCl, as noticed earlier in case of Ni(salen)/NaOCl system¹⁰, confirmed the formation of small amounts of catalytically inactive nickel peroxide¹⁰ in the reacting system. The results in Table 1 suggest that the complexes **1-4** can efficiently catalyze the epoxidation of olefins under investigation using NaOCl. In order to examine the effectiveness of various terminal oxidants, cyclohexene was chosen as the representative olefin and the results of complexes **1-4** catalyzed epoxidation of cyclohexene in the presence of various single oxygen donors viz. NaOCl, KHSO₅, H₂O₂, *t*-BuOOH, PyO are summarized in Table 2. The results in Table 2 imply that either NaOCl or KHSO₅ are capable of participating complexes **1-4** oxo-transfer process. Other oxidants like H₂O₂, *t*-BuOOH, PyO were noticeably inactive. Although no long lived intermediate could be spectroscopically detected in the present studies, a square pyramidal (tentative) Ni(IV)-oxo intermediate reportedly suggested earlier in the case of [Ni(cyclam)]²⁺/PhIO (ref. 8) and [Ni(salen)]/OCl⁻ (ref. 10) systems is proposed herein for being responsible for olefin epoxidation. The overall catalytic process may be represented as follows:



(L = Schiff base ligand; S = olefin; SO = epoxide)

It is worth mentioning here, that no direct evidence in favour of putative Ni(IV)-oxo intermediate is reported in the literature^{8,10,15}. Nonetheless, postulation of nickel(IV)-oxo intermediate (formed in the reaction of Ni^{II}L with oxidant XO) in the proposed mechanism allows explanations of all of the observed experimental facets of complexes **1-4** catalyzed olefin epoxidation as per Eqs 1 and 2. The inability of H₂O₂, *t*-BuOOH and PyO to achieve olefin epoxidation with any of the complexes **1-4** may be explicated as follows: Reduction of peroxide by transition metal complexes involves generally η² mode of coordination of peroxide followed by inner-sphere electron transfer process¹⁶ to yield high-valent metal oxo-species. In the present case, complexes **1-4** were found to be inert towards binding peroxides (a general term for H₂O₂, *t*-BuOOH) as none of the catalyst complexes (**1-4**) had displayed appreciable spectral changes even after 4 h of reaction with H₂O₂/*t*-BuOOH. The fact is further supported by the lack of reports on Ni(II)-complexes containing N, O donor ligands binding with molecular oxygen or peroxide to form oxo-nickel species^{17,18}. Moreover, it has been ascertained in a recent report¹⁹ that the macrocyclic nickel(II) complex undergoes one electron oxidation

^aTable 1—Complexes **1-4** catalyzed epoxidation of olefins with NaOCl

Substrate	Product ^b	Yields(%) ^c			
		1	2	3	4
Cyclohexene	Cyclohexene epoxide	18	23	31	21
1-Hexene	1-Hexene epoxide	21	32	41	26
Cyclohexane	Cyclohexanol	d	d	d	d
	Cyclohexanone	d	d	d	d
Toluene	Benzyl alcohol	d	d	d	d
	Benzaldehyde	d	d	d	d

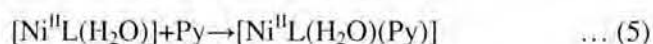
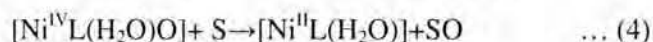
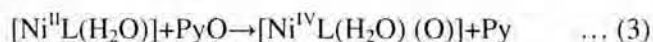
^asee experimental for reaction conditions, ^bafter 4hrs of reaction, ^cbased on substrate taken, ^dno product.

^aTable 2—Effect of oxidants on **1-4** catalyzed epoxidation of cyclohexene

Catalyst	NaOCl	KHSO ₅	H ₂ O ₂	<i>t</i> -BuOOH	PyO
1	18 ^b	14 ^b	c	c	trace
2	23 ^b	21 ^b	c	c	trace
3	31 ^b	23 ^b	c	c	trace
4	21 ^b	15 ^b	c	c	trace

^asee experimental for reaction conditions, catalyst = 0.1mmol, oxidant = 5.0 mmol, cyclohexene = 5.0 mmol ^b% yield of cyclohexene epoxide (calculated based on cyclohexene concentration) after 4hr of reaction, ^c no product.

with *t*-butylhydroperoxide resulting in the formation of the corresponding nickel(III)-complex, but not the high valent oxo-nickel species that necessarily contrives the oxo-functionalization of C=C bond in olefins. Formation of no oxidation products seems to be consistent with the above reported observations¹⁷⁻¹⁹. Trace amounts of epoxide obtained in case of PyO suggest the fact that though oxo-transfer process is operative, the catalyst complexes (**1-4**) are disabled by coordination of pyridine resulting in the decomposition of PyO in the catalytic process (Eq. 3-5).



Incorporation of a small amount of pyridine in the reacting system decreased the yield of epoxide substantially. This is probably due to the fact that the formation of nickel(IV)-oxo species (catalytically active intermediate) is kinetically not favoured as it involves the coordination of OCl^- through the substitution of axially coordinated pyridine (which is a stronger nucleophile than OCl^-) in $[\text{Ni}^{\text{II}}\text{L}(\text{H}_2\text{O})(\text{Py})]$ species.

Though the results in Table 1, indicate that the relative reactivity of various olefins falls into a narrow range, slightly greater reactivity of 1-hexene than that of cyclohexene may be attributed to the fact that the linear olefins are sterically more accessible to the oxo-species than cyclic olefins. The present reacting systems are completely inactive toward C-H bond activation (Table 1) as no reaction products are gas chromatographically evidenced for oxidation cyclohexane and toluene. Probably, nickel(IV)-oxo intermediate complexes in open macrocyclic Schiff-base frame with N, O donors environment are less prone towards hydrogen atom/hydride abstraction to effect oxo-functionalisation of C-H bond of saturated hydrocarbons.

The reasonable yields of epoxides observed in the present system is perhaps associated with the catalyst inactivation owing to the formation of catalytically inactive μ -oxo $[\text{LNi}^{\text{III}}\text{ONi}^{\text{III}}\text{L}]$ dimer. In the presence of a stronger coordinating agent (pyridine), the system became catalytically inert which is evocative of the fact that the transient coordination of terminal oxidant in the axial position of the nickel(II) catalyst

complexes is the key-step in the formation of high-valent Ni(IV)-oxo intermediate which effects oxo-transfer to olefins.

Conclusion

Comparison of the results of the present study and those reported^{8-10,15} for other Ni^{II} -complexes containing tetradentate Schiff-base ligands (with N, O donors) reveals that catalytic properties of nickel(II) complexes of this category are quite similar with regards to the olefin epoxidation and none of the complexes are effective towards catalyzing oxidation of C-H bond of saturated hydrocarbons.

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