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Synthesis, structural characterization and catalytic activity study of Mn(II), Fe(III), Ni(II), Cu(II) and Zn(II) complexes of quinoxaline-2-carboxalidine-2-amino-5-methylphenol: Crystal structure of the nickel(II) complex

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ABSTRACT

Five new transition metal complexes $[MnL(OAc)]\cdot H_2O(1)$, $[FeLCl_2](2)$, $[NiL_2]\cdot H_2O(3)$, [CuLCl](4) and $[ZnL_2]\cdot 2H_2O(5)$ have been synthesized using a tridentate Schiff base ligand, HL (quinoxaline-2-carboxalidine-2-amino-5-methylphenol) and the complexes have been characterized by physicochemical and spectroscopic techniques. The spectral analyses reveal an octahedral geometry for **3**, square pyramidal structure for **2** and square planar structure for **4**. Analytical and physicochemical data indicate tetrahedral structure for **1** and octahedral structure for **5**. The crystallographic study reveals that $[NiL_2]\cdot H_2O$ shows distorted octahedral geometry with a *cis* arrangement of N_4O_2 donor set of the bis Schiff base and exhibits a two-dimensional polymeric structure parallel to $[0\ 1\ 0]$ plane. The complexes were screened for catalytic phenol hydroxylation reaction. Coordinatively unsaturated manganese(II), iron(III) and copper(II) complexes were found to be active catalysts. The poor catalytic activity of the nickel(II) complex is due to coordinatively saturated octahedral nature of the complex. Maximum conversion of phenol was observed for the copper(II) complex and the major product was catechol.

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1. Introduction

Transition metal complexes containing nitrogen and phenolic oxygen donor atoms are of considerable interest due to their potential application in catalysis, medicine and material science [1–4]. They are often used to construct extended network structures and coordination polymers with high structural stability and special topologies [5-8]. Some of the metal complexes find wide applications as oxidation catalysts in the production of bulk and fine chemicals and in the elimination of organic pollutants like phenol. Liquid phase hydroxylation of phenol to catechol and hydroquinone using simple oxidants like O₂ and H₂O₂ is a reaction of industrial importance. There is a continuing interest in the production of dihydroxybenzenes by the direct hydroxylation of phenol with the environmentally benign oxidant, hydrogen peroxide (H₂O₂) [9]. Catechol and hydroquinone are two of the many phenolic derivatives of high value. They are widely used as photographic chemicals, antioxidants [10,11], polymerization inhibitors, flavoring agents, and medicine [12,13]. A number of novel estrane skeletons have been synthesized using catechol estrogens [14]. The

catalytic hydroxylation of phenols in heterogenized systems has been reported in many cases [15–18].

We have recently reported the Schiff base, quinoxaline-2-carboxalidine-2-amino-5-methylphenol, and its cobalt(II) complex [19]. In continuation of our work, we present here the synthesis and characterization of manganese(II), iron(III), nickel(II), copper(II) and zinc(II) complexes of the Schiff base HL. The crystal structure of $[NiL_2]$ ·H₂O is studied. All the prepared complexes are screened for their catalytic activity for the liquid phase hydroxylation of phenol. Suitable reaction conditions have been optimized to give maximum hydroxylation.

2. Experimental

2.1. Materials

2-Amino-5-methylphenol (Aldrich), manganese(II) acetate tetrahydrate (Merck), ferric chloride anhydrous (Merck), nickel(II) acetate tetrahydrate (Qualigens), copper(II) chloride dihydrate (Merck) and zinc(II) acetate dihydrate (Merck) were used as supplied. The synthesis of quinoxaline-2-carboxaldehyde was carried out as reported in the literature [20,21]. The Schiff base HL was prepared by the reported procedure [19] by stirring methanolic



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solution (60 mL) of quinoxaline-2-carboxaldehyde (1.58 g, 10.0 mmol) and 2-amino-5-methylphenol (1.23 g, 10.0 mmol). Structure of the Schiff base is given in Fig. 1.

2.2. Preparation of complexes

A solution of the Schiff base (2.63 g, 10.0 mmol) in 1:1 chloroform-methanol (50 mL) was added to a solution of manganese(II) acetate tetrahydrate (2.45 g, 10.0 mmol), ferric chloride (1.62 g, 0.01 mol), nickel(II) acetate tetrahydrate (1.24 g, 5.0 mmol), copper(II) chloride dihydrate (1.71 g, 10.0 mmol) or zinc(II) acetate dihydrate (1.10 g, 5.0 mmol) in methanol (15 mL). The solution was then refluxed for 3 h and left to cool at room temperature $(27 \pm 2 \text{ °C})$ overnight. The crystalline complexes that separated out were filtered, washed with ether and dried in vacuum over anhydrous calcium chloride.

[MnL(OAc)]·H₂O (**1**). Yield: 65%, color: red, M.P: 295–297 °C, λ_m (DMF): 15 ohm⁻¹ cm² mol⁻¹, μ_{eff} (B.M): 5.94. Elemental *Anal.* Calc. for C₁₈H₁₇N₃O₄Mn: C, 54.83; H, 4.35; N, 10.66; Mn, 13.93. Found: C, 54.78; H, 3.98; N, 10.69; Mn, 13.96%.

[FeLCl₂] (**2**). Yield: 70%, color: black, M.P: 260–263 °C, λ_m (DMF): 9 ohm⁻¹ cm² mol⁻¹, μ_{eff} (B.M):4.01. Elemental *Anal.* Calc. for C₁₆H₁₂Cl₂N₃OFe: C, 49.40; H, 3.11; N, 10.80; Fe, 14.35. Found: C, 49.67; H, 3.15; N, 10.69; Fe, 14.31%.

[NiL₂]·H₂O (**3**). Yield: 80%, color: blue, M.P: 300–302 °C, λ_m (DMF): 12 ohm⁻¹ cm² mol⁻¹, μ_{eff} (B.M): 3.2. Elemental *Anal.* Calc. for C₃₂H₂₆N₆O₃Ni: C, 63.92; H, 4.36; N, 13.98; Ni, 9.76. Found: C, 63.70; H, 3.99; N, 13.93; Ni, 9.74%. Blue crystals suitable for X-ray analysis of species (**3**) were obtained by slow diffusion of methanolic solution of the complex.

[CuLCl] (4). Yield: 70%, color: violet, M.P: 240 °C, λ_m (DMF): 13 ohm⁻¹ cm² mol⁻¹, μ_{eff} (B.M): 1.95. Elemental *Anal.* Calc. for C₁₆H₁₂N₃ClOCu: C, 53.19; H, 3.35; N, 11.63; Cu, 17.59. Found: C, 53.16; H, 3.36; N, 11.67; Cu, 17.64%.

[ZnL₂]·2H₂O (**5**). Yield: 85%, color: violet, M.P: 245–247 °C, λ_m (DMF): 8 ohm⁻¹ cm² mol⁻¹, μ_{eff} (B.M): 0. Elemental *Anal.* Calc. for C₃₂H₂₈N₆O₄Zn: C, 61.40; H, 4.51; N, 13.42; Zn, 10.45. Found: C, 61.75; H, 4.12; N, 13.79; Zn, 10.42%.

2.3. Physical measurements

Elemental analysis of the Schiff base and complexes were done on a Vario EL III CHNS analyzer. The estimation of metal ions was carried out on a Thermo Electron Corporation, M series Atomic Absorption Spectrophotometer. Far-IR spectra of the complexes were recorded using polyethylene pellets in the 500–100 cm⁻¹ region on a Nicolet Mega 550 FTIR Instrument. The molar conductivities of the complexes were measured using a Systronic conductivity bridge type 305 in DMF. ¹H NMR spectra were recorded in CDCl₃ or DMSO-d₆ on a Bruker AVAVCE III 400 MHz -NMR spectrometer using TMS as the internal standard. The IR spectra were recorded on a JASCO FTIR-4100 spectrophotometer using KBr pellets in the range 4000–400 cm⁻¹. The electronic spectra of the complexes were recorded on a Thermoelectron Nicolet evolution 300 UV-Vis spectrophotometer. Magnetic susceptibility measurements were done at room temperature on a Magway MSB Mk 1 Magnetic Susceptibility Balance. The EPR spectrum of the copper



Fig. 1. Structure of quinoxaline-2-carboxalidine-2-amino-5-methylphenol.

complex was recorded on a Varian E-112 spectrometer using TCNE as the standard. TG-DTA analyses were carried out on a Perkin Elmer Pyris Diamond TG/DTA analyser. The products of the catalytic reaction were analyzed using a Chemito 8510 gas chromatograph fitted with FID detector.

2.4. Catalytic activity study: oxidation of phenol

The catalytic activity study towards the hydroxylation of phenol was carried out in a 50 mL two necked RB flask fitted with a water cooled condenser. In a typical reaction, an aqueous solution of 30% H_2O_2 (2.67 mL, 25 mmol) and phenol (2.2 mL, 25 mmol) were mixed in acetonitrile (10 mL) and the reaction mixture was heated at 343 K with continuous stirring in an oil bath. The complex (0.015 mmol) was added to the reaction mixture and the reaction was considered to be started at this time. During the reaction, the products were analyzed using a gas chromatograph after specific interval of time by withdrawing small aliquots. The effects of various parameters such as amount of oxidant, catalyst, temperature and time of the reaction were studied to see their effect on the reaction product pattern.

2.5. X-ray crystallography

X-ray crystal structure determination was performed with a Bruker SMART APEX CCD X-ray diffractometer, using graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å, φ and ω scans). The data was reduced using sAINTPLUS [22] and a multiscan absorption correction using sADABS was performed [23]. The structure was solved using sHELXS-97, and full matrix least squares refinement against F^2 was carried out using sHELXL-97 in anisotropic approximation for non-hydrogen atoms [24]. The hydrogen atoms of the ligands were positioned geometrically, and allowed to ride on their parent carbon atoms. The hydrogen atoms of the water molecules were located in the difference Fourier map and refined isotropically. All hydrogen atoms were assigned using fixed U_{iso} values, equal to 1.2 U_{eq} of the parent atom for the ligand carbons and 1.5 for hydrogen atoms of water. A summary of crystallographic data and refinement parameters are given in Table 1.

3. Results and discussion

All the five complexes are soluble in polar organic solvents like methanol, CH_3CN , DMF and DMSO. The molar conductivity measurements in 10^{-3} M DMF solutions revealed the non-electrolytic

Crystal data summary for $[NiL_2]$ ·H ₂ O.				
Formula	C32 H26 Ni N6 O3			
Formula weight	601.30			
Crystal system	Monoclinic			
Space group	$P2_1/n$			
a (Å)	13.677(4)			
b (Å)	13.760(3)			
c (Å)	14.572(4)			
β (°)	96.445(5)			
V (Å ³)	2725.1(12)			
Ζ	4			
T (K)	298			
$Dc (mg m^{-3})$	1.466			
μ (Mo K $lpha$) (mm ⁻¹)	0.76			
F(000)	1248			
θ range for data collection (°)	1.94-25.00			
Reflections collected/unique	12261/4797			
Goodness-of-fit (GOF) on F^2	1.194			
$R_1, wR_2 [I > 2\sigma(I)]$	0.0694, 0.1579			
R_1 , wR_2 (all data)	0.1007, 0.1650			

 $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma |F_o|, \ wR_2 = [\Sigma w (F_o^2 - F_c^2) 2 / \Sigma w (F_o^2) 2] 0.5.$

nature of the complexes [25]. The analytical data clearly give the evidence of formation of 1:2 complexes in the case of nickel(II) and zinc(II) complexes while others are formed in 1:1 ratio of metal to ligand. The 1:2 metal ligand ratio itself suggests an octahedral geometry for the Ni(II) and Zn(II) complexes, while the 1:1 complexes may form four, five or six coordinated complexes depending upon the solvent molecules and anions in the coordination sphere.

3.1. ¹H NMR spectrum of [ZnL₂]·2H₂O

The NMR spectrum of the zinc(II) complex is taken in DMSO-d₆. The phenolic OH signal at 9.70 ppm observed in the spectrum of the ligand is not seen in the spectrum of the Zn(II) complex indicating the participation of the phenolic OH group in chelation with proton displacement. The signal due to azomethine proton gets shifted upon complexation, which might probably be due to the donation of the lone pair of electrons by the nitrogen to the central metal atom, resulting in the formation of a coordinate linkage (M \leftarrow N). The aromatic and quinoxaline protons resonate as a complex multiplet in the region δ 7.46–8.20 ppm. The signal due to methyl group attached to the phenolic ring is observed almost at the same chemical shift for that in spectrum of the ligand. A broad singlet appeared in the region 3.91–4.26 indicates the presence of water molecules in the complex.

3.2. Infrared spectra

The most important IR spectral bands of the ligand and its metal complexes are listed in Table 2. The ν (C=N) band at 1626 cm⁻¹ of the Schiff base shifts to lower frequencies in complexes indicating weakening of the azomethine bond due to coordination to the metal [26]. For the Schiff base, the C=N- stretching of quinoxaline ring is observed as a strong band at 1549 cm⁻¹. This band undergoes a small shift ($\sim 5 \text{ cm}^{-1}$) on complexation; such small shifts have been reported when ring nitrogens are involved in coordination to the metal [19]. The v(C-O) band for all the complexes appears at lower frequencies compared to that for the free ligand, which is due to the participation of phenolic oxygen on chelation [27]. Thus the Schiff base behaves as a monobasic tridentate ligand. In the spectra of complexes [MnL(OAc)]·H₂O, [NiL₂]·H₂O and $[ZnL_2] \cdot 2H_2O$ the broad band observed at 3300–3400 cm⁻¹ is due to the presence of water in the lattice. Appearance of new bands in the spectra of all complexes in the regions 490-450 and 450–400 cm⁻¹ has been attributed to v(M-O) and v(M-N) [2], respectively. The IR spectra of the chloro complexes, (2) and (4), reveal an additional new band at 346 and 332 cm⁻¹ which can be assigned to v(M–Cl) [28]. The IR spectrum of the acetato complex, (1), displays v_{asym} (COO⁻) and v_{sym} (COO⁻) at 1577 and 1390 cm⁻¹ which is consistent with monodentate acetato coordination [29].

3.3. Magnetic susceptibility and electronic spectra measurements

Electronic spectra of the Schiff base and its complexes were taken in methanol in the range 50 000–10 000 cm⁻¹. The absorption maxima are listed in the Table 2. The UV–Vis spectrum of the Schiff base shows two strong bands at 42 550 and 25 970 cm⁻¹ due to π – π * transitions. [30]. For all the complexes, the π – π * bands are not altered to a greater extent on coordination.

The spectrum of the Mn(II) complex shows three shoulders at 16 645, 22 765 and 27 765 cm⁻¹ assignable to ${}^{6}A_{1} \rightarrow {}^{4}T_{1}$, ${}^{6}A_{1} \rightarrow {}^{4}T_{2}(G)$ and ${}^{6}A_{1} \rightarrow {}^{4}T_{2}(D)$ transitions, respectively. The μ_{eff} value of the Mn(II) complex was found to be 5.94 B.M. at room temperature as expected for high spin d⁵ system [31,32].

The electronic spectrum of the iron(III) complex shows a weak broad band in the near IR region at 6890 cm⁻¹ indicating a square pyramidal structure. Similar observations have been made by Martin and White for the five coordinated iron(III) dithiocarbamate complex, which shows characteristic band in the near IR region due to low lying spin forbidden states [33,34]. The charge transfer band observed at 29 000 cm⁻¹ obscure the rest of the d–d transitions. The iron(III) complex shows a magnetic moment of 4.01 B.M., which confirms that iron(III) complex is five coordinated.

For the nickel(II) complex, the band at 17 450 cm⁻¹ is due to the ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ transition of nickel(II) in octahedral environment. The intensity of this d–d band is considerably increased possibly due to the influence of nearby intense charge-transfer transitions [33]. The complex has a room temperature magnetic moment value of 3.1 B.M., which is in the normal range observed for octahedral Ni(II) complexes.

The spectrum of [CuLCI] shows two bands in the visible region, at 22 220 and 15 950 cm⁻¹ assignable to ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ and ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ transitions, respectively [33,35] indicating the square planar geometry of the copper(II) complex. The magnetic moment of the complex is found to be 1.95 B.M. The zinc(II) complex exhibits a charge transfer transition at 18315 cm⁻¹.

3.4. Thermal analysis

Thermal stability of the Schiff base and the complexes were investigated using TG-DTA under nitrogen atmosphere with a heating rate of 10 °C min⁻¹ over a temperature range of 40–1000 °C. The Schiff base HL exhibits a one stage decomposition which begins at 160 °C. The weight loss below 200 °C observed in complexes **1**, **3** and **5** indicate the presence of lattice water. All the complexes are found to be thermally stable and exhibit multi stage decomposition pattern. The thermal data upto 200 °C of the complexes is given in Table 3. The decomposition of the organic part occurs above 200 °C for all complexes. TG results show good agreement with the formula of the complexes arrived from the analytical data.

3.5. EPR spectral studies

The X band EPR spectrum (Fig. 2) of the copper(II) complex is taken in DMF at 77 K. The ESR spectrum of the copper(II) complex gives a spectrum with $g_{||}$ and g_{\perp} values at 2.28 and 2.12, respectively. The trend $g_{||} > g_{\perp} > g_e$ (g_e is the g value of free electron) observed for the copper(II) complex suggests that the unpaired

Table 2

Infrared and electronic spectra of the Schiff base HL and its complexes.

Compound IR data (cm ⁻¹)			Electronic spectral data ^a			
	v (O–H)	v (C=N)	v (C-O)	v (M–O)	v (M–N)	Absorption maxima (log ε)
HL	3365	1626	1262			42550 (3.96), 25970 (3.81)
$[MnL(OAc)] \cdot H_2O(1)$	3317	1605	1257	465	413	41270 (3.56), 32540 (3.25), 27765 (3.30), 22765 (3.27), 16645 (1.67)
[FeLCl ₂] (2)		1609	1254	490	424	42110 (4.12), 35730 (3.96), 29000 (3.70), 6890 (1.24)
[NiL ₂]·H ₂ O (3)	3373	1579	1253	457	432	41150 (4.13), 27855 (3.88), 17450 (3.83)
[CuLCl] (4)		1612	1250	425	409	40325 (3.74), 37735 (3.65), 22220 (2.65), 15950 (1.27)
$[ZnL_2] \cdot 2H_2O(5)$	3381	1587	1251	465	418	42195 (3.72), 30395 (3.30), 25840 (3.31), 18315 (3.36)

^a Absorption maxima in cm⁻¹ and ε in L mol⁻¹ cm⁻¹.

Table 3 Thermal decomposition data (below 200 °C) for complexes.

Compound	TG temperature range/°C	% Weight loss (fragment lost)
$[MnL(OAc)] \cdot H_2O(1)$	46-101	4.5 (1 H ₂ O)
[NiL_2] \cdot H_2O(3)	50-130	3.1 (1 H ₂ O)
[7nL_2] \cdot 2H_2O(5)	46-101	2.9 (2 H ₂ O)

For complexes 2 and 4, there is no weight loss below 200 °C.



Fig. 2. ESR spectrum of the copper(II) complex.

electron is most likely localized in $d_x^2 - d_y^2$ orbital of copper(II) ion and the complex has an axial symmetry [36,37].

3.6. Crystal structure of $[Ni(L)_2] \cdot H_2O$

Single crystal X-ray diffraction analysis reveals that complex **3** forms a two-dimensional polymeric chain due to the aggregation of the discrete monomeric entities through classical intermolecular $O-H\cdots O$ and $O-H\cdots N$ hydrogen bonds. The asymmetric unit as illustrated in the ORTEP diagram (Fig. 3), consists of a monomeric Ni{(CH₃)C₆H₄(O)N=CH-C₈H₅N₂)₂ unit with a solvent water molecule present in the lattice. In the complex, the ligand quinoxaline-2-carboxalidine-2-amino-5-methyl phenol behaves as a monoanionic, tridentate Schiff base with its NNO donor set which coordinates to the metal center through one imine nitrogen, one quinoxaline ring nitrogen atom and a deprotonated phenolic oxygen atom in a *cis* arrangement. The nickel(II) center adopts a distorted octahedral geometry being chelated by two units of such tridentate Schiff base ligands.

Selected bond lengths and angles are listed in Table 4. The Ni–N (imine) distances are comparable to those observed for the similar kind of complexes present in the literature [38–40]. The three *trans*-angles at nickel(II) are 176.00(18), 157.68(16) and 159.61(17)° for N(3)–Ni(1)–N(6), O(1)–Ni(1)–N(1) and O(2)–Ni(1)–N(4), and the *cis* angles are in the range 76.64(18)–106.03(17). The bite angles show deviation from ideal value due to the rigid structure of the Schiff base.

A further insight into the structure of $\mathbf{3}$ reveals the presence of a C2 symmetry axis, and the complex is expected to exhibit optical isomerism. However both the enantiomers co-exist in the unit



Fig. 3. Ortep representation of the complex 3, with 50% probability ellipsoid (hydrogen atoms are omitted for clarity).

Table 4	
Selected bond lengths (Å) and angles (°) for $[\text{NiL}_2]{\cdot}\text{H}$	₂ 0.

Ni(1)-N(3)	1.988(4)	Ni(1)-N(4)	2.226(4)
Ni(1)-N(6)	1.992(4)	Ni(1)-N(1)	2.290(4)
Ni(1)-O(2)	2.033(4)	N(3)-C(9)	1.273(6)
Ni(1)-O(1)	2.044(4)	N(3)-C(10)	1.391(6)
N(3)-Ni(1)-N(6)	176.00(18)	O(1)-Ni(1)-N(1)	157.68(16)
O(2)-Ni(1)-N(4)	159.61(17)	C(9)-N(3)-C(10)	127.6(5)



Fig. 4. Packing diagram of the complex 3, view along b axis.

cell, as shown in Fig. 4, since the crystal belongs to a centrosymmetric space group. Both hydrogens of the uncoordinated water molecule are involved in the intermolecular hydrogen bonding with the neighbouring phenolic oxygen atom and uncoordinated quinoxaline nitrogen atom through O(3)-H(1w)···N(5) and O(3)-H(2w)···O(1) interactions (H(1w) and H(2w) are the hydrogens of water molecule). Similarly there are some weak intermolecular and intramolecular hydrogen bondings in the lattice. There is π - π stacking interaction between phenolic ring and symmetry related quinoxaline. A few significant hydrogen bonding parameters are listed in Table 5. All these interactions afford an infinite two-dimensional chain propagating along [0 1 0] direction as shown in Fig. 5.

Based on the above physicochemical, spectral and crystallographic analyses, the suggested structures of the complexes are given in Fig. 6.

Table 5

Selected hydrogen bond interactions in the complex.

D–H···A	Symmetry	Distances (Å)		Angles (°) D–H···A
		D···A	H···A	
O(3)– H(1w)····N(5)	1/2 + x, $3/2 - y$, -1/2 + z	3.015(7)	2.33	135
O(3)– H(2w)···O(1)	1 - x, 1 - y, 1 - z	2.862(7)	2.02	144



Fig. 5. Two-dimensional polymeric structure of [NiL₂]·H₂O.

3.7. Oxidation of phenol

Liquid phase hydroxylation of phenol catalyzed by the Schiff base complexes using H_2O_2 as an oxidant has been studied in CH₃CN. As the hydroxyl group present on phenol is *ortho* and *para* directing, the hydroxylation of phenol is expected to give two products viz. catechol and hydroquinone. Table 6 presents the results for phenol hydroxylation reaction with the manganese(II), iron(III) and copper(II) complexes of HL. The Schiff base and the nickel(II) and zinc(II) complexes do not catalyze the reaction. In order to acquire suitable reaction conditions for maximum transformation of phenol, [CuLCI] (the complex which showed highest activity during the screening studies) was studied in detail by varying the following reaction conditions: the amount of catalyst (the copper complex), temperature, concentration of H_2O_2 and time.

3.7.1. Effect of the amount of catalyst

Effect of variation of concentration of the catalyst on the rate of reaction is illustrated in Table 7. Five different concentrations (5, 10, 15, 20 and 25 mmol) of the catalyst [CuLCl] were used for the fixed amount of phenol (2.2 mL, 25 mmol) and oxidant (2.67 mL,

Table 6

Result of phenol hydroxylation reaction catalyzed by complexes of the Schiff base HL.

Catalyst	Phenol conversion (%)	Product distribution		TON ^b
		Catechol	Hydroquinone	
[MnL(OAc)]·H ₂ O [FeLCl ₂] [CuLCl]	11.70 9.29 16.10	10.30 7.95 14.48	1.40 1.34 1.62	200 167 268

Reaction time, 2 h; reaction temperature, 343 K; phenol: H_2O_2 (molar ratio) = 1:1; acetonitrile = 10 mL; catalyst, 0.015 mol.

^a TON: total turnover number, moles of products formed per mole of catalyst.



Fig. 6. Suggested structures of the complexes 1, 2, 3, 4 and 5.

Table 7The influence of the amount of catalyst.

Catalyst weight,	Phenol	Product dist	Product distribution	
(mmol)	conversion (%)	Catechol	Hydroquinone	
5	3.30	3.27	0.03	
10	14.38	13.54	0.84	
15	16.10	14.48	1.62	
20	14.36	12.90	1.46	
25	13.01	10.32	2.69	

Reaction time, 2 h; reaction temperature, 343 K; phenol: H_2O_2 (molar ratio) = 1:1; acetonitrile = 10 mL.

25 mmol) in 10 mL CH₃CN. An amount of 10–20 mmol for the catalyst gave comparable results in both cases with ca. 14–16% phenol conversion in 2 h of reaction time at 343 K. Lowering the amount of catalyst resulted in the poor conversion [17]. Thus, 15 mmol of the catalyst was considered to be sufficient enough to give good performance.

3.7.2. Effect of temperature

Table 8 presents the data with regard to variation of reaction temperature on hydroxylation of phenol. Five different temperatures (303, 323, 333, 343 and 353 K) were considered, while keeping other parameters constant (*i.e.*, 2.2 mL phenol, 2.67 mL H_2O_2 and 15 mmol catalyst), for the catalytic performance in 10 mL of CH₃CN. Below 343 K, conversion of phenol was very poor. Above 343 K the decomposition of H_2O_2 would be accelerated, which is not beneficial to phenol hydroxylation [41]. Thus, 343 K is considered as, the minimum required temperature to supply sufficient energy to reach the energy barrier of phenol transformation.

3.8. Effect of time

The appropriate reaction time is the main assurance for the perfect reaction. Too long a time appears to be unfavorable for phenol hydroxylation [41]. Table 9 shows that the optimum reaction time is 2 h. There was no significant change in the conversion and selective formation of catechol beyond 3 h.

Table 8	
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The influence of temperature.

Temperature (K)	Phenol conversion (%)	Product distribution	
		Catechol	Hydroquinone
303	0	0	0
323	1.23	1.23	0
333	8.20	7.23	0.97
343	16.10	14.48	1.62
353	16.57	14.40	2.17

Reaction time, 2 h; catalyst, 0.015 mol; phenol: H_2O_2 (molar ratio) = 1:1; aceto-nitrile = 10 mL.

Table 9

The influence of reaction time.

Time (h)	Phenol conversion (%)	Product dist	Product distribution	
		Catechol	Hydroquinone	
1	11.66	11.25	0.41	
2	16.10	14.48	1.62	
3	14.19	12.00	2.19	
4	15.88	13.01	2.87	
5	17.31	13.51	3.80	

Reaction temperature, 343 K; catalyst, 0.015 mol; phenol: H_2O_2 (molar ratio) = 1:1; acetonitrile = 10 mL.

3.9. Effect of H₂O₂ concentration

Table 10 presents the effect of H_2O_2 concentration on reaction rate. The influence of oxidant on reaction was monitored using five different concentrations of aqueous 30% H_2O_2 viz. 15, 20, 25, 30 and 35 mmol for a fixed amount of phenol (2.2 mL) and catalyst (5 mg) in 10 mL CH₃CN. The lowest H_2O_2 concentration results in only ca. 3% phenol hydroxylation. Other two concentrations gave comparable results. This information suggests that H_2O_2 /phenol ratio of 1:1 is ideal for the maximum conversion as well as maximum efficiency. Thus, excess oxidant is not an essential condition to maximize phenol conversion.

The proposed mechanism of the phenol hydroxylation reaction for the copper(II) complex is given in Scheme 1. The copper(II) complex is square planar and it interacts with H_2O_2 and produces the active species (Cu–OOH) [42]. This active species subsequently interacts with phenol and produces the intermediate (Cu–phenol– OOH) as shown in Scheme 1. The intermediate facilitates the attack of OOH at the *ortho* and *para* position of phenol producing catechol and hydroquinone. The intermolecular oxidation–reduction reaction between the hydrogen peroxide and phenol seems to be an intramolecular electron transfer reaction in the intermediate species (phenol–Cu–OOH), which might decrease the activation energy for the oxidation of phenol resulting in significant enhancement of the rate. The proposed Scheme can correlate with geometry of the complex. The complexes **1**, **2** and **4** which contain vacant coordination positions are found to catalyze phenol hydroxylation

Table 10

The influence of H₂O₂ concentration.

Hydrogen peroxide	Phenol conversion	Product distribution		
(mmol)	(%)	Catechol	Hydroquinone	
15	3.27	3.27	0	
20	7.57	7.44	0.13	
25	16.10	14.48	1.62	
30	13.37	11.81	1.56	
35	15.00	13.17	1.83	

Reaction time, 3 h; reaction temperature, 343 K; catalyst, 0.015 mol; acetonitrile = 10 mL.



Scheme 1. Proposed mechanism for hydroxylation of phenol.

while complexes **3** and **5** which do not contain coordinatively unsaturated locations are inactive.

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4. Conclusion

In summary we have successfully prepared five complexes of the Schiff base HL and demonstrated that manganese(II), iron(III) and copper(II) complexes can serve as catalyst for phenol hydroxylation reaction. Only the manganese(II), iron(III) and copper(II) complexes with vacant coordination sites show good activity in phenol hydroxylation. The nickel(II) complex, which is a coordinatively saturated octahedral complex, is not active. Thus the activity can be correlated with geometry of the complex. Absence of the catalytic activity of Zn(II) complex might be due to its octahedral structure and its incapability to have variable oxidation states. The molecular structure of the nickel(II) complex was confirmed by X-ray crystallography. The crystal is a racemic mixture of two crystallographically independent enantiomers of the complex. The molecules exhibit a two-dimensional polymeric structure parallel to [0 1 0] plane, formed by O-H···N and O-H···O intermolecular hydrogen bonding and π - π stacking interaction. We, therefore, conclude that the monomeric unit can act as a good template in establishing an ordered supramolecular structure.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.08.016.

CCDC 750227 contains the supplementary crystallographic data for [NiL₂]·H₂O. 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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