



Synthesis, spectral, electrochemical and catalytic properties of Cu(II), Ni(II) and Co(II) complexes containing N, O donors

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ABSTRACT

Metal(II) chelates of Schiff bases derived from the condensation of multi-substituted aniline with mono- and di-substituted salicylaldehyde have been prepared and characterized by ¹H NMR, IR, electronic, EPR, magnetic and cyclic voltammetry measurements. The complexes are of the type M(X-DPMP)₂ [(M = Cu(II), Ni(II) or Co(II)), DPMP = 2-[(2,6-diisopropylphenylimino)methyl]phenol, X = Br, Cl, I, BrCl].

The Schiff bases behave as monobasic bidentate ligand in their complexes. The spectral data indicate that the ligand coordinates through the phenolic oxygen and the azomethine nitrogen atoms. The observed A₁₁ values in the Cu(II) complexes indicate a tetrahedrally distorted square planar structure. The cyclic voltammetric redox potential of copper(II) and nickel(II) complexes suggest the existence of irreversible pairs in acetonitrile. Cu(Br-DPMP)₂ was found to be an efficient catalyst for cyanosilylation of aldehydes under mild conditions.

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1. Introduction

Metal complexes of Schiff bases derived from substituted salicylaldehydes and various amines have been widely investigated because of their wide applicability [1]. These ligands are readily available and versatile and depending on the nature of the starting materials they exhibit various lenticities and functionalities [2]. There is a continuing interest in metal complexes of Schiff bases because of the presence of both nitrogen and oxygen donor atoms in the backbones of these ligands [3–7]. They readily coordinate with a wide range of transition metal ions, yielding stable and intensely coloured metal complexes, which exhibit interesting physical, chemical, biological and catalytic properties [8–15]. In particular, metal–Schiff base complexes were found to be very efficient catalysts in the oxidation processes [16]. New kinds of chemotherapeutic agents containing Schiff bases have gained significant attention among biochemists. Hence, a systematic understanding on the structure has warranted synthesis and characterization of a variety of Schiff base complexes containing different disubstituted 2-hydroxy aromatic moieties. Although there are many Schiff

bases reported in literature, multisubstituted ligand systems are hardly reported. With this in view and our continuing interest [17–23] in the synthesis of metal complexes and their catalytic activity, the present report accounts for the synthesis and characterization of new multisubstituted Schiff bases and their metal(II) complex (Fig. 1) with a special emphasis on their spectral and electrochemical investigations. Further, the catalytic behavior of copper complexes on cyanosilylation reaction has been reported.

2. Experimental

2.1. Materials

Chemicals used for the preparation of the ligands and complexes were purchased from Aldrich and used as such. The purity of ligands and metal complexes were checked by TLC.

2.2. Physical measurements

The magnetic moment of each complex in the solid state was determined on a Gouy balance at room temperature using Hg[Co(SCN)₄] as calibrant. The IR spectra of the ligands and complexes in KBr (4000–400 cm⁻¹) were recorded on a Perkin Elmer 577 grating spectrophotometer. The electronic spectra in MeCN were obtained on a Shimadzu-160 UV–vis. spectrophotometer.

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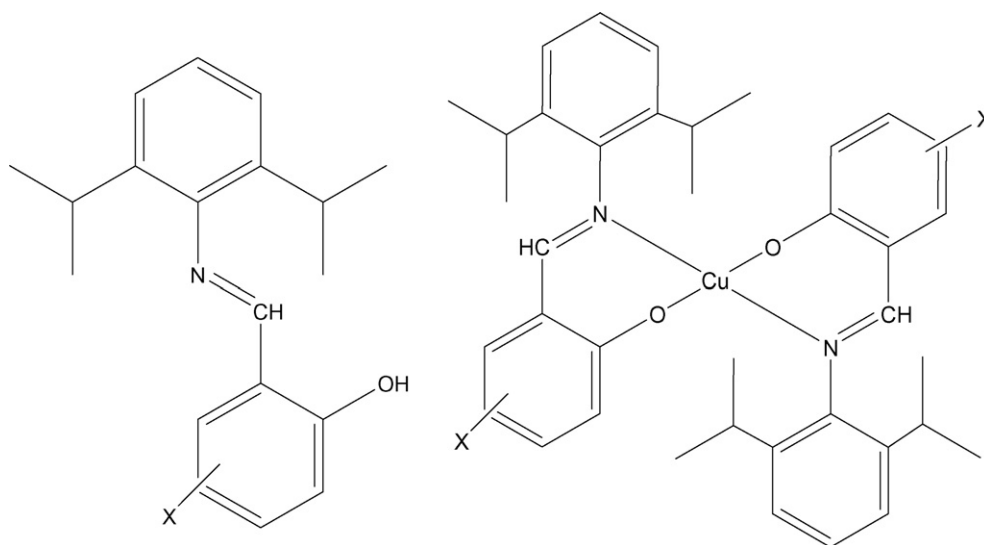


Fig. 1. The chemical structure of Schiff base ligand [X = 5-Br, 5-Cl, 5-I, 3Br5Cl, Ph] and copper complex.

Microanalyses for the carbon, hydrogen and nitrogen content of the new complexes were carried out by the CDRI, Lucknow, India. The metal contents of the complexes were estimated by incinerating them to their oxides in the presence of ammonium oxalate. ^1H NMR spectra were recorded in CDCl_3 with TMS as an internal standard on a Bruker 300 MHz spectrometer. X-band EPR spectra were recorded on a Varian-E-12 spectrometer with a quartz Dewar for measurements at the liquid N_2 temperature and the spectra were calibrated with DPPH. Cyclic voltammetric measurements were made in MeCN (HPLC grade) using a BAS-CV50 electrochemical analyzer. The three electrode cell was comprised of a reference Ag/AgCl , an auxiliary Pt and a working glassy carbon electrodes. Bu_4NClO_4 was used as supporting electrolyte.

2.3. Synthesis of ligands

An ethanolic solution of 2,6-diisopropylaniline [2 mmol] was magnetically stirred in a round bottom flask followed by dropwise addition of 5-chlorosalicylaldehyde [2 mmol]. The reaction mixture was then refluxed for 3 h and upon cooling to 0°C , a yellow solid precipitated from the reaction mixture. The solid which separated out was filtered, washed with ice cold ethanol and dried over anhydrous CaCl_2 .

2.3.1. 4-Chloro-2-[(2,6-diisopropylphenylimino)methyl]phenol [Cl-DPMP]

Overall yield 70%. Anal. Calc. $\text{C}_{19}\text{H}_{22}\text{ClON}$: C, 72.28; H, 6.97; N, 4.44. Found: C, 72.08; H, 6.87; N, 4.34%.

^1H NMR (CDCl_3) 410 MHz: δ ppm 13.12 (s, 1H), 8.27 (s, 1H), 7.12 (d, 1H), 7.22–7.49 (m, 5H), 2.98 (m, 2H), 1.19–1.23 (d, 12H).

^{13}C NMR (CDCl_3): δ 165.33, 159.64, 145.62, 138.45, 132.95, 131.13, 125.67, 123.61, 123.25, 119.29, 118.86, 28.22, 23.58.

2.3.2. 4-Bromo-2-chloro-6-[(2,6-diisopropylphenylimino)methyl]phenol [Br,Cl-DPMP]

Overall yield 75%. Anal. Calc. $\text{C}_{19}\text{H}_{21}\text{BrClON}$: C, 57.82; H, 5.33; N, 3.55. Found: C, 57.68; H, 5.22; N, 3.45%. δ ppm: 14.1 (s, 1H), 8.23 (s, 1H), 7.68–7.70 (d, 1H), 7.33–7.34 (d, 1H), 7.22–7.28 (m, 3H), 2.91–2.98 (m, 2H), 1.18–1.21 (d, 12H).

^{13}C NMR (CDCl_3): δ ppm: 164.87, 156.81, 144.81, 138.62, 135.65, 130.44, 126.09, 123.80, 123.34, 119.43, 111.82, 28.27, 23.63.

2.3.3. 4-Bromo-2-[(2,6-diisopropylphenylimino)methyl]phenol [Br-DPMP]

Overall yield 75%. Anal. Calc. $\text{C}_{19}\text{H}_{22}\text{BrON}$: C, 63.35; H, 6.11; N, 3.89. Found: C, 63.25; H, 6.25; N, 3.99%. δ ppm: 12.95 (s, 1H), 8.28 (s, 1H), 7.03 (d, 1H), 7.23–7.41 (m, 5H), 2.95–3.02 (m, 2H), 1.20–1.23 (d, 12H).

2.3.4. 2-[(2,6-Diisopropylphenylimino)methyl]-4-iodophenol [I-DPMP]

Overall yield 70%. Anal. Calc. $\text{C}_{19}\text{H}_{22}\text{ION}$: C, 56.03; H, 5.41; N, 3.44. Found: C, 56.23; H, 5.60; N, 3.63%. δ ppm: 13.19 (s, 1H), 8.25 (s, 1H), 7.68–7.71 (m, 2H), 7.28 (s, 3H), 6.86–6.91 (d, 1H), 2.90–3.04 (m, 2H), 1.18–1.22 (d, 12H).

^{13}C NMR (CDCl_3): δ ppm: 165.12, 160.83, 145.54, 141.46, 140.16, 138.46, 121.68, 123.25, 120.75, 119.78, 28.22, 23.59.

2.4. Synthesis of complexes

All the complexes were prepared by using the following general procedure. Methanolic solution (20 mL) of the Schiff base (1 mmol) and the metal acetate (0.5 mmol) in methanol (10 mL) were mixed thoroughly and the mixture was boiled under reflux for 4 h and then cooled to room temperature. The resulting precipitate was filtered, washed in ice cold methanol and dried *in vacuo*.

2.5. Typical procedure for cyanosilylation of benzaldehyde

To a stirred solution of benzaldehyde (1 mmol), catalyst (2 mol%) and *N*-methylmorpholine-*N*-oxide (NMO) (2 mol%) in dry THF (1 mL) trimethylsilyl cyanide (TMSCN) (1.5 equiv.) was added dropwise. The resulting solution was stirred continuously and progress of the reaction was followed by TLC. After 2 h, the reaction mixture was purified by silica gel flash chromatography by using a $\text{EtOAc}/\text{hexanes}$ (1:9) mixture as eluent. The desired 2-phenyl-2-(trimethylsilyloxy)acetonitrile was obtained as a colourless oil (yield: 80%). ^1H NMR (CDCl_3 , 200 MHz): δ = 0.25 (s, 9H), 5.52 (s, 1H), 7.42–7.47 (m, 5H). ^{13}C NMR (CDCl_3 , 50 MHz): δ = -0.33, 63.59, 119.12, 126.29, 128.87, 129.27, 136.18. The other silyl ethers thus obtained were identified by NMR data which are consistent with the structure.

Table 1
Colour, magnetic moment and absorption maxima of metal complexes.

Metal	Complex (mole. formula)	Colour	F.W.	Found, % (calculated)				$\mu_{\text{eff.}}$ (B.M.)	$\lambda_{\text{max.}}$ (cm ⁻¹)
				C	H	N	M		
Copper	1. Cu(Br-DPMP) ₂	Lustrous dark brown	781.34	58.26	5.28	3.38	8.03	1.80	13810
	Cu(C ₁₉ H ₂₁ BrON) ₂			58.36	5.38	3.58	8.13		
	2. Cu(Cl-DPMP) ₂	Brown	692.42	65.71	6.17	4.14	9.03	1.92	13790
	Cu(C ₁₉ H ₂₁ ClON) ₂			65.86	6.07	4.04	9.18		
	3. Cu(Br,ClDPMP) ₂	Lustrous dark brown	850.24	53.51	4.60	3.39	7.22	2.10	13140
Nickel	Cu(C ₁₉ H ₂₀ BrClON) ₂			53.63	4.70	3.29	7.47		
	4. Cu(I-DPMP) ₂	Brown	875.32	52.19	4.49	3.29	7.11	1.71	13870
	Cu(C ₁₉ H ₂₁ ION) ₂			52.09	4.79	3.19	7.26		
	5. Cu(Np-DPMP) ₂	Greenish Brown	723.52	76.39	6.71	3.67	8.88	2.12	14184
	Cu(C ₂₃ H ₂₄ NO) ₂			76.29	6.91	3.87	8.78		
Cobalt	1. Ni (Br-DPMP) ₂	Lustrous dark green	776.51	58.42	5.21	3.71	7.66	3.85	12500
	Ni (C ₁₉ H ₂₁ BrON) ₂			58.72	5.41	3.61	7.56		
	2. Ni (Cl-DPMP) ₂	Green	687.59	66.02	6.21	4.17	8.44	3.90	12100
	Ni (C ₁₉ H ₂₁ ClON) ₂			66.32	6.11	4.07	8.54		
	3. Ni (Br,ClDPMP) ₂	Lustrous dark green	845.41	53.84	4.83	3.42	6.84	3.94	13500
Nickel	Ni (C ₁₉ H ₂₀ BrClON) ₂			53.94	4.73	3.31	6.94		
	4. Ni (I-DPMP) ₂	Light green	870.49	52.48	4.93	3.33	6.85	3.84	13200
	Ni (C ₁₉ H ₂₁ ION) ₂			52.38	4.82	3.22	6.74		
	5. Ni (Np-DPMP) ₂	Light green	718.91	76.92	6.86	3.99	8.29	3.81	12300
	Ni (C ₂₃ H ₂₄ NO) ₂			76.81	6.96	3.89	8.17		
Cobalt	1. Co (Br-DPMP) ₂	Deep red	776.73	58.82	5.52	3.73	7.39	4.51	10800
	Co (C ₁₉ H ₂₁ BrON) ₂			58.71	5.41	3.60	7.59		
	2. Co (Cl-DPMP) ₂	Brick red	687.81	66.19	6.22	4.19	8.69	4.48	11100
	Co (C ₁₉ H ₂₁ ClON) ₂			66.29	6.11	4.07	8.57		
	3. Co (Br,ClDPMP) ₂	Reddish orange	845.63	53.82	4.63	3.01	6.87	4.50	11500
Cobalt	Co (C ₁₉ H ₂₀ BrClON) ₂			53.92	4.73	3.31	6.97		
	4. Co (I-DPMP) ₂	Reddish orange	870.71	52.57	4.95	3.33	6.87	4.53	10600
	Co (C ₁₉ H ₂₁ ION) ₂			52.37	4.82	3.22	6.77		
	5. Co (Np-DPMP) ₂	Brick red	718.91	76.88	6.75	3.79	8.09	4.47	11300
	Co (C ₂₃ H ₂₄ NO) ₂			76.78	6.95	3.89	8.19		

2.5.1. Typical procedure for cyanosilylation of acetophenone

The same procedure was also applied to acetophenone. The desired 2-trimethylsilyloxy-2-phenylpropanenitrile was obtained as a colourless oil (yield: 83 %). ¹H NMR (CDCl₃, 200 MHz): δ = 0.16 (s, 9H), 1.84 (s, 3H), 7.35–7.56 (m, 5H). ¹³C NMR (CDCl₃, 100 MHz): δ = 0.89, 33.41, 71.46, 121.45, 124.46, 128.48, 141.87.

3. Results and discussion

The colour, magnetic moments and absorption maxima of metal complexes are given in Table 1. The metal to ligand ratio of all the complexes was found to be 1:2. The chelates are soluble in CH₃CN and DMSO but insoluble in water.

3.1. Magnetic measurements

The magnetic susceptibility measurements in the solid state show that the present complexes are paramagnetic at room temperature. The $\mu_{\text{eff.}}$ value of the copper(II) complexes fall in the 1.80–2.12 B.M. range corresponding to one unpaired electron. For Ni(II) and Co(II) complexes, the observed magnetic moment values suggest a high spin octahedral structure.

3.2. Electronic spectra

The electronic spectra of ligands show characteristic bands in the 32,787 cm⁻¹ and 25,773 cm⁻¹ region representing intraligand charge transfer transitions. The electronic spectra of the copper complexes in CHCl₃ or CH₃CN solution exhibit a broad band in the 13,141–14,184 cm⁻¹ region which may be assigned to ²B_{1g} → ²B_{2g} transition in a square planar geometry. In addition to this, there is a shoulder observed around 21,900 cm⁻¹ [24].

The nickel(II) complexes exhibit a band in the 12,100–14,800 cm⁻¹ region assigned to octahedral environment [25]. The

peak observed for cobalt complexes in the 10,500–11,500 and 21,000–21,500 cm⁻¹ regions assigned to ⁴T_{1g} [F] → ⁴T_{2g} and ⁴T_{1g} [F] → ⁴T_{2g} [P] respectively, are characteristic of an octahedral configuration [26].

3.3. IR spectra

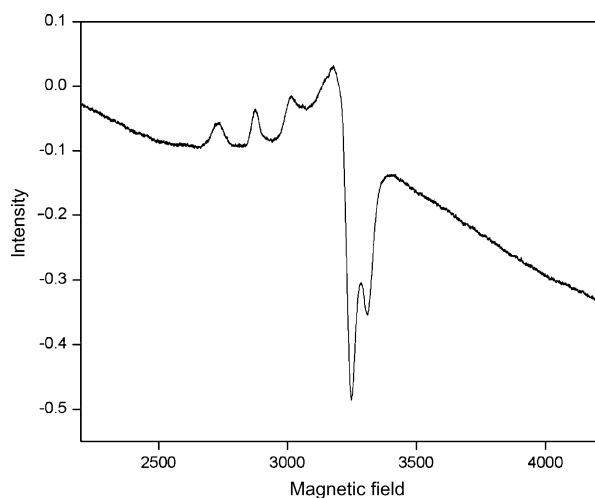
The characteristic IR frequencies of the free ligands and their metal(II) chelates are given in Table 2. IR spectra of the ligands show absorption around 3440 cm⁻¹ with medium intensity due to $\nu(\text{OH})$. The absence of bands characteristic of the amino group of 2,6-diisopropylaniline and the carbonyl group of substituted aldehydes and the appearance of a new strong intensity band around 1625 cm⁻¹ characteristic of azomethine group, $\nu(\text{C}=\text{N})$ confirm that condensation between the aforesaid reactants has taken place [27]. The $\nu(\text{C}=\text{N})$ undergoes a negative shift of 15–30 cm⁻¹ in the complexes, which may be attributed to the coordination of the nitrogen atom of azomethine group to the metal ion [28]. A band around 600 cm⁻¹ in the complexes is assigned to $\nu(\text{M}-\text{O})$ and the values of $\nu(\text{M}-\text{O})$ follow the order Cu > Ni > Co, in parallel with the crystal field stabilization energies [29].

3.4. EPR spectra

The X-band EPR spectra of copper complexes were recorded in acetonitrile solution. The EPR spectral parameters derived from their respective spectra are presented in Table 3. Representative EPR spectrum of Cu(II) complex is given in Fig. 2. The EPR spectra of copper complexes in solution exhibit a set of four well-resolved peaks in the high field region. The “g” tensor values of the copper(II) complexes can be used to obtain the ground state [30–32]. In axially elongated octahedral and square planar complexes, the unpaired electron occupies the $d_{x^2-y^2}$ orbital with ²B_{1g} ground state resulting in $g_{\parallel} > g_{\perp}$. However, in a compressed octahedron

Table 2
Infrared spectral bands for the ligands and their metal complexes.

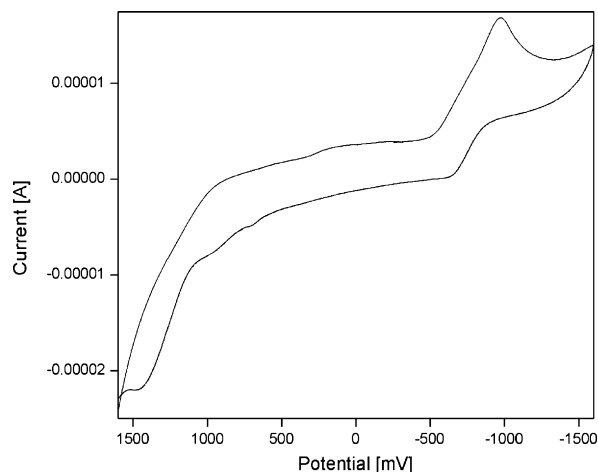
S. no.	Ligand and complex	$\nu(\text{OH})$	$\nu(\text{CH}=\text{N})$
Free ligand			
1	Br DPMP	3444	1624
2	Cl DPMP	3444	1624
3	BrCl DPMP	3436	1623
4	I DPMP	3435	1623
5	Np DPMP	3444	1623
Copper complex			
1	Cu(Br-DPMP) ₂	–	1608
2	Cu(Cl-DPMP) ₂	–	1605
3	Cu(Br,Cl-DPMP) ₂	–	1606
4	Cu(I-DPMP) ₂	–	1600
5	Cu(Np-DPMP) ₂	–	1608
Nickel complex			
1	Ni(Br-DPMP) ₂	–	1606
2	Ni(Cl-DPMP) ₂	–	1600
3	Ni(Br,Cl-DPMP) ₂	–	1604
4	Ni(I-DPMP) ₂	–	1604
5	Ni(Np-DPMP) ₂	–	1608
Cobalt complex			
1	Co (Br-DPMP) ₂	–	1600
2	Co (Cl-DPMP) ₂	–	1593
3	Co (Br,Cl-DPMP) ₂	–	1596
4	Co (I-DPMP) ₂	–	1595
5	Co (Np-DPMP) ₂	–	1600

**Fig. 2.** ESR spectra of Cu(Br-DPMP)₂ at LNT.

the unpaired electron occupies the d_z^2 orbital with $^2A_{1g}$ ground state having $g_{\perp} > g_{\parallel}$. The observed “g” values suggest that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital. The quotient $g_{\parallel}/A_{\parallel}$ are empirically treated as a measure of the distortion from planarity. The range of our values (158–160) for copper(II) complexes of Br and Cl substituents at the fifth position clearly indicate a slight tetrahedral distortion. For a naphthyl derivative the observed A_{\parallel} values suggest delocalization of the unpaired electron on copper(II) making the coordination plane more planar [33,34].

Table 3
ESR spectral parameters of the copper(II) complexes.

S. no.	Copper Complex	g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}	$g_{\parallel}/A_{\parallel}$	α_{Cu}^2
1	Cu(Br-DPMP) ₂	2.2522	2.0751	140	70	160	0.7778
2	Cu(Cl-DPMP) ₂	2.2545	2.0820	145	52	155	0.8056
3	Cu(Br,Cl-DPMP) ₂	2.2603	2.0733	143	60	158	0.7944
4	Cu(I-DPMP) ₂	2.2332	2.0985	173	56	129	0.9610
5	Cu(Np-DPMP) ₂	2.2290	2.0844	186	90	120	0.9818

**Fig. 3.** Cyclic voltammogram of Cu(Br,Cl-DPMP)₂ in CH₃CN.**Table 4**
Electrochemical data of copper complexes.

S. no.	Copper complex	E_p^a	E_p^c	ΔE_p
1	Cu(Br-DPMP) ₂	–1344	–657	687
2	Cu(Cl-DPMP) ₂	–976	–648	328
3	Cu(Br,Cl-DPMP) ₂	–1165	–646	519
4	Cu(I-DPMP) ₂	–1176	–634	542
5	Cu(Np-DPMP) ₂	–1127	–649	478

The α^2 values fall in the 0.7–0.9 range, indicating a fair degree of metal–ligand covalency [35].

3.5. Cyclic voltammetry

Cyclic voltammograms of the present complexes were recorded in CH₃CN with tetrabutylammonium perchlorate as the supporting electrolyte in the potential +1.6 V to –1.6 V range.

3.5.1. Copper complexes

A typical voltammogram of Cu is displayed in Fig. 3. Copper complexes show an irreversible redox value [$E_p^c = -646$ to -657 mV, $E_{p1}^a = -976$ to -1334 mV] with an additional oxidation wave [E_{p2}^a] in the 683–987 mV range (Table 4). The cyclic voltammogram shows that the electron transfer occurring for reduction reactions is two-electron reduction [$\text{Cu}^{2+} \rightarrow \text{Cu}^0$, E_p^c] and the corresponding oxidation reaction occurs in two steps [$\text{Cu}^0 \rightarrow \text{Cu}^+$, $\text{Cu}^+ \rightarrow \text{Cu}^{2+}$, E_{p1}^a , E_{p2}^a]. The electrochemical behavior of Cu(I-DPMP)₂ and Cu(Np-DPMP)₂ are different from that observed for others. These two complexes exhibit two-step reduction waves and two oxidation waves. The change in separation of the peak potential reflects the stability of the copper complexes of different oxidation states. The result indicates that the stability of the low oxidation state of copper complex is greater than that of the high oxidation state copper complex [36]. Similar observations were reported for copper(II) mononuclear complexes containing substituted salicylaldehydes [37].

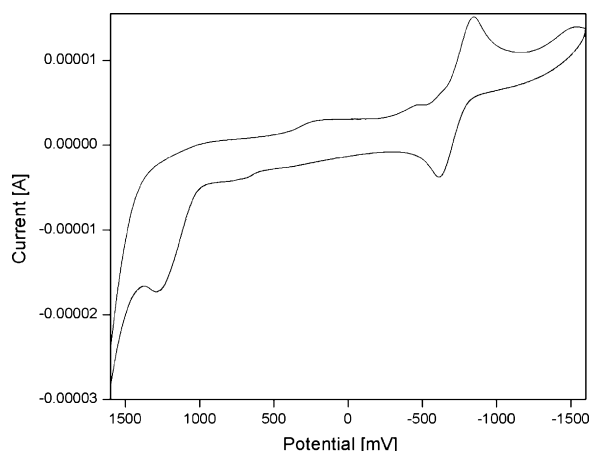


Fig. 4. Cyclic voltammogram of Ni(Br,Cl-DPMP)₂ in CH₃CN.

Table 5
Electrochemical data of nickel(II) complexes.

S. no.	Nickel complex	E_p^a	E_p^c	ΔE_p
1	Ni (Br-DPMP) ₂	-868	-591	277
2	Ni (Cl-DPMP) ₂	-848	-610	238
3	Ni (Br,Cl-DPMP) ₂	-1061	-560	501
4	Ni (I-DPMP) ₂	-896	-588	308

The cyclic voltammogram of nickel(II) complexes measured in CH₃CN vs Ag–AgCl are shown in Fig. 4 and the electrochemical data of Ni complexes are listed in Table 5.

For the Ni(II)–Ni(I) reduction, the half wave potentials are in the –560 to –610 mV range. The corresponding separations between the reduction and oxidation peaks are in the 277–501 mV range for scanning rates of 100 mVs⁻¹. The M(II)–M(I) reductions are irreversible in every case.

The redox behaviour of Cu(II) and Ni(II) complexes at glassy carbon electrode surface follows a diffusion-controlled process which is evident from the plot of \sqrt{SR} vs peak current (Figs. 5 and 6). A straight line was obtained for lower scanning rates (25–125 mV s⁻¹).

3.5.2. Effect of bases

The cyclic voltammograms were recorded in order to examine the effect of axially coordinating ligands on the redox behaviour of the Cu(I-DPMP)₂ complex (Fig. 7). The cyclic voltammograms were recorded in acetonitrile after the addition of an appropriate quantity of bases. The results are summarized in Table 6. The

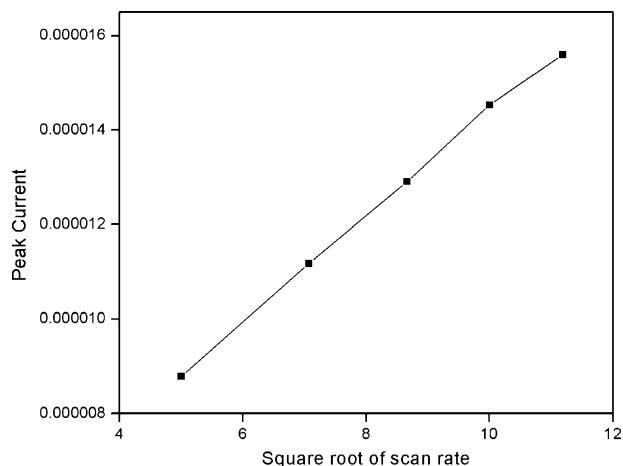


Fig. 5. Plot of $\sqrt{\text{scan rate}}$ vs peak current for Cu(I-DPMP)₂.

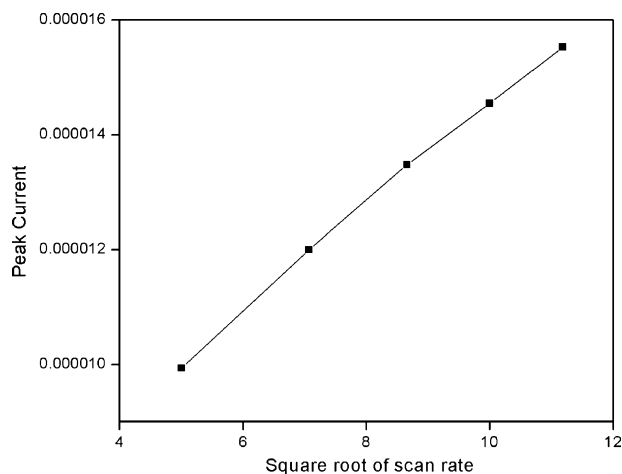


Fig. 6. Plot of $\sqrt{\text{scan rate}}$ vs peak current for Ni(Br,Cl-DPMP)₂.

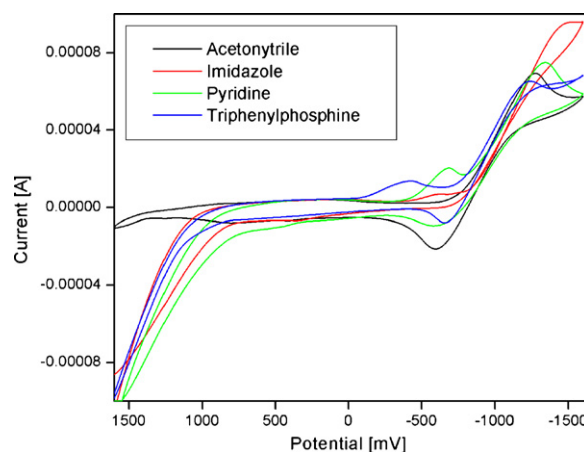


Fig. 7. Effect of added bases on Cu(I-DPMP)₂.

cathodic peak potential of the copper complex is shifted towards the more negative region on the addition of bases. This result can be explained on the basis that the added bases contribute a net additional charge to the central metal atom, which is evident from a shift in the potential values.

3.6. Catalytic studies

The catalytic addition reaction of trimethylsilyl cyanide to carbonyl compounds is an area of active study due to the synthetic versatility of cyanohydrins. This can be elaborated into a variety of useful synthetic building blocks such as α -hydroxyacids, α -hydroxyaldehydes, 1,2-diols, and α -amino alcohols [38]. Many metal complexes have been employed as Lewis acid catalysts for the addition of HCN or TMSCN to aldehydes and ketones, for example, magnesium, zirconium, titanium, aluminium, yttrium, lanthanum, samarium, vanadium and gadolinium complexes containing mono- or polydentate ligands [39]. Metal halides, such as AlCl₃, BiBr₃, InX₃, LnCl₃ (Ln = La, Ce, Sm), MgBr₂, SnCl₄, TiCl₄, ZnI₂ and Cu(OTf)₂, are known to be Lewis acid catalysts for cyanosilylation of aldehydes

Table 6
Electrochemical results (in mV) of added bases.

S. no.	Cu(I-DPMP) ₂ in	CH ₃ CN	Imidazole	Pyridine	Triphenylphosphine
1	E_p^a	-592	-633	-592	-663
2	E_p^c	-1270	-1468	-1335	-1231

Table 7
Cyanosilylation of benzaldehyde under various conditions in THF.

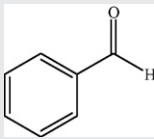
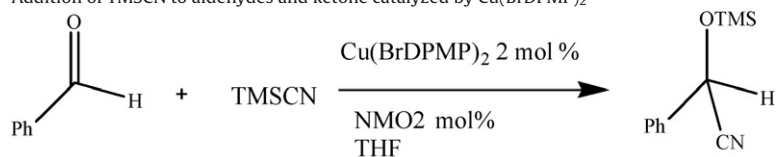
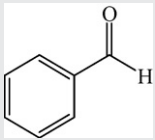
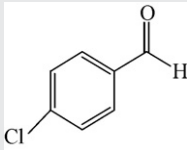
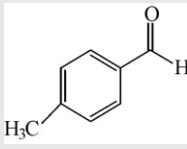
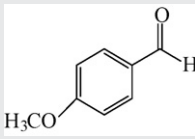
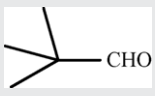
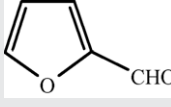
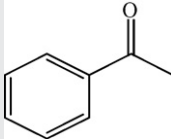
S. no.	Substrate	Catalyst (mol %)	Additive (NMO) (mol %)	Time (h)	Yield (%)
1		1	2	3.30	78
2		2	2	2	80
3		3	2	1	81
4		4	2	1	83
5		5	2	1	82
6		–	2	4	Trace
7		2	–	4	No reaction

Table 8
Addition of TMSCN to aldehydes and ketone catalyzed by Cu(BrDPMP)₂



Entry	Substrate	Time (h)	Yield (%) ^a	Literature values	
				Time (h)	Yield (%)
1		2	80	24	70 ^b
				3	81 ^c
2		2	83	3	75 ^d
				2	80
3		2	78	12	80 ^e
4		2.15	85		
5		2	80		
6		1.45	85		
7		4	83		

^a Isolated yield.

^b [50].

^c [51].

^d [52].

^e [53].

[40]. Lithium chloride acts as a highly effective catalyst for cyanosilylation of various aldehydes and ketones [41].

The chiral Cu complex catalysts for asymmetric reactions such as aziridination [42], Diels–Alder reactions [43], cyclopropanation [44], carbenoid insertion of diazoacetates into the Si–H bond of silanes [45,46] have been studied and recently the complexes of Cu(II) with chiral bidentate ligands of bisoxazolines for asymmetric Henry reaction have shown promising results [47].

Though several salen based metal complexes have been used for cyanosilylation of aldehydes, no work has been reported for copper salen complexes. The catalytic activity of Cu(Br–DPMP)₂ was tested with benzaldehyde as a model substrate (Table 7). When a mixture of benzaldehyde (1 mmol) and TMSCN (1.2 equiv.) was treated with various amounts of copper complex (1–5 mol%) and NMO as additive at room temperature, the cyanide addition occurs smoothly (entries 1–5). The amount of catalyst appeared to be an important parameter for the reduction of reaction time. With increased quantity of catalyst, the reaction took place more rapidly (entries 1 and 2). We have found that 2 mol% of copper catalyst is the optimal condition for a good yield (80%) at room temperature. Further reduction in catalytic loading requires longer reaction time. No reaction takes place without copper complex or without NMO (entry 6).

The scope of copper complex catalyzed cyanosilylation was explored by using substituted aromatic aldehydes. Table 8 summarizes the most significant results obtained under optimized conditions. In all cases, aromatic aldehydes were converted into the corresponding silyl ethers in moderate to good yields. The copper catalyzed system is still a better method in terms of reaction time and catalyst loading because only 2 mol% catalytic loading is required for effective reaction to take place. LiClO₄-catalyzed cyanosilylation requires 100 mol% of catalytic loading [48] and Zr(KPO₄)₂-catalyzed reaction proceeds with 35 mol% of catalyst for complete conversion of benzaldehyde [49]. It should be noted that the sterically hindered pivalaldehyde was transformed into the corresponding silyl ether in 80% yield. Furfural, a heterocyclic aldehyde gives corresponding silyl ether in a good yield (85%). As shown in Table 8, our catalytic system requires moderate catalytic loading and short reaction time compared to the previous studies. The procedure tolerates a wide variety of substrates due to the Lewis acid property of copper.

We tested the cyanosilylation of ketones using the same catalytic conditions. Using acetophenone as the substrate, the cyanosilylation reaction took 4 h and gave an 83% yield. The difference in structure between aldehydes and ketones appeared to change the required reaction time from 2 h (aldehydes) to 4 h (acetophenone). The detailed results for the cyanosilylation of ketones will be published later. Further investigations to clarify the reaction mechanism and the recovery and reuse of the catalyst are in progress.

4. Conclusions

Copper(II), Nickel(II) and Cobalt(II) complexes of multisubstituted Schiff base ligands have been prepared and characterized. The magnetic and spectral evidence shows that the complexes are formed through the coordination of phenolic oxygen and the azomethine nitrogen atoms. The EPR spectral data of copper complexes reveal that there is a slight distortion of the complexes. The redox behaviour of Cu(II) and Ni(II) complexes at glassy carbon electrode surface follows a diffusion controlled process. The newly prepared copper complex possesses a good catalytic ability for cyanosilylation of aldehydes under mild conditions.

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