

Synthesis, Characterization, Thermal, and Electrochemical Properties of Co(II) and Cu(II) Pseudohalide Complexes with 2-mercapto-3-phenyl-quinazolin-4(3H)-one and ethylendiamine or 1,10-phenanthroline as Ligands

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Several complexes of the type $[M(L)(en \text{ or phen})(H_2O)X]$ (1a-4a and 1b-4b); where M = Co(II) and Cu(II); L = 2-mercapto-3-phenyl-quinazolin-4(3H)-one; en = ethylenediamine, phen = 1,10-phenanthroline; $X = N_3^-$ and NCS⁻ have been prepared and characterized. The complex formation occurred through both nitrogen and sulphur atom of the ligand L. Electronic spectra and magnetic moment values suggest octahedral geometry for all complexes. The thermal behavior of the complexes revealed that the phen complexes are thermally more stable than the en complexes. The electrochemical behavior of the Cu(II) complexes showed that phen complexes appeared at more positive potential than corresponding en complexes.

Keywords mixed ligands, quinazolinone derivatives, thermal studies, cyclic voltammetry

INTRODUCTION

The coordination chemistry of transition metal complexes with hybrid ligands are of current interest because they can provide new materials with useful properties such as magnetic exchange,^[1,2] electrical conductivity,^[3] photoluminescence,^[4] nonlinear optical property,^[5] and antimicrobial activity.^[6] Among various ligands quinazolinone containing nitrogen, sulphur donor atoms have received much attention in recent years. These compounds exhibit varieties of biological properties, especially anti-inflammatory,^[7] anticonvulsant,^[8] antihypertensive,^[9] anticancer,^[10,11] antimalarial,^[12] antibacterial,^[13] etc. The presence of endocyclic hard N-donor and exocyclic soft S-donor atoms in the backbone of these ligands enable them to react readily with transition metal ions to form stable complexes with unusual structural and chemical properties. Owing to their versatile bioactivities and the potential applications in various fields, the coordinating behavior of quinazolinone ligands with transition metal ions has been studied extensively.^[14-17] Ethylenediamine and 1,10-phenanthroline chelators are also good nitrogen donors, and the complexes formed serve as building blocks for the synthesis of metallodendrimers, as a molecular scaffolding for supramolecular assemblies, and in analytical chemistry, catalysis, electrochemistry, ring-opening metathesis polymerization.^[18–21] They also act as potential antitumor agents and show better antitumor activity if they form water soluble neutral complexes with transition metal ions.^[22] Pseudohalides, especially azide (N_3^-) and thiocynate (NCS^-) , are known for construction of monomeric, dimeric, or polymeric complexes because of their versatile coordination modes and ability to mediate strong magnetic coupling.

In continuation of our earlier work on structural characterization of transition metal complexes containing quinazolinone ligands,^[23] here we report the synthesis, properties and molecular structure of Co(II) and Cu(II) complexes of 2-mercapto-3-phenyl-quinazolin-4(3H)-one (L) with ethylenediamine (**en**) or 1,10-phenanthroline (**phen**) and N_3^- or NCS⁻ as coligands. The complexes were characterized on the basis of elemental analysis, molar conductance, magnetic moment, spectroscopic (IR, UV-visible and ESR), and thermal studies. The redox behavior of Cu(II) complexes has also been studied by cyclic voltammetry.

EXPERIMENTAL

Reagents

All the chemicals used were pure and of analytical grade. 2-mercapto-3-phenyl-quinazolin-4(3H)-one was synthesized by reported method.^[24] Cu(NO₃)₂·3H₂O (E-Merk India), Co(NO₃)₂·6H₂O (E-Merk India), NaN₃ (Aldrich, USA), NH₄NCS (Aldrich, USA), ethylenediamine, 1,10-phenanthroline (Alfa Aesar) were purchased from the respective concerns and were used as received.

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FIG. 1. Proposed molecular structure of the complexes (M = Co(II) or Cu(II); $X = N_3$ or NCS).

Physical Measurements

Elemental analysis (C, H, N and S) were performed on a Thermo Finnigan FLASH EA-112 CHNS analyzer. Molar conductance (Λ_M) was measured on the Elico (CM-185) conductivity bridge using ca. 10^{-3} M DMF solution. Electronic spectra were recorded on a Shimadzu 3600 UV-visible-NIR spectrophotometer. Magnetic susceptibility was measured on Gouy balance at room temperature using Hg[Co(NCS)₄] as a calibrant. IR spectra were recorded on Perkin Elmer FT-IR spectrometer 2000 as KBr pellets in the 4000–400 cm⁻¹ spectral range. The X-band ESR spectra of Cu(II) complexes have been recorded in the polycrystalline state at room temperature and in DMF solution at 77K on Varian E-112 spectrometer using TCNE as the standard marker. Thermal analysis of the complexes was carried out on a Perkin Elmer thermal analyzer in nitrogen atmosphere at a heating rate of 10°C/min. Cyclic voltammetry measurements were performed with Electrochemical Quartz Crystal Microbalance CHI-400. A standard three electrode system, consisting of Pt disk working electrode, Pt wire counter electrode, and Ag/AgCl reference electrode containing aqueous 3M KCl were used. All potentials were converted to SCE scale.

Synthesis of Complexes

Preparation of Azido Complexes (1a-4a)

To a methanolic solution (5 mL) of appropriate metal salt (1 mmol, 0.291 g, $Co(NO_3)_2.6H_2O$, 0.241 g $Cu(NO_3)_2.3H_2O$), a methanolic solution of **L** (1 mmol, 0.256 g) was added while stirring. To this, a methanolic solution (5 mL) of **en** (1 mmol, 0.060 g) or **phen** (1 mmol, 0.198 g) was added, followed by the addition of NaN₃(1 mmol, 0.065 g) in warm methanol. The resultant mixture was refluxed for 3 h. The solid product obtained was filtered, washed with methanol, and dried under vacuum over CaCl₂.

Preparation of Thiocyanato Complexes (1b-4b)

A methanolic solution (5 mL) of ligand L (1 mmol, 0.256 g) was added drop wise to a solution (5 mL) of appropriate metal salt (1 mmol, 0.291 g, $Co(NO_3)_2.6H_2O$, 0.241 g $Cu(NO_3)_2.3H_2O$) in the same solvent followed by addition of en (1 mmol, 0.060 g) or phen (1 mmol, 0.198 g) and NH₄NCS (1 mmol, 0.076 g) in warm methanol. The resultant mixture was



FIG. 2. ESR spectrum of 4b in DMF solution at 77 K.



FIG. 3. TG, DTG and DTA curves of 4b.

refluxed for 3 h. The product obtained was filtered, washed with methanol and dried under vacuum over CaCl₂.

RESULTS AND DISCUSSION

The reaction of ligand \mathbf{L} with metal(II) salts in presence of ethylenediamine or 1,10-phenanthroline and NaN₃ or NH₄NCS yielded the complexes of the type [M(L)(en or phen)(H₂O)(N₃ or NCS)], as shown in Figure 1. The general reaction for the formation of the complexes is shown as

$$\begin{split} M(NO_3)_2 \cdot nH_2O + \mathbf{L} + \textbf{en} \text{ or } \textbf{phen} + NaN_3 \rightarrow & [M(\mathbf{L})(\textbf{en} \text{ or } \textbf{phen})(H_2O)(N_3)] \ \textbf{(1a-4a)} \end{split}$$

$$\begin{split} M(NO_3)_2 \cdot nH_2O + \mathbf{L} + \mathbf{en} \text{ or } \mathbf{phen} + NH_4NCS \rightarrow [M(\mathbf{L})(\mathbf{en} \\ \text{ or } \mathbf{phen})(H_2O)(NCS)] \ (\mathbf{1b-4b}) \end{split}$$

 $M = Co(II) \{n = 6\}$ and $Cu(II) \{n = 3\}$; L = 2-mercapto-3-phenyl-quinazolin-4(3H)-one; **en** = ethylenediamine, **phen** = 1,10-phenanthroline

The results of the elemental analysis of all the complexes are in good agreement with those required by the proposed formula. The complexes are insoluble in common organic solvents except DMF and DMSO. The molar conductivity values of the compounds in DMF $(10^{-3} \text{mol dm}^{-3})$ (Table 1) indicates that they are non-electrolytic in nature.

Infrared Spectra

The main stretching frequencies of the IR spectra of the complexes are presented in Table 2. In the IR spectra of L, v(NH) band appear at 3248 cm⁻¹ and absence of v(SH) band near 2600 cm⁻¹ indicates the thione structural form of the ligand in solid state. The absence of v(NH) band in the spectra of all the complexes provides strong evidence for involvement of ligand coordination in deprotonated form.^[25] The characteristic ν (C=O) frequency of ligand L occurs at 1680 cm⁻¹ remains unaltered in all complexes, ruling out the possibility of coordination through carbonyl group of quinazoline ligand. The ligand L contains a thioamide group (-HN-C=S) and gives rise to four characteristic thioamide bands (I-IV) at 1533, 1339, 988, and 842 cm⁻¹.^[26] The thioamide band-I [δ (NH) + δ (C-N)] observed at 1533 cm⁻¹ in L splits up in the spectra of the complexes suggest the coordination through imino nitrogen atom of L. The two bands appearing at the frequency 1339 cm⁻¹ [ν (C=N) + δ (NH) + δ (CH) + ν (C=S)] thioamide band-II and 842 cm⁻¹ [ν (C=S)] thioamide band-IV in the spectra of L shifted to lower frequencies in the range 1305–1326 cm^{-1} and 832–839 cm^{-1} indicating coordination of thione/thiolato sulfur. The thioamide band-III observed at

					Analytical da	ta % found (calculated)		- -
	M.F.	Yield							$\Lambda_M \Omega^{-1} cm^2$
Complex	Color	%	M.P. °C	Μ	C	Н	Z	S	mol ⁻¹
$[Co(L)(en)(H_2O)N_3]$ (1a) C_{10}	6H19N7O2SCo (light green)	74	>300	13.69 (13.63)	44.17 (44.45)	4.21 (4.43) 2	2.47 (22.68)	7.11 (7.42)	24.42
$[Cu(L)(en)(H_2O)N_3]$ (2a) $C_{1(1)}$	6H19N7O2SCu (dark green)	76	>300	14.67 (14.54)	43.67 (43.98)	4.01 (4.38) 2	(22.53 (22.44)	7.01 (7.34)	22.30
$[Co(L)(phen)(H_2O)N_3]$ (3a) C_{20}	6H19N7O2SCo (dark yellow)	72	>300	10.47 (10.67)	56.13 (56.52)	3.11 (3.47) 1	7.63 (17.75)	5.37 (5.80)	23.36
$[Cu(L)(phen)(H_2O)N_3]$ (4a) C_{20}	6H19N7O2SCu (green)	78	>300	11.23 (11.41)	56.28 (56.06)	3.31 (3.44) 1	7.79 (17.60)	5.61 (5.76)	25.48
$[Co(L)(en)(H_2O)NCS] (1b) C_{17}$	7H19N5O2S2Co (light green)	79	>300	13.19 (13.14)	45.11 (45.53)	4.09 (4.27) 1	5.39 (15.62)	(13.93 (14.30)	20.17
$[Cu(L)(en)(H_2O)NCS] (2b) C_{13}$	7H19N5O2S2Cu (dark green)	76	>300	14.19 (14.03)	44.93 (45.07)	4.11 (4.23) 1	5.13 (15.46)	13.83 (14.16)	22.30
$[Co(L)(phen)(H_2O)NCS] (3b) C_{23}$	7H19N5O2S2Co (yellow)	83	>300	10.41 (10.37)	56.83 (57.04)	3.23 (3.37) 1	2.03 (12.32)	(11.02 (11.28)	25.48
$[Cu(L)(phen)(H_2O)NCS] (4b) C_{2}$	$_7H_{19}N_5O_2S_2Cu$ (green)	74	>300	10.81 (11.09)	56.21 (56.58)	3.21 (3.34) 1	2.17 (12.22)	(11.03 (11.21)	29.73

TABLE 1 Analytical and physico-chemical data of the metal complexes

 TABLE 2

 Infrared spectral data of metal complexes

					Thioa	umide b	ands		Selected	
Compound	$\nu H_2 O$	νNH_2	ν C= Ο	$\nu N_3 / \nu NCS$	Ι	Π	III	IV	ν (phen)	vM-N
1a	3447, 816	3237, 3296	1704	2056, 1345	1562, 1543	1317	988	839	-	469
2a	3479, 818	3243, 3292	1675	2057, 1346	1573, 1540	1320	986	835	-	465
3a	3442, 816	-	1688	2046, 1344	1573, 1540	1314	979	838	1506, 1434, 848, 716	472
4 a	3428, 820	-	1707	2056, 1342	1568, 1542	1310	978	836	1505, 1445, 847, 719	464
1b	3430, 816	3242, 3308	1693	2071, 764, 499	1562, 1534	1317	978	832	-	469
2b	3489, 817	3243, 3292	1675	2073, 762, 485	1573, 1526	1305	976	835	-	469
3b	3407, 819	-	1688	2070, 759, 495	1573, 1540	1326	974	832	1513, 1423, 845, 724	469
4b	3422, 819	-	1698	2076, 762, 489	1578, 1542	1316	978	835	1510, 1426, 845, 724	454

Thioamide bands: Band-I (δ NH + δ C-N) Band-II (ν C=N + δ NH + δ CH + ν C=S) Band-III (ν C=S + ν C=N) Band-IV (ν C=S)

988 cm $^{-1}$ in L also reduced in intensity on coordination with metal ion. $^{\left[27\right] }$

The spectra of mixed en complexes (1a, 1b, 2a and 2b) shows two characteristic bands at around 3232 and 3300 cm⁻¹ assigned to v_{sym} and v_{asym}vibration of NH₂ suggesting coordination through NH₂.^[28] The bands observed at around 1510, 1426, 845, and 720 in the mixed phen complexes (3a,3b, 4a and **4b**) due to ν (C=N), ν (C=C) and out-of-plane CH stretching vibrations of 1,10-phenanthroline, confirms the presence of **phen** ligand in the coordination sphere of the complexes. The azido complexes (1a-4a) show a sharp band at ~ 2055 cm^{-1} and a strong band at ~1346 cm^{-1} . These are assigned to v_a and v_s vibrations of the coordinated azido group.^[29] The thiocynate complexes (1b-4b) exhibit a strong sharp band at \sim 2075 cm⁻¹, a weak band at \sim 762 cm⁻¹ and another weak band at ~485 cm⁻¹, which can be attributed to v(CN), v(CS)and v(NCS), respectively. These values are typical for N-bonded thiocynate complexes.^[30] In the spectra of all the complexes, a broad band centered at \sim 3440 cm⁻¹ together with a new band at \sim 820 cm⁻¹ indicates presence of water molecules in the coordination sphere of the complexes.

Electronic Spectra and Magnetic Moments

The electronic spectra in dimethylformamide $(10^{-4} \text{ mol} \text{ dm}^{-3})$ and magnetic moment values of the metal complexes are listed in Table 3. The transitions below 400 nm observed in complexes may be attributed to usual $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions occurring within ligand orbitals. The electronic spectra of Co(II) complexes (**1a**, **1b**, **3a** and **3b**) display two bands in the range of 652–698 and 484–496 nm that may be assigned to ${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}A_{2g}({}^{4}F) (\nu_{2})$ and ${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}T_{1g}({}^{4}P) (\nu_{3})$, indicating octahedral configuration around Co(II). The absorption band due to ${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}T_{2g}({}^{4}F) (\nu_{1})$ is not often observed. This might be due to presence of this band near IR region around 1237–1242 nm. The μ_{eff} value measured for the Co(II) complexes are in the range 4.79–4.88 μ_B , which is fairly close

to those reported for the unpaired electrons of Co(II) ion in an octahedral environment.^[31] The electronic spectra of Cu(II) complexes (**2a**, **2b**, **4a**, and **4b**) shows a broad band centered at around 690 nm that may be due to ${}^{2}\text{Eg} \rightarrow {}^{2}\text{T}_{2g}$ transition in octahedral environment. The observed magnetic moment of 1.84–1.89 μ_{B} for all the Cu(II) complexes support octahedral geometry around Cu(II).^[32]

ESR Spectra

The X-band ESR spectra of the Cu(II) complexes were recorded in polycrystalline state at room temperature and in DMF solution at 77 K. The ESR spectral assignments of the complexes along with the spin Hamiltonian and orbital reduction parameters are summarized in Table 4.

The room temperature ESR spectra of all the Cu(II) complexes (**2a**, **2b**, **4a** and **4b**) in the polycrystalline state show typical axial behavior with slightly different g_{\parallel} and g_{\perp} values. The geometric parameter G, which is a measure of exchange interaction between the copper centers in polycrystalline

TABLE 3 Electronic spectra and magnetic moment values of the metal complexes

Compound	$\mu_{\mathrm{eff}} \mu_{\mathrm{B}}$	$\pi \to \pi^*$ and $n \to \pi^*$ transitions and charge transfer transitions (nm)	$d \rightarrow d$ transitions (nm)
1a	4.83	262, 299, 348	492, 662
2a	1.89	274, 304, 350	704
3a	4.88	260, 304, 364	496, 698
4 a	1.87	264, 296, 374	694
1b	4.88	258, 274, 336	486, 652
2b	1.87	274, 296, 393	726
3b	4.79	266, 304, 348	484, 688
4b	1.84	278, 304, 392	698



FIG. 4. Cyclic voltammogram of 4a.

compound, is calculated using the equation $G = (g_{\parallel} - 2.0023)/(g_{\perp} > 2.0023)$. In all the Cu(II) complexes, $g_{\parallel} > g_{\perp} > 2.0023$ and G values within the range 3.69–4.04 are consistent with the d_{x2-y2} ground state.^[33]

The ESR spectra of all the Cu(II) complexes in DMF solution at 77K (Figure 2) possesses well resolved hyperfine spectra that was unresolved at room temperature suggesting that complexes are monomer. No band corresponding to forbidden magnetic dipolar transition ($\Delta Ms = \pm 2$) was observed in the spectra of the complexes also support the complexes are mononuclear. The spectra presents four lines in the g_{\parallel} region giving $g_{\parallel} > g_{\perp} >$ 2.0023, corresponding to the presence of an unpaired electron in the d_{x2-y2} orbital. The g_{\parallel} values for all the Cu(II) complexes are less than 2.3, which is an indication of significant covalent bonding in these complexes.

The ESR parameters g_{\parallel} , g_{\perp} , g_{av} , A_{\parallel} and A_{\perp} and the energies of the d-d transitions were used to evaluate the bonding parameters α^2 , β^2 and γ^2 , which may be regarded as measures of covalency of the in-plane σ -bonding, in-plane π -bonding and out-of-plane π -bonding, respectively, and orbital reduction factor K. The values of bonding parameters α^2 , β^2 and $\gamma^2 < 1.0$ indicate significant in-plane σ -bonding and in-plane π -bonding. The value of K_{||} and K_⊥, which are the parallel and perpendicular components of orbital reduction factor, also provides information about the nature of bonding in the complexes. The complexes show the value of K_{||} and K_⊥ in order K_{||} < K_⊥, which suggest the considerable in-plane π -bonding in the complexes.

The Fermi contact hyperfine interaction term K were obtained from the equation.^[34]

$$K = A_{av}/P\beta^2 + (g_{av} - 2.00277)/\beta^2$$

where P is the free ion dipolar term and its value is 0.036. K is dimensionless quantity and is generally found to have a value of 0.30. The K values obtained for all the complexes are in agreement with those reported for Cu(II) complexes.^[35,36]

Thermal Analysis

The thermal decomposition studies of all Cu(II) complexes were carried out up to 1200°C under N₂ atmosphere. Typical TG, DTG, and DTA curves of **4b** are presented in Figure 3, and thermal analysis data is summarized in Table 5.

The thermal decomposition process of azide complexes 2a and 4a involves four decomposition stages. The first stage takes place in the range 158–189°C and 179–213°C, with endothermic DTA peaks at 176°C (2a) and 201°C (4a), respectively, corresponding to mass loss 4.57 and 3.62% of coordinated water molecule (Calc. % = 4.12 and 3.23). The second stage occurs in the range 189–276°C and 213–354°C accompanied by a mass loss of 9.87 and 7.71%, respectively, and may be attributed to the decomposition of the azide ion with endothermic DTA peaks at 228°C (2a) and 296°C (4a) (Calc. % = 9.61 and 7.54). The third stage corresponding to the mass loss of 31.26 and 46.08% may be attributed to the decomposition of half molecule of the 'L' and ethylenediamine or 1,10-phenanthroline (Calc. % =31.39 and 46.19) in the 276–568°C and 354–673°C range, respectively. The DTA curve gives endothermic peaks at 380 and 457°C for complex 2a and at 454 and 562°C for 4a. In the fourth stage (568-1070 and 673-1182°C), a mass loss of 40.24 and 31.46% corresponding to the decomposition of the rest of

 TABLE 4

 ESR spectral assignments for Cu(II) complexes in polycrystalline state (298 K) and solution (77 K)

	Polycrystalline state (298 K)				DMF solution (77 K)											
Complex	g∥	g_{\perp}	g _{av}	g_	g⊥	g _{av}	$A^{\mathrm{a}}_{\parallel}$	A_{\perp}^{a}	$A_{\rm av}^{\rm a}$	G	α^2	β^2	γ^2	K_{\parallel}	K_{\perp}	K
2a	2.239	2.066	2.124	2.271	2.073	2.139	158.9	18.7	65.4	3.80	0.780	0.738	0.777	0.575	0.606	0.43
2b	2.208	2.056	2.107	2.227	2.063	2.118	163.6	15.8	65.1	3.69	0.746	0.657	0.713	0.490	0.531	0.45
4 a	2.167	2.053	2.091	2.249	2.066	2.127	163.6	21.5	68.8	3.82	0.768	0.668	0.699	0.513	0.537	0.47
4b	2.271	2.066	2.134	2.263	2.066	2.132	154.3	18.7	65.4	4.04	0.756	0.745	0.741	0.563	0.560	0.42

^{*a*} Expressed in units of cm^{-1} multiplied by a factor of 10^{-4} .

	Therm	nogravimetry (TG)		Mass	s loss (%)	
Compound	Stage	Temp. range (°C)	DTA peak (°C)	found	calculated	Decomposition product loss
2a	Ι	158–189	176	4.57	4.12	H ₂ O
	II	189-276	228	9.87	9.61	N_3
	III	276-568	380, 457	31.26	31.39	$C_2H_8N_2, C_6H_5$
	IV	568-1070	985	40.24	40.32	$C_8H_4N_2OS$
2b	Ι	147–194	168	3.84	3.97	H_2O
	II	194-288	212	12.94	12.82	NCS
	III	288-547	334, 496	30.19	30.27	$C_2H_8N_2, C_6H_5$
	IV	547-1064	870	38.73	38.89	$C_8H_4N_2OS$
4 a	Ι	179-213	201	3.62	3.23	H_2O
	II	213-354	296	7.71	7.54	$\bar{N_3}$
	III	354-673	454, 562	46.08	46.19	$C_{12}H_8N_2, C_6H_5$
	IV	673-1182	1107	31.46	31.62	$C_8H_4N_2OS$
4b	Ι	161-225	210	3.09	3.14	H_2O
	II	225-373	304	10.07	10.13	NCS
	III	373-679	412, 552	44.77	44.89	$C_{12}H_8N_2, C_6H_5$
	IV	679–1152	1090	30.62	30.74	$C_8H_4N_2OS$

 TABLE 5

 Thermal behavior of Cu(II) complexes

the molecule of 'L' was obtained leaving anhydrous CuO (Calc. % = 40.32 and 31.62).

In thiocynate complexes 2b and 4b, the first stage takes place in the 147–194°C and 161–225°C range, corresponding to mass loss of 3.84 and 3.09%, respectively, due to loss of coordinated water molecule (Calc. % = 3.97 and 3.14) with endothermic DTA peaks at 168°C (2b) and 210°C (4b). The second stage occurs in the 194-288°C and 225-373°C range accompanied by a mass loss of 12.94 and 10.07%, respectively, corresponding to the decomposition of the thiocynate ion (Calc. % = 12.82and 10.13) with endothermic DTA peaks at 212°C (2b) and 304°C (4b). The third stage takes place in the 288–547°C and 373-679°C range, corresponding to the mass loss of 30.19 and 44.77%, respectively, and may be attributed to the decomposition of half molecule of the 'L' and ethylenediamine or 1,10phenanthroline (Calc. % = 30.27 and 44.89). The DTA curve gives two endothermic peaks at 334 and 496°C for complex 2b and 412 and 552°C for 4b. The fourth stage takes place in the 547-1064 and 679-1152°C range corresponding to the mass loss of 38.73 and 30.62%, respectively, corresponding to the decomposition of the remaining half molecule of 'L', leaving anhydrous CuO (Calc. % = 38.89 and 30.74).

Cyclic Voltammetry

Electrochemical properties of the Cu(II) complexes (**2a**, **2b**, **4a** and **4b**) were investigated in DMF solutions (10^{-3} mol dm⁻³) at room temperature in the potential range +1 to -1.5 V with scan rate 50 mVs⁻¹. Typical cyclic voltammogram (CV) of complex **4a** is shown in Figure 4 and the electrochemical data obtained is represented in Table 6.

The electrochemical potentials of the Cu(II) complexes were characterized by well-defined redox process in positive potential side. Since the ligand used in this work is not reversibly oxidized or reduced in the applied potential range, the redox processes are assigned to the metal centers only. In positive potential side, all the complexes exhibit reduction peak at E_{pc} , 1.021 to 1.058 V with direct re-oxidation peak at E_{pa} , 1.001 to 1.026 V corresponding to the Cu(II)/Cu(III) couple. The values of the limiting peak-to-peak separation (ΔEp) ranging from 0.012–0.036 V reveal that the process is reversible as the limiting peak potential is lower than 59 mV. Further, the redox processes for Cu(II) complexes of **phen** (**4a** and **4b**) appear at more positive potential (1.022 to 1.042 V) as compared to those for corresponding **en** complexes **2a** and **2b** (1.013 to 1.021 V). This trend

TABLE 6 Electrochemical data of Cu(II) complexes

		Metal o	xidation	L	Ligand re	Ligand reduction			
Compound	E _{pa} (V)	E _{pc} (V)	ΔE_p (V)	E _{1/2} (V)	E _{pa} (V)	E _{pa} (V)			
2a	1.001	1.025	0.024	1.013	-0.140	-0.961			
2b	1.009	1.021	0.012	1.021	-0.056	-1.034			
4 a	1.004	1.040	0.036	1.022	-0.076	-0.941			
4b	1.026	1.058	0.032	1.042	-0.020	-0.953			

Supporting electrolyte: *n*-Bu₄NClO₄ (0.05 M); complex: 0.001 M; solvent: DMF; $\Delta E_p = E_{pa}$ - E_{pc} where, E_{pa} and E_{pc} are anodic and cathodic potentials, respectively; $E_{1/2} = \frac{1}{2}(E_{pa} + E_{pc})$; scan rate: 50 mVs⁻¹.

may be due to the strong σ -donor tendency of the ethylenediamine moiety and the strong π -acceptor ability of 1,10phenanthroline ligand. These results are consistent with those reported in the literature.^[18]

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