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Research Article

Cobalt(II) and Copper(II) Complexes of a Novel Mannich Base Derived From 8-Hydoxyquinoline: Synthesis, Spectral, Thermal, Electrochemical, and Biological Studies

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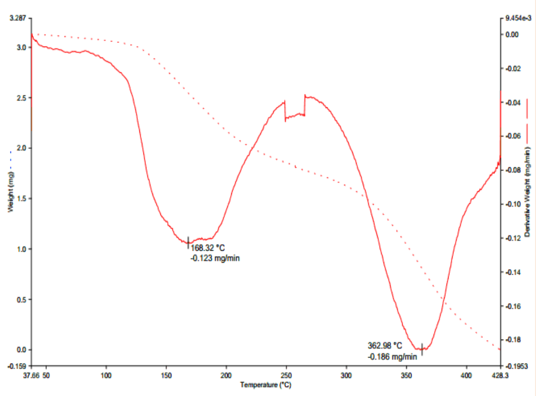
Abstract

A novel Mannich base of 8-hydroxyquninoline namely 7-diethylaminobenzyl-8-hydroxyqunioline(L) was synthesized and characterized by elemental analysis and spectral studies. Chelates of the Mannich base with cobalt(II) and copper(II) were isolated and structurally characterized by elemental analysis, chemical conductance, magnetic susceptibility measurement,IR,UV-Vis, EPR and Mass spectral data. The Mannich base ligand is found to chelate through the phenolic oxygen and the aliphatic tertiary amino nitrogen atoms. Based on the magnetic and electronic spectral data all the Co^{II} complexes and Cu^{II} nitrato complex are assigned a tetrahegral geometry and the Cu^{II} chloro and sulphato complexes are assigned a distorted octahedral geometry. The cyclic voltammetric studies on the Mannich base ligand indicates two redox couples,one involving the phenolic OH group and other due to the aliphalic tertiary amino group. The cyclic voltammograms of $CoCl_2$.L indicates the quasi-reversible nature of the Co^{II}/Co^{I} redox couple. The electrochemical behaviour of $CuCl_2$.L.$2H_2O$ shows the quasi-reversible one electron transfer involving Cu^{II}/Cu^{I} couple.

The antimicrobial screening of the Mannich base and its metal chloro complexes shows that the Mannich base is possessing higher activity than its metal chelates. Among the chelates Cu^{II} chelate is more potent than Co^{II} chelate.



Keywords: 8-Hydroxyquinoline, Antimicrobial screening, Cyclic voltammetry, Thermogramal decomposition.

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Introduction

Heterocyclic compounds containing quinoline moiety are of great interest to synthetic chemists and pharmacologists due to their unique chemical and biological properties[1-6].Quinoline derivatives exhibit versatile pharmacological properties[7-20]such as anti-inflammatory, antibacterial, antifungal, antiallergic, antidepressant, antiasthmatic, antimalarial, antiviral, antitumour, neuroleptic, antihypertensive, cytotoxic, hypnotic, sedative and bronchodilator activities.8-Hydroxyquinoline is toxic if injected directly but its derivatives are useful as medicine in view of their antimicrobial, antiamoebic, antimalarial, antinflammatory and other biological activities . 8-Hydroxyquinoline is much useful in analytical chemistry also due to its chelating ability[21]. When 8-hydroxyquinoline is subjected to Mannich condensation with aldehydes and secondary amines it yields Mannich bases which could display more potent pharmacological properties and stronger chelating tendencies. Mannich base coordination chemistry has been a popular area of research due to the diverse range of biological, analytical and industrial applications of the Mannich base metal ion complexes[22-25]. Earlier studies have reported that some drugs show improved curative value when administered as metal chelates rather then as free organic compounds. Hence in this work metal chelates of a novel Mannich base 7-diethylaminobenzyl-8-hydroxyquinoline have been synthesized, characterized and their antimicrobial potency screened against a few pathogenic micro- organisms.

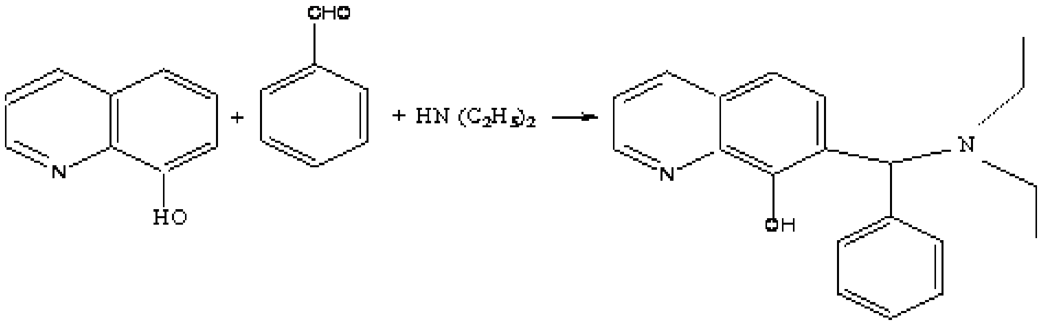
Experimental

Materials and Methods

All the chemicals and solvents used were AR grade products. The microelemental analyses were performed using Carlo Erba 1108 CHN analyzer. Metals and anions were estimated by conventional wet chemical analyses[21]. Molar conductivities were measured in ~ 10^{-3} M DMF solutions at room temperature using Systronics Conductivity Meter 304. FT-IR spectral measurements were made with Perkin - Elmer Spectrum – 1 FT-IR Spectrometer as KBr pellets. Mass spectra were recorded using JEOL D-300 (EI) Mass Spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL GSX-400 FT NMR Spectrometer (400 MHz) employing TMS as internal reference and DMSO-d_6 as solvent. Electronic absorption spectra were measured in DMF solutions using Perkin - Elmer EZ301 Spectrophotometer. Magnetic susceptibility measurements were made on a Gouy magnetic balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. EPR spectra of Cu^{II} complexes were recorded with a JEOL JES-TES 100 EPR spectrometer operating at X-band frequencies. Cyclic voltammetry was performed on a CH instrument (TX,USA) Model – 400 Potentiostat with a conventional three electrode cell.The three electrode cell consisted of a Ag/AgCl [sat .KCl] reference electrode, Pt wire counter electrode and a glassy carbon working electrode. Simultaneous TG/DTA thermograms were recorded on a Perkin-Elmer Thermal analyzer.

Synthesis of 7-Diethylaminobenzyl-8-hydroxyquinoline (L)

The Mannich base (L) was synthesized[26,27] by interacting 8-hydroxyquinoline(14.51g, 0.l mole) with benzaldehyde(10.6g, 0.1mole) and diethylamine (7.31g, 0.1 mole) in acetone medium at room temperature. The brownish-yellow solid compound formed was filtered and purified by recrystallization in ethanol (Yield ~ 70%, melting point: 63 – 64^0C).



Scheme 1 Formation of 7-Diethylaminobenzyl-8-hydroxyquinoline

Preparation of Co^{II} and Cu^{II} Complexes of Mannich Base (L)

The metal complexes were isolated from hot ethanolic medium. The hot ethanolic solution of the respective hydrated metal salt (0.01 mole) was slowly added with constant stirring to the hot ethanolic solution of ligand (0.01 or 0.02 mole). The mixture was digested on a hot water bath for half an hour and the precipitated complex was filtered, washed with hot ethanol and dried in a hot air oven at ~70^0C.

Invitro Antimicrobial Screening

Antimicrobial screening of the organic ligand and some of its metal complexes was carried out by agar well diffusion technique [28,29]. *S.aureus* and *E.coli* were the bacterial strains and *P.Chryogenum* and *A.niger* were the fungal species employed. The concentrations of test samples in DMSO solutions were 50 and 100 µg/mL. Antimicrobial activities of samples were determined by measuring the diameters of zones of inhibition (mm) in Muller Hinton agar medium after 24 hours of incubation for bacterial species and after 48 hours of incubation for fungal species.Growth inhibition produced by a particular sample has been compared with that of the standard bacterial drug ampicillin and standard fungal drug amphotericin-B.

Results and Discussion

Structural Characterization of L

Elemental composition Calculated for $C_{2O}H_{22}N_2O$: C 78.43; H 7.189; N 9.15% Found C 78.44; H 7.20; N 9.16%, FT-IR absorption frequencies (cm^{-1} in KBr) : 3392 ν_{OH} ; 3049,3100 ν_{CH} ; 1579, 1471-1409 $\nu_{C=C}$ and $\nu_{C=N}$ aromatic ; 1379 $\nu_{CN\,;}$ 1284 – 1275 $\nu_{CNC\,.}$UV – Vis data (λ in nm, in DMF): 316 n- $\pi^*_{;}$ 260 π - $\pi^*_{.}$ ^{1}H NMR chemical shifts (δ in ppm) : 7.2 – 8.2 pyridine ring protons; 6.9 – 7.2 benzene ring protons, 6.4 benzylic proton; 2.2 $N(CH_2)_2$ proton; 1.3CH_3 proton, 6.6 OH proton. ^{13}C NMR chemical shifts (δ in ppm) : 137.6 ,127.6 bridgehead carbons in quinoline moiety; 126.3 -129.3 other aromatic carbons,7.3 benzylic carbon;45 $N(CH_2)_2$ carbons;148.1 carbon with OH group. Mass spectral data of molecular ion (m/z):306.

Based on these physico – chemical data the structure of L is confirmed as given below:

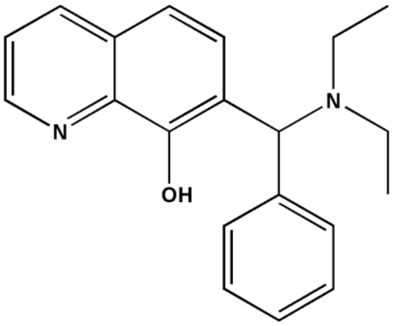


Figure 1 Chemical Structure of L

Structural Characterization of Metal Complexes

The analytical and conductivity data of the metal complexes of L are provided in Table1. These data indicate that the isolated metal complexes have 1:1 or 1:2 stoichiometry and are non-ionic in behavior[30]. The non-electrolytic behaviour of metal complexes suggests the bonding of anions to the respective metal ion.

Infrared Spectral Studies

The significant IR absorption frequencies measured for the metal complexes are provided in Table 2. A broad absorption band observed at 3392 cm^{-1} is ascribed to the presence of a phenolic OH group[31] in the quinoline moiety of the ligand molecule. In the spectra of the metal complexes this band has split and shifted to 3420-3236 cm^{-1} region indicating the coordination of the phenolic oxygen to the metal centre.

Normally 8-hydroxyquinoline in aqueous medium chelates through quinoline N and phenolate O^- to a metal ion to precipitate the coordination compound. But, when complex preparation is attempted in an ethanolic medium, the ionization of the phenolic OH into O^- may not be easy.

Further the presence of anions(Cl^-,NO^-_3,SO^{2-}_4) in the complex species rules out the existence of phenolate(O^-) anion in the coordination compounds. Also, those vibrations of the pyridine ring which are normally observed at about 604 cm^{-1} (inplane ring deformation) and 405 cm^{-1} (out–of–plane ring deformation) are not shifted to higher frequencies in the spectra of the complexes studied due to non-involvement of pyridine ring N atom in the coordination process[32].

In the free ligand IR spectrum, the absorption bands observed at 1284-1275 cm^{-1} are attributed to the C-N-C stretching vibrations of the $N(C_2H_5)_2$ moiety. But the inspection of the IR spectra of the metal complexes shows that this vibration has shifted to the region of 1280-1165cm^{-1} indicating the binding of the aliphatic tertiary amino nitrogen atom to the metal ion[33]. Though the coordination of tertiary amino nitrogen is not sterically favoured, the possibility for chelation leads to its coordination to a metal centre. Further, the appearance of new non-ligand bands in the regions of 581-520 and 520-457 cm^{-1} may be due to ν_{MO} and ν_{MN} vibrations[34] respectively. The unidentate coordination of nitrato groups in both Co^{II} and Cu^{II} complexes is suggested on the basis of the following absorptions:1458-1455(ν_5), 1384 (ν_1) and 1031 cm^{-1} (ν_2). Very low separation between ν_5 and ν_1 peaks (75-71 cm^{-1})

confirms the unidentate coordination behaviour nitrato groups. The bidentate chelation behaviour of sulphato group is also inferred from its IR absorption bands. In the Co^{II} sulphato complex the relevant absorptions are 1371,1139,1032 cm^{-1} (ν_3); 822 cm^{-1} (ν_1) and 700, 668, 634 cm^{-1} (ν_4), while in the Cu^{II} sulphato complex they are at 1464,1374,1112 cm^{-1} (ν_3); 980 cm^{-1} (ν_1) and 723,618 cm^{-1} (ν_4). Also the presence of coordinated water [34] in the Cu^{II} chloro complex is suggested based on the absorptions observed at 3420,1607,822,634 and 581 cm^{-1}.

Table 1 Analytical and Molar Conductance Data for L and its Metal Complexes

Compound	Analysis % Found (Calculated)					λ_M
	C	H	N	M	X	(ohm^{-1} cm^2 mol^{-1})
L ($C_{20}H_{22}N_2O$)	78.4 (78.43)	7.20 (7.189)	9.16 (9.15)	-	-	-
$CoCl_2$.L	55.16 55.06)	5.14 (5.04)	6.55 (6.42)	13.61 (13.52)	16.27 (16.26)	35
$Co(NO_3)_2$.L	49.09 (49.08)	4.56 (4.49)	11.49 (11.45)	12.15 (12.05)	- (25.36)	27
$CoSO_4$.L	52.1 (52.06)	4.8 (4.77)	6.09 (6.07)	12.65 (12.78)	20.9 (20.82)	32
Cu $CuCl_2$.L.$2H_2O$	50.38 (5.37)	5.47 (5.45)	5.9 (5.87)	13.32 (13.33)	14.85 (14.88)	25
$Cu(NO_3)_2$.L	48.7 (48.62)	4.5 (4.45)	11.23 (13.34)	12.85 (12.87)	- (25.12)	19
$CuSO_4$.2L	62.25 (62.21)	5.75 (5.70)	7.1 (7.25)	8.27 (8.23)	12.37 (12.44)	37

Note: X = Anion

Table 2 IR Spectral Data of L and its Metal Complexes (cm^{-1})

Compound	ν_{OH}	$\nu_{C=N}$	ν_{CNC}	ν_{MO}	ν_{MN}
L ($C_{20}H_{22}N_2O$)	3392	1624	1284-1275	-	-
$CoCl_2$.L	3368	1604	1210	520	420
$Co(NO_3)_2$.L	3368	1578	1224	529	471
$CoSO_4$.L	3236	1616	1223	531	420
$CuCl_2$.L.$2H_2O$	3420	1607	1237-1215	581	457
$Cu(NO_3)_2$.L	3396	1595	1165	553	526
$CuSO_4$.2L	3365	1615	1280-1235	550	520

Magnetic and Electronic Spectral Studies

The colours, magnetic moments and the electronic absorptions of the bivalent Co and Cu complexes[35] are summarized in Tabel 3. The chloro, nitrato and sulphato complexes of Co^{II} exhibit electronic absorption bands at 3910, 3948 and 3196 cm^{-1} respectively due to ${}^4A_2 \rightarrow {}^4T_2$ (F) transition; at 6800,6813 and 6828 cm^{-1} respectively due to ${}^4A_2 \rightarrow {}^4T_1$ (F) transition; and at 15120,15180 and 15100cm^{-1} respectively due to ${}^4A_2 \rightarrow {}^4T_1$(P) transition. Absorption bands observed at 29300,28900 and 28867 cm^{-1} respectively are assigned to charge transfer transition in the chloro, nitrato and sulphato complexes of cobalt(II). The values of ν_2/ν_1 ratio for Co^{II} chloro, nitrato and sulphato complexes are 1.74,1.73 and 1.74 respectively. These values are lower than 1.80. The room temperature magnetic moments measured for the chloro, nitrato and sulphato complexes of cobalt(II) are 4.30, 4.48 and 4.69 BM. The spectral features and magnetic moments indicate a tetrahedral environment of Co^{II} in these complexes.

Table 3 Magnetic and Electronic Spectral Data for the Metal Complexes

Complex	Colour (μ_{eff} BM)	Coordination Environment	Absorption Maxima (cm^{-1})	Transition Assignments
			3910	$^4A_2 \rightarrow {}^4T_2(F)$
$CoCl_2.L$	Green (4.3)		6800	$^4A_2 \rightarrow {}^4T_1(F)$
		$[CoNOCl_2]$	15120	$^4A_2 \rightarrow {}^4T_1(P)$
			29300	CT
$Co(NO_3)_2.L$	Green (4.48)	$[CoNO_3]$	3948	$^4A_2 \rightarrow {}^4T_2(F)$
			6813	$^4A_2 \rightarrow {}^4T_1(F)$
			15180	$^4A_2 \rightarrow {}^4T_1(P)$
			28900	CT
$CoSO_4.L$	Green (4.69)	$[CoNO_3]$	3196	$^4A_2 \rightarrow {}^4T_2(F)$
			6828	$^4A_2 \rightarrow {}^4T_1(F)$
			15100	$^4A_2 \rightarrow {}^4T_1(P)$
			28867	CT
$CuCl_2.L.2H_2O$	Yellow Green	$[CuNO_3Cl_2]$	8130	$^2B_{1g} \rightarrow A_{1g}$
	(1.79)		11437	$^2B_{1g} \rightarrow {}^2B_{2g}$
			14925	$^2E_g \rightarrow {}^2T_{2g}$
			27570	CT
$Cu(NO_3)_2.L$	Blue (1.95)	$[CuNO_3]$	9166	$^2B_{1g} \rightarrow A_{1g}$
			10238	$^2B_{1g} \rightarrow {}^2B_{2g}$
			11792	$^2E_g \rightarrow {}^2T_{2g}$
			24070	CT
$CuSO_4.2L$	Yellow Green	$[CuN_2O_4]$	8236	
	(1.70)		11329	$^2B_{1g} \rightarrow {}^2A_{1g}$
			14541	$^2B_{1g} \rightarrow {}^2B_{2g}$
			24371	$^2E_g \rightarrow {}^2T_{2g}$
				CT

The chloro and sulphato complexes of Cu^{II} are green while the nitrato complexe is blue in colour. The chloro and sulphato complexes exhibit absorption bands at 8130 and 8236 cm^{-1} respectively due to $^2B_{1g} \rightarrow {}^2A_{1g}$ transition and at 14925 and 14541 cm^{-1} respectively due to $^2E_g \rightarrow {}^2T_{2g}$ transition. The bands observed at 27570 and 24371 cm^{-1} may be due to charge transfer transition in the Cu^{II} chloro and sulphato complexes respectively. Also the chloro and sulphato complexes measure magnetic moments at 1.79 and 1.70 BM respectively. Thus the spectral features and magnetic moments suggest a tetragonally distorted octahedral geometry for the Cu^{II} chloro and sulphato complexes.

The Cu^{II} nitrato complex shows absorptions at 9166,10238 and 11792 cm^{-1} which are attributed to $^2B_{1g} \rightarrow {}^2A_{1g}$; $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2E_g \rightarrow {}^2T_{2g}$ transitions respectively. The absorption found at 24070 cm^{-1} is assigned to a charge transfer transition. The room temperature magnetic moment for the nitrato complex is 1.95 BM. Thus the Cu^{II} nitrato complex is tentatively assigned a distorted tetrahedral geometry.

EPR Studies on Copper(II) Complexes

The X band EPR spectra of polycrystalline chloro, nitrato and sulphato complexes of copper ion have been recorded at room temperature [36]. The spin Hamiltonian parameters are provided in Table 4. The EPR spectra of chloro and sulphato complexes of copper(II) ion shows axial symmetry indicating the distorted octahedral symmetry. In both copper(II) chloro and sulphato complexes the g values are in the order $g_{\|} > g_{\perp} > g_e$ signifying the presence of unpaired electron predominantly in the $d_{X^2-Y^2}$ orbital. The $g_{\|}$ values of the chloro and sulphato complexes of copper are less than 2.3 indicating that in these complexes the metal – ligand bonding is covalent in nature. The axial symmetry parameter(G) values are much less than 4 in both chloro and sulphato complexes showing the existence of some interaction between the two copper centres in solid state. The EPR spectrum of the Cu^{II} nitrato complex recorded at room temperature is shown in Fig 2. The spectrum is isotropic. The g_{iso} value measured at 2.1133 indicates that the symmetry of the copper complex is cubic.

Table 4 EPR spectral Parameters for the Copper(II) complexes at Room Temperature

Complex	**g_{iso}**	**$g_{\perp}$**	**$g_{\|}$**	**G**
$CuCl_2.L.2H_2O$	-	2.1007	2.1635	1.64
$Cu(NO_3)_2.L$	2.1133	-	-	-
$CuSO_4.2L$	-	2.1065	2.2744	2.62

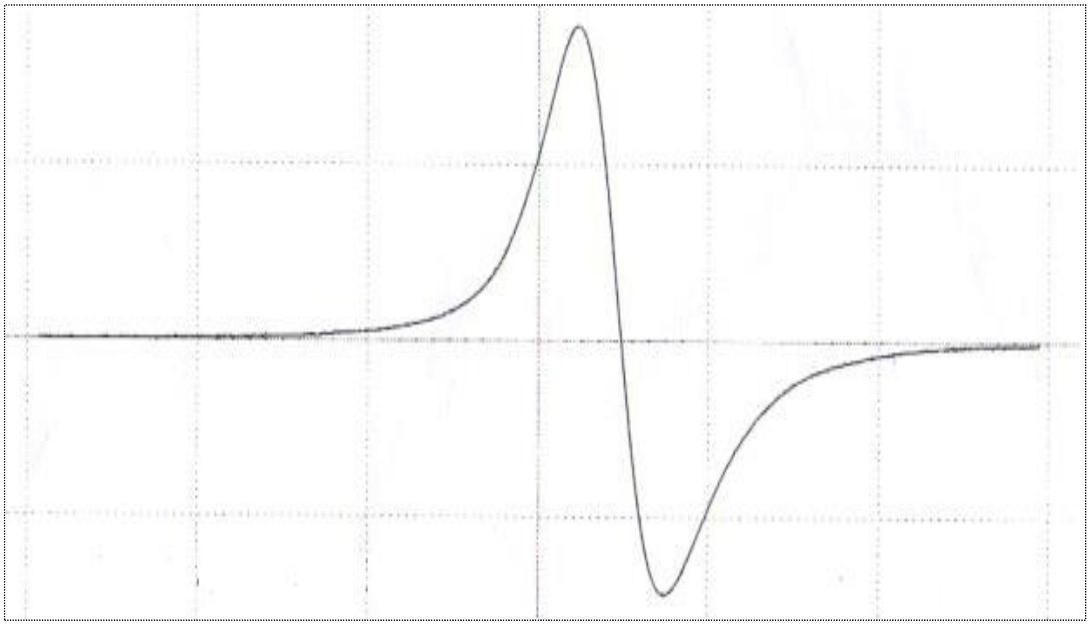


Figure 2 EPR Spectrum of $Cu(NO_3)_2L$

Electrochemical Behaviour of L

Cyclic voltammetry [37,38] of the Mannich base 7-diethylamniobenzyl-8-hydroxyquinoline,L was performed in DMSO solution with 0.1 M $LiClO_4$ as a supporting electrolyte at scan rates50-500 mVs^{-1}. The cyclic voltammogram of L at 50 mVs^{-1} is shown Figure.3. The organic compound shows two redox couples with border peaks.The cathodic peak potential E_{pc} and anodic peak potential E_{pa} at 50 mVs^{-1} are observed at -0.03 and 0.33V respectively for the first redox couple .This is most probably due to the presence of the phenolic OH group in the free ligand, which loses the hydrogen atom thereby facilitating the anodic reaction in the first step. The peak separation (ΔE_p) is 0.3V at scan rate 50mVs^{-1} .The second redox couple shows E_{pa} and E_{pc} values at -0.53 and -0.31V with peak separation (ΔE_p) of 0.22V. The second redox couple may be due to the aliphatic tertiary amino group[$-N(C_2H_5)_2$] which gets reduced in the second step. It is observed for both cases, that by increasing the scan rate, the peak separation is increased .This indicate the quasi-reversible nature of the redox process. The linear variation of cathodic peak current, I_{pc} with square root of scan rate, $\nu^{1/2}$ shows the electrode process to be diffusion controlled.

Table 5 Redox Properties of L and its Chloro Complex

Compound	**Scan rate (mVs^{-1})**	**E_{pc1} (V)**	**I_{pc1} ($x10^5$) (μA)**	**E_{pa1} (V)**	**I_{pa1} ($x10^5$) (μA)**	**E_{pc2} (V)**	**I_{pc2} ($x10^5$) (μA)**	**E_{pa2} (V)**	**I_{pa2} ($x10^5$) (μA)**
L ($C_{20}H_{22}N_2O$)	50	-0.03	1.43	0.33	-1.81	-0.53	2.65	-0.31	-0.43
	250	-0.09	3.10	0.37	-3.51	-0.63	4.68	-0.29	-1.16
	500	-0.18	4.20	0.52	-5.46	-0.71	6.55	-0.19	-2.46
$CoCl_2$.L	50	-1.22	4.92	-0.63	-0.19	-	-	-	-
	250	-1.29	5.97	-0.54	-0.60	-	-	-	-
	500	-1.37	7.24	-0.39	-1.99	-	-	-	-
$CuCl_2$.L.$2H_2O$	50	-1.09	3.10	-0.43	-0.34	-	-	-	-
	250	-1.22	5.65	-0.31	-1.60	-	-	-	-
	500	-1.31	7.35	-0.11	-2.55	-	-	-	-

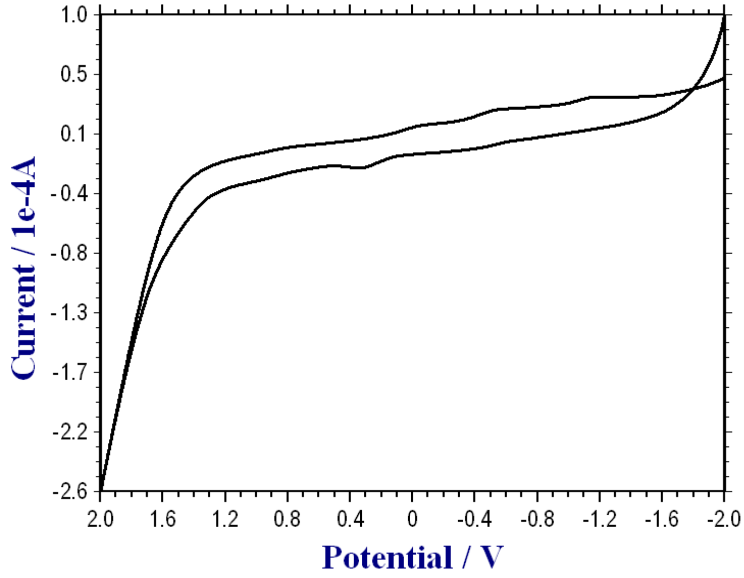


Figure 3 Cyclic voltammogram of Mannich base(L) at 50 mVs^{-1}

Electrochemical behavior of $CoC1_2$.L

The cyclic voltammogram of $CoC1_2$. L in DMSO solution at $50mVs^{-1}$ shows a well defined redox couple (Fig.3) with reduction peak potential,(E_{pc}) at -1.22V and the corresponding oxidation peak potential(E_{pa})at-0.63V. The peak separation of the redox couple is 0.59V.As the scan rate increases, the potential shift increases confirming the quasi-reversible nature of the Co^{II}/Co^{I} redox couple. The ratio of the cathodic peak current, I_{pc} and anodic peak current ,Ipa is found to be less then one which indicates that the electron transfer does not follow a chemical reaction. The linear variation of peak current with square root of the scan rate, $v^{1/2}$ may be attributed to the diffusion controlled electrode process.

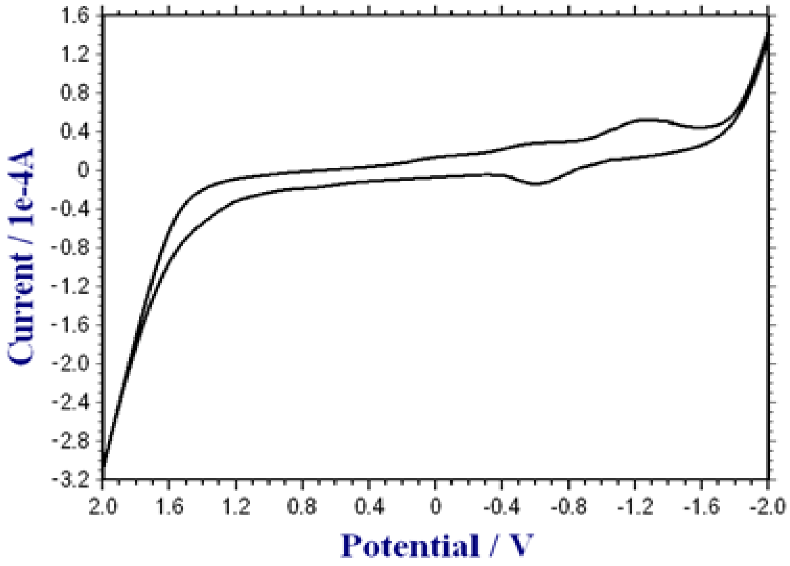


Figure 4 Cyclic voltammogram of $CoCl_2$.L at 50 mVs^{-1}

The cyclic voltammogram of the complex $CoC1_2$. L does not show the redox peaks corresponding to the phenolic OH and aliphatic tertiary amino N indicating that these groups are involved in coordination to the Co^{II} centre. Double potential step chronocoulometry was also performed for the complex in DMSO solution versus Ag/AgCl [KCl saturated] with initial potential -2.0V and final potential +2.0V. The plot of charge (Q) versus square root of time($t^{1/2}$) is linear and no sharp decrease is observed .This confirms the diffusion controlled redox process.

Electrochemical behaviour of $CuCl_2^{\cdot}$ $L^{\cdot}2H_2O$

The complex exhibited a redox couple with reduction peak (E_{pc}) at-1.09V with an associated oxidation peak (E_{pa}) at -0.43V at the scan rate of 50 mVs^{-1}.At 50 mVs^{-1} the peak separation (ΔE_p) is 0.66V and peak separation increases with increasing scan rate. The ΔE_p values are 0.91 and 1.2V at scan rates 250 and 500 mVs^{-1} respectively. An increase in potential shift with increase in scan rates confirms the quasi-reversibility of the electron transfer process. The cyclic voltammetric responses at different scan rates offer evidence for the quasi-reversible one electron redox process involving the Cu^{II} complex as Cu^{II}/Cu^{I} couple. Also the linear variation of cathodic peak current, I_{pc} with square root of scan rate, $\nu^{1/2}$ indicates diffusion controlled process. When compared to the free ligand, the Cu^{II} complex does not show redox peaks corresponding to the phenolic OH and the aliphatic tertiary amino groups. This may indicate the involvement of these groups in coordination to the metal centre.

Double potential step chronocoulometric studies were also performed for this complex in DMSO solution with initial and final potentials at -2.0 and +2.0V versus Ag/AgCl [KCl saturated]. A linear plot was obtained by plotting charge(Q) versus square root of time ($t^{1/2}$) and no sharp variation was observed. This suggests the process to be diffusion controlled which implies that the complex is not adsorbed onto the electrode surface.

Thermal Decomposition Studies

Thermal studies [39,40] have been carried out on the Mannich base ligand (L) and $CuSO_4$ 2L. The ligand is thermally stable upto 130^{0}C. It undergoes the first stage of decomposition in the temperature range of 130-200^{0}C. This is shown by the broad DTG peak centered at 168^{0}C. The thermogram shows the existence of an intermediate in the temperature range 200-300^{0}C, the composition of ligand which is not clearly understood. The intermediate undergoes further decomposition and complete weight loss at about 430^{0}C. The decomposition of the intermediate is shown by another DTG peak centered at 363^{0}C. However the DTA plot is not very clear.

The TG plot of $CuSO_4$.2L shows that the complex compound is stable upto 90^{0}C. Above 90^{0}C it undergoes gradual weight loss and decomposition perhaps to produce the intermediate complex of $CuSO_4$.L, which further undergoes decomposition and weight loss to form $CuSO_4$ as the final residue. The decomposition of $CuSO_4$.L is indicated by the DTG peak found at 358^{0}C. A very weak endotherm at about 90^{0}C is supporting the decomposition of $CuSO_4$.2L to give $CuSO_4$.L.

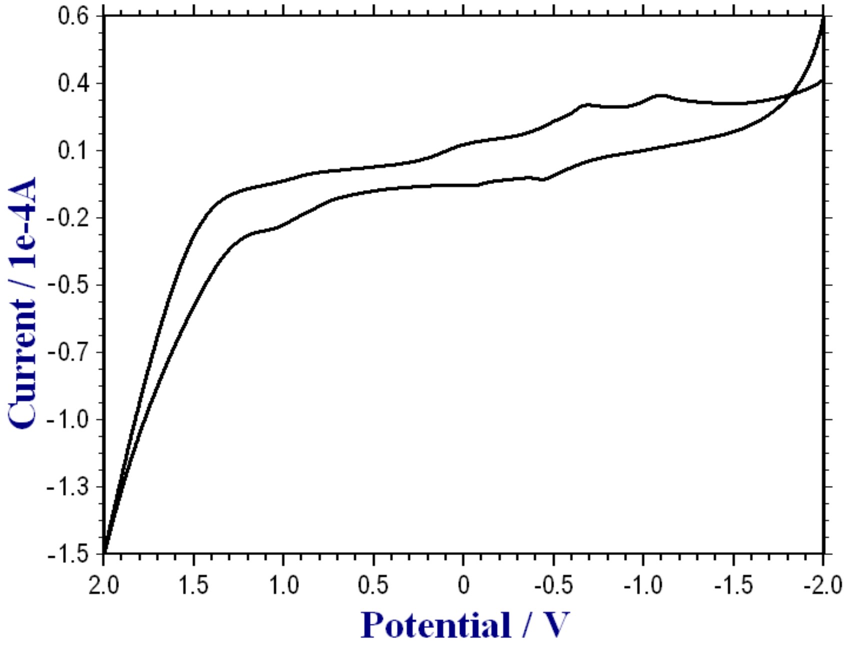


Figure 5 Cyclic voltammogram of $CuCl_2$.L.$2H_2O$ at 50 mVs^{-1}

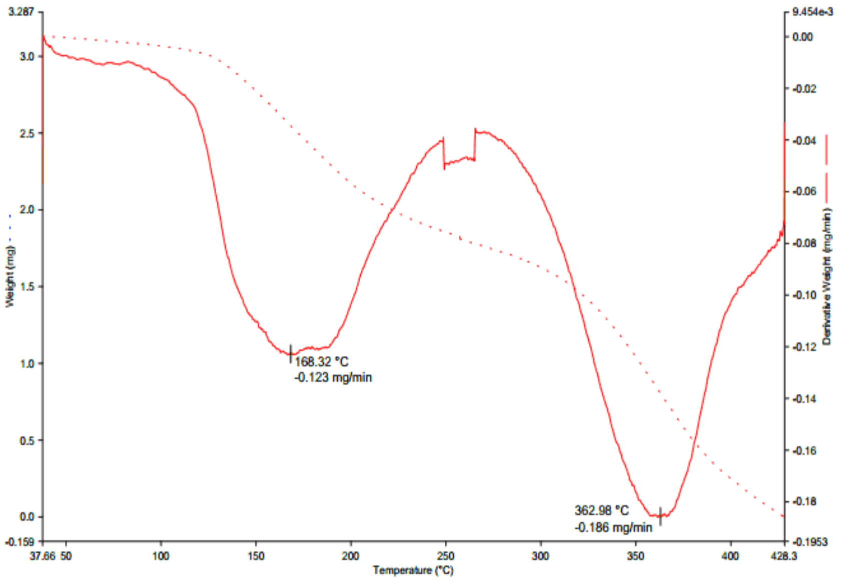


Figure 6 TG/DTG of L

Antimicrobial Studies

The Mannich base ligand (L) and its Co^{II} and Cu^{II} chloro complexes have been screened for antimicrobial activity against *E.coli*, *S.aureus*, *A.niger* and *P.chrysogenum*. The levels of antimicrobial activity in terms of the zones of inhibition produced by the test compounds are presented in Table 7. The Mannich base is active against both the bacterial and the fungal strains tested. The Mannich base ligand exhibits comparable activity with standard antibacterial drug used (Ampicillin). But antifangal activity the Mannich base, is superior to that of the standard drug (Amphotericin – B) used. It shows that this organic compound may very well be used as an antifungal antibiotic. Considering cobalt(II) and copper(II) chloro complexes, the copper(II) complex exhibits significant activity against both the bacterial and the fungal organisms tested.

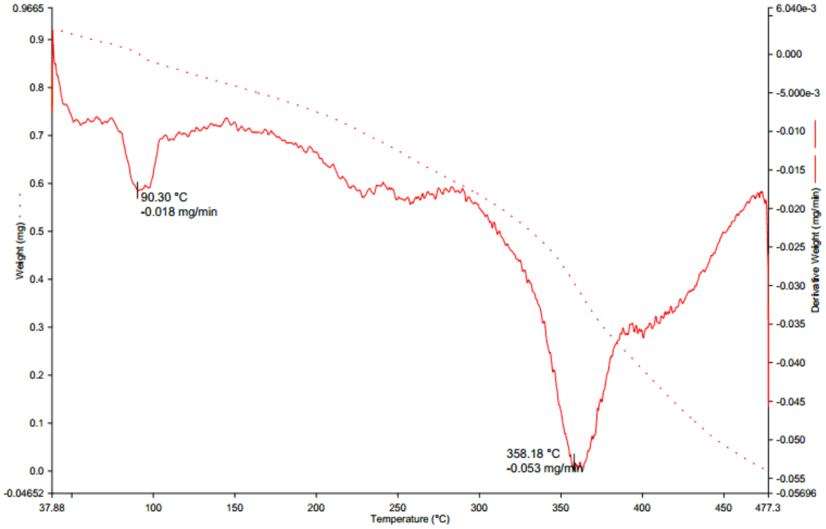


Figure 7 TG/DTG of L.$CuSO_4$

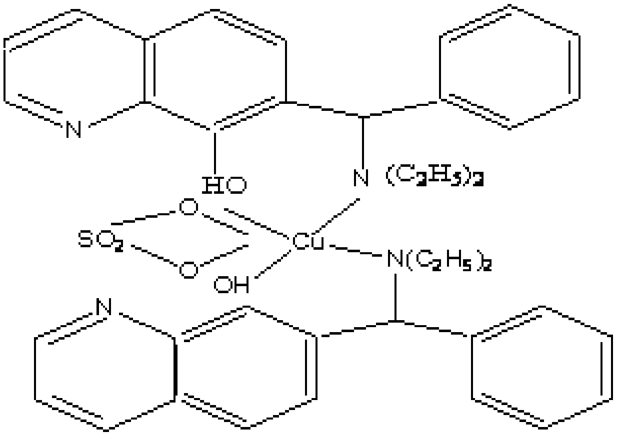


Figure 8c Structure of $CuSO_4$.2L

Conclusion

7-Diethylaminobenzyl-8-hydroxyquinoline and its Co^{II} and Cu^{II} complexes have been synthesized and their spectral, electrochemical, thermal and biological properties studied. The Mannich base ligand prefers to coordinate through the phenolic oxygen and aliphatic amino nitrogen atoms. Based on analytical and spectral studies, the structures of the coordination complexes are established as shown in Fig 8a, b, c. The electrochemical behaviours of both the ligand and a selected few complexes indicate that the ligand molecule shows two redox couples, while the metal complexes show only one redox couple vizCo^{II} / Co^{I} or Cu^{II} / Cu^{I} redox couple. From antimicrobial screening studies, it is seen that the Mannich base ligand is more potent than the metal complexes. The ligand exhibits much higher level of activity than the standard drugs used. The Cu^{II} complex exhibits more significant activity, while the Co^{II} complex shows very feasible activity.

Table 6 Antimicrobial activity of L and its Chloro complexes

Compound	**Zone of Inhibition (mm)**							
	E.coli **P.chrysogenum**		**S.aureus**		**A.niger**			
	50 (µg/mL)	100 (µg/mL)	50 (µg/mL)	100 (µg/mL)	50 (µg/mL)	100 (µg/mL)	50 (µg/mL)	100 (µg/mL)
L ($C_{20}H_{22}N_2O$)	18	24	39	41	17	19	19	24
$CoCl_2$.L	-	10	-	10	-	10	-	-
Cu $CuCl_2$.L.$2H_2O$	15	19	20	24	17	22	16	18
Ampicillin	-	27	-	28	-	-	-	-
Amphotericin-B	-	-	-	-	-	11	-	10

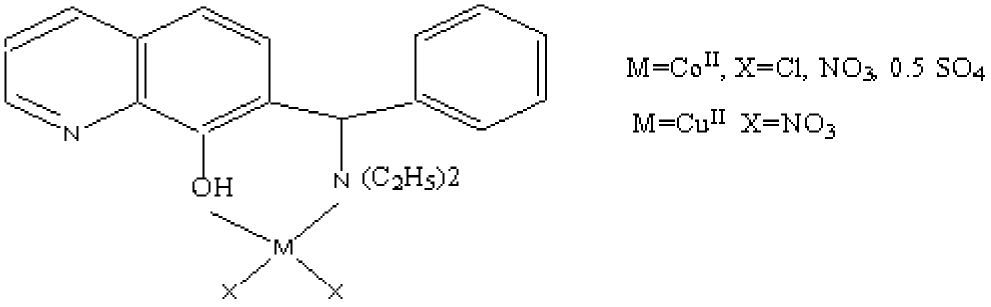


Figure 8a Structure of $CoCl_2$, $Co(NO_3)_2$.L

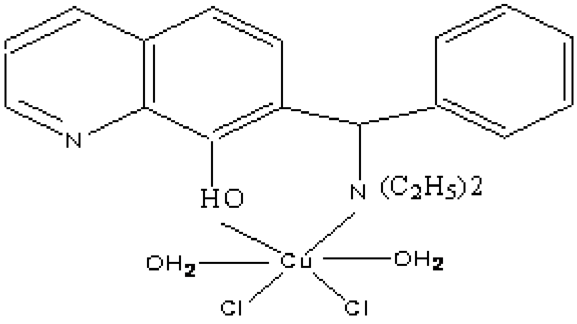


Figure 8b Structure of $CuCl_2$.L.$2H_2O$

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