

Synthesis, Characterization and Antimicrobial Activity of Cobalt (II) and Nickel (II) Complexes with a Novel Mannich Base 2-(Diethylaminomethyl)isoindoline-1,3-dione

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Abstract: A new Mannich base 2-(diethylaminomethyl)isoindoline-1,3-dione and its metal complexes with cobalt(II) and nickel(II) ions have been synthesized and characterized. Their structural features have been established on the basis of analytical, magnetic, conductance, IR, UV-visible, Mass, ^1H and ^{13}C NMR spectra. Simultaneous TG/DTA patterns of a selected few compounds were recorded and discussed. The non-electrolytic nature of the complexes was inferred from their low molar conductance values. On the basis of colour, magnetic moments and electronic spectral data, the geometries of Co(II) and Ni(II) complexes have been assigned. Cyclic voltammetric analysis of a cobalt(II) complex was discussed to understand its redox behaviour. The antimicrobial activity of the ligand and a selected few complexes has been studied with the microorganisms such as *Escherchia coli*, *Staphylococcus aureus*, *Aspergillus niger* and *Candida albicans*, employing agar-well diffusion method. Both the organic ligand and the complexes possess significant antimicrobial activity comparable to that of the standard drugs.

Keywords: Mannich base, metal complexes, geometry, antimicrobial activity, thermal analysis, redox behaviour.

INTRODUCTION

Mannich bases and their coordination compounds have been reported to show a broad spectrum of biological properties and pharmaceutical applications[1]. Metal ion complexes of Mannich bases have been studied extensively in the recent years due to their selectivity and sensitivity towards biologically important metal ions[2-7]. Cyclic imides possess a structural feature $-\text{CO}-\text{N}(\text{R})-\text{CO}-$ and an imide ring which help them to be biologically active and pharmaceutically useful. Phthalimides have received much attention due to their antibacterial, antifungal, analgesic, antitumour, anxiolytic and anti HIV-1 activities[8-12]. When phthalimide (isoindoline-1,3-dione) is subjected to Mannich condensation, it may yield Mannich bases which may display more potent biological activities[13-15] than phthalimide. In view of these facts and continuation of our earlier work[16] on Mannich base complexes, we report herein the synthesis, characterization and antimicrobial screening of the new Mannich base 2-(diethylaminomethyl)isoindoline-1,3-dione and its cobalt(II) and nickel(II) complexes.

EXPERIMENTAL

Chemicals and Methods

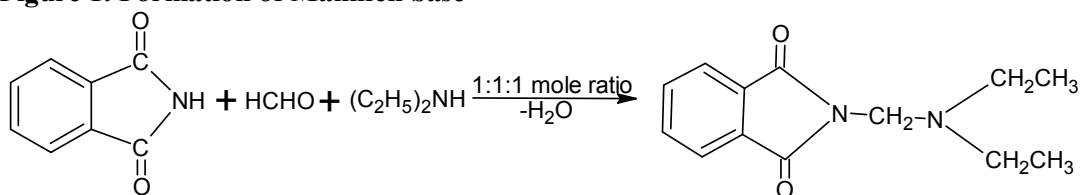
Reagents such as formaldehyde, diethylamine, phthalimide, various metal salts and solvents used were analytical grade Merck products and were used as such without further purification. Elemental(C, H, N) analyses were performed using Carlo Erba 1108 CH analyzer and Coleman N analyzer. The molar conductivities of the metal complexes were measured in $\sim 10^{-3}\text{M}$ DMF solutions at room temperature using Systronics direct reading conductivity meter 304. Infrared spectra of the synthesized compounds were recorded on a Perkin Elmer 337 FT-IR spectrophotometer in the form of KBr pellets. The UV-visible absorption spectra of the compounds were recorded on a Perkin Elmer EZ 301 spectrophotometer. Both ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL GSX-400

spectrometer employing TMS as internal reference and $\text{DMSO}-d_6$ as solvent at ambient temperature. The mass spectral study of the ligand was carried out using JEOL D-300 (EI) mass spectrometer. Magnetic susceptibility measurements were carried out using a Gouy magnetic balance at room temperature. $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as a standard and diamagnetic corrections were made with Pascal's constants[17]. Wet chemical analyses for metal ions and anions (chloride and sulphate) were performed using standard methods[18]. Nitrate was not estimated separately. Antimicrobial screening of the test compounds was carried out using agar-well diffusion method. Simultaneous TG/DTA patterns of a selected few compounds were recorded on a Perkin Elmer Diamond TG/DTA analyzer. TG was derivatized to get DTG by the software associated with the instrument. An electrochemical analyzer CHI- 620A, USA was used for the cyclic voltammetric analysis of a Co(II) complex. Glassy carbon working electrode, Ag/AgCl reference electrode and Pt foil auxiliary electrode were used in the cell assembly. NaClO_4 was used as supporting electrolyte in DMF.

Synthesis and Characterization of 2-(Diethylaminomethyl)isoindoline-1, 3-dione (L)

2-(Diethylaminomethyl)isoindoline-1,3-dione(L) is commonly known as N-(diethyl-aminomethyl) phthalimide. It was prepared by the Mannich condensation of phthalimide, diethylamine and aqueous formaldehyde. Phthalimide (14.71g, 0.1mol) was mixed with 37% aqueous formaldehyde (7.5mL, 0.1mol) and then with diethylamine (9.6mL, 0.1mol) with constant stirring at room temperature. The oily solution obtained was kept aside for two hours. The colourless solid product formed was suction filtered, washed with distilled water several times and finally with a small amount of acetone. It was dried at 60°C and recrystallized from ethanol (Yield 86%). It melts at 139°C . The formation of the new Mannich base 2-(diethylaminomethyl)isoindoline-1,3-dione is shown in Figure1.

Figure 1. Formation of Mannich base



Synthesis of Metal Complexes

An ethanolic solution (20mL) of the Mannich base ligand L (0.01mol) was added to a hot ethanolic solution (20mL) of the metal salt (0.01mol) taken in a 100ml beaker with constant stirring. The content of the beaker was digested on a boiling water bath for an hour. The solid product thrown out was filtered, washed with ethanol and dried under vacuum in a desiccator. The metal complexes thus obtained were preserved in a vacuum desiccator.

Antimicrobial Activity Screening

The synthesized Mannich base and its Co(II) and Ni(II) complexes have been screened for their antibacterial and antifungal activities[19,20] by agar well diffusion method using Mueller-Hinton agar(MHA) and Rose Bengal Chloromphenicol agar medium respectively. The antibacterial and antifungal activities were determined at 25, 50, 75 and 100 μ g/mL concentrations of test compounds in DMF solvent using bacteria (*E.coli* and *S.aureus*) and fungi (*A.niger* and *C.albicans*). These bacterial strains were incubated for 24h at 37°C and fungal strains were incubated for 72h at 37°C. Kanamycin, tetracycline, amphotericin and nystatin were used as standard drugs against *E.coli*, *S.aureus*, *A.niger* and *C.albicans* respectively

for comparison under similar conditions. Activity was determined by measuring the diameter of the zone showing complete inhibition (mm).

RESULTS AND DISCUSSION

Structural Characterization of the Mannich Base (L)

Based on analytical and spectral data, the structure of the ligand has been confirmed. The analytical and spectral data obtained for the ligand are summarized in Table1. The spectral data obtained for the ligand are furnished below:

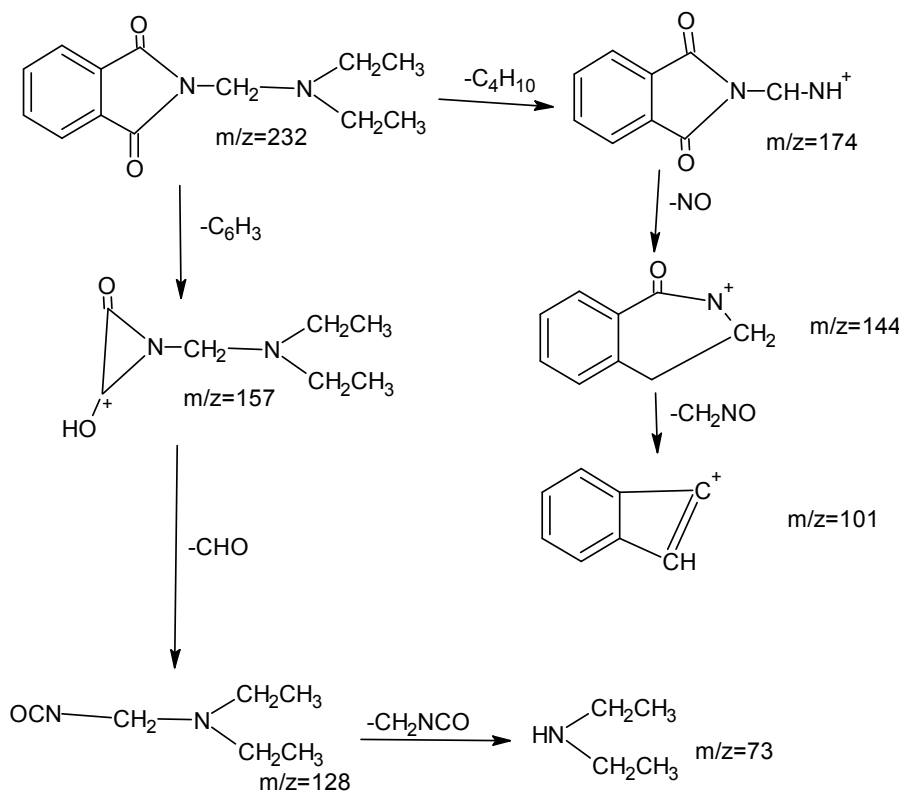
FT-IR (KBr, cm^{-1}): 2927, 2854(C-H), 1773(sh), 1706 (C=O), 1352 (C-N), 1147 (C-N-C)

^1H NMR (DMSO- d_6 , δ ppm): 3.03 (4H, $\text{N}(\text{CH}_2)_2$), 1.16(6H, CH_3), 4.80(2H, $\text{N-CH}_2\text{-N}$),

7.86-7.05 (4H, aromatic) **^{13}C NMR** (DMSO- d_6 , δ ppm): 13.40-11.12(2C, CH_3) 42.05 - 37.69(2C, $\text{N}(\text{CH}_2)_2$), 62.96 (1C, $\text{N-CH}_2\text{-N}$), 129.57-122.89 (4C, aromatic), 133.68(2C, aromatic bridgehead), 171.71 (2C, C=O) **Mass** (m/z): 231.38 (M^+ peak).

Further fragmentation pattern of the molecular ion (Figure 2) confirms the structure of the ligand(L).

Figure 2: Fragmentation Pattern of L



Characterization of Metal Complexes

The analytical and molar conductance data of the cobalt(II) and nickel(II) complexes are provided in **Table 1**. The conductance data [21] indicate that all the metal complexes synthesized are non-electrolytes. The non-electrolytic nature of the metal complexes suggests that the anions of the salts have coordinated to the metal ions in the formation of metal complexes.

Infrared Spectra

The characteristic IR absorption bands of the Co(II) and Ni(II) complexes have been compared with those of the free ligand L (**Table 2**) in order to get a meaningful information regarding the bonding sites. In the ligand L spectrum, the infrared bands observed at 1773(sh) and 1706(s) cm^{-1} , have been assigned to ν_{CO} of the phthalimide moiety. But in the IR spectra of metal complexes the band at 1706 cm^{-1} has undergone splitting and lowering into two bands one at a higher position(1720-1709 cm^{-1}) and another at a lower position(1627-1595 cm^{-1}) indicating the coordination of one of the two carbonyl oxygens of the ligand to the metal ion. Based on such observations in the study of imidato complexes, Adams *et al* [22] and Fairlamb *et al*[23] have also proposed the bonding of only one carbonyl oxygen of the ligand moiety to the metal centre. Further, the binding of both the carbonyl oxygens to the same metal centre is not sterically possible. The binding of carbonyl oxygen to the metal

ion has also been confirmed by the appearance of bands due to ν_{MO} in the far IR region at 536 – 461 cm^{-1} .

The ligand L exhibits a vibrational absorption band at 1147 cm^{-1} which is assigned to ν_{CNC} of the diethylamino moiety. This band has shifted to lower region (1144 -1058 cm^{-1}) in the metal ion complex spectra indicating the coordination of the tertiary amino nitrogen atom to the metal ion. The appearance of bands due to ν_{MN} in the far IR region at 461-413 cm^{-1} is also an indication of metal-nitrogen bonding in the metal complexes. Though the coordination of an aliphatic tertiary amino nitrogen is not sterically favoured, the high electron density available on the tertiary amino nitrogen favours its coordination to a metal ion where there is a possibility for chelation[24].

The metal nitrate complexes have shown IR absorptions in the three regions at about 1460(ν_5), 1380(ν_1) and 1080 cm^{-1} (ν_2) suggesting unidentate nitrate coordination. But the metal sulphato complexes absorb at ~1250, 1175, 1050 cm^{-1} (ν_3) and at ~725, 625, 565 cm^{-1} (ν_4) suggesting chelating bidentate coordination. In the case of metal chloro complexes, observation of absorptions at 330-312 cm^{-1} points to the binding of chloro groups to the metal ion. The presence of coordinated water molecules in the chloro and sulphato complexes of cobalt(II) and the nitrate and sulphato complexes of nickel(II) is inferred from the appearance of bands at 3489-3433, 1629-1595, 847-841, 636-626 and 531-475 cm^{-1} which are assigned to ν_{OH} , δ_{HOH} , ρ_{HOH} , ρ_{WHOH} and ν_{MO} respectively[25].

TABLE-1: Analytical and Molar Conductance Data for L and its Metal Complexes

Compound	% Analysis Found (Calculated)					$\Lambda_M \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
	C	H	N	Metal	Anion	
L ($\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_2$)	67.18 (67.24)	6.93 (6.89)	12.11 (12.06)	-	-	-
$\text{CoCl}_2 \cdot \text{L} \cdot 2\text{H}_2\text{O}$	47.74 (47.71)	6.08 (6.12)	8.58 (8.56)	18.07 (18.03)	21.70 (21.72)	26
$\text{Co}(\text{NO}_3)_2 \cdot 2\text{L}$	48.28 (48.23)	4.97 (4.95)	12.94 (12.98)	9.13 (9.11)	-- (19.17)	19
$2\text{CoSO}_4 \cdot \text{L} \cdot \text{H}_2\text{O}$	22.54 (22.50)	3.41 (3.46)	4.87 (4.85)	20.35 (20.40)	33.28 (33.23)	31
$\text{NiCl}_2 \cdot 2\text{L}$	52.52 (52.55)	5.42 (5.39)	8.12 (8.08)	9.89 (9.93)	11.91 (11.96)	15
$\text{Ni}(\text{NO}_3)_2 \cdot \text{L} \cdot 2\text{H}_2\text{O}$	36.10 (36.05)	4.57 (4.62)	12.98 (12.94)	13.51 (13.56)	-- (28.66)	43
$2\text{NiSO}_4 \cdot \text{L} \cdot \text{H}_2\text{O}$	24.67 (24.63)	3.11 (3.19)	4.48 (4.42)	18.51 (18.53)	39.19 (39.16)	37

TABLE-2: Infrared Spectral Data of L and its Complexes with Co(II) and Ni(II) Ions (cm⁻¹)

Compounds	$\nu_{C=O}$	ν_{C-N-C}	ν_{M-O}	ν_{M-N}	ν_{M-X}	ν_{OH}
L (C ₁₃ H ₁₆ N ₂ O ₂)	1773,1706	1147	--	--	--	--
CoCl ₂ .L.2H ₂ O	1766,1709,1599	1144	529	443	336	3485
Co(NO ₃) ₂ .2L	1771,1720,1601	1144,1084	536	461	--	--
2CoSO ₄ .L. H ₂ O	1769,1709,1595	1144	531	452	--	3186
NiCl ₂ .2L	1718,1627	1107	461	421	312	--
Ni(NO ₃) ₂ .L.2H ₂ O	1768,1714,1629	1086	475	413	--	3433
2NiSO ₄ .L. H ₂ O	1771,1710,1608	1144,1058	531	439	--	3489

Electronic Spectra and Magnetic Moments

The colours, magnetic moments and electronic spectral data of the Co(II) and Ni(II) complexes are summarized in **Table 3**. The electronic spectra of the chloro and nitrate Co(II) complexes display absorption bands in the regions 7500-7000, 15600-14800, 18950-18850 and ~ 29000cm⁻¹, which may be assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and charge transfer transitions respectively which indicate an octahedral stereochemistry[26] for the chloro and nitrate complexes of Co(II) ion. The determined magnetic moment values

(5.13 and 5.21BM) also support the same. The sulphato complex of Co(II) absorbs at 3926,6842,14620 and 28826cm⁻¹, which may be assigned ${}^4A_2(F) \rightarrow {}^4T_2(F)$, ${}^4A_2(F) \rightarrow {}^4T_1(F)$, ${}^4A_2(F) \rightarrow {}^4T_1(P)$ and charge transfer transitions[26-32] respectively. These spectral features indicate a tetrahedral stereochemistry for the Co(II) sulphato complex and it is further supported by the observed magnetic moment value at 4.32BM.

TABLE-3: Colours, Electronic Spectral Bands, Transition Assignments and Magnetic Moment Values of Complexes

Compound	Colour	Magnetic moment B.M	Absorption maxima	Transition Assignment
CoCl ₂ .L.2H ₂ O	Violet	5.13	7026 14815 18868 29622	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ CT
Co(NO ₃) ₂ .2L	Pink	5.21	7486 15680 18962 32268	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ CT
2CoSO ₄ .L. H ₂ O	Blue	4.32	3926 6842 14620 28826	${}^4A_2(F) \rightarrow {}^4T_2(F)$ ${}^4A_2(F) \rightarrow {}^4T_1(F)$ ${}^4A_2(F) \rightarrow {}^4T_1(P)$ CT
NiCl ₂ .2L	Green	2.87	9168 15127 25966 35461	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ CT
Ni(NO ₃) ₂ .L.2H ₂ O	Light green	3.16	9174 15212 25195 32066	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ CT
2NiSO ₄ .L. H ₂ O	Apple green	1.12	3926 8418 14964 29320	${}^3T_1(F) \rightarrow {}^3T_2(F)$ ${}^3T_1(F) \rightarrow {}^3A_2(F)$ ${}^3T_1(F) \rightarrow {}^3T_1(P)$ CT

TABLE- 4: Ligand Field Parameters of Co(II) and Ni(II) Complexes

Compound	v_2/v_1	B cm^{-1}	Dq	β	$\beta\%$
$\text{CoCl}_2 \cdot \text{L} \cdot 2\text{H}_2\text{O}$	2.11	840	778.9	0.865	13.50
$\text{Co}(\text{NO}_3)_2 \cdot 2\text{L}$	2.10	812	746.8	0.836	16.40
$2\text{CoSO}_4 \cdot \text{L} \cdot \text{H}_2\text{O}$	1.74	645	378.6	0.664	33.60
$\text{NiCl}_2 \cdot 2\text{L}$	1.65	906	916.8	0.870	13.00
$\text{Ni}(\text{NO}_3)_2 \cdot \text{L} \cdot 2\text{H}_2\text{O}$	1.66	859	917.4	0.825	17.50
$2\text{NiSO}_4 \cdot \text{L} \cdot \text{H}_2\text{O}$	2.14	773	449.2	0.743	25.70

The ligand field parameters for the cobalt (II) complexes have been computed and presented in Table 4. The observed v_2/v_1 ratios for Co(II) chloro and nitrate complexes are 2.11 and 2.10 respectively suggesting the octahedral geometry of Co(II). The v_2/v_1 ratio for Co(II) sulphato complex is 1.74 which is much below 1.80 indicating tetrahedral geometry around Co(II). The order of Dq values (779, 747 cm^{-1}) among the octahedral Co(II) complexes is found to be $\text{CoCl}_2 \cdot \text{L} > \text{Co}(\text{NO}_3)_2 \cdot \text{L}$. This trend is in accordance with the position of anions in the spectrochemical series. From the calculated $\beta\%$ values (13.50, 16.40 and 33.60%) for the Co(II) chloro, nitrate and sulphato complexes covalent character of the Co(II) complexes is established.

The Ni(II) chloro and nitrate complexes exhibit electronic absorption bands at 9100, 15100, 25100 and $\sim 32000 \text{cm}^{-1}$ which are assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ and charge transfer transition respectively, which indicate octahedral geometry of Ni(II). The observed magnetic moments at 2.87 and 3.16 BM also support the octahedral stereochemistry of Ni(II) in $\text{NiCl}_2 \cdot 2\text{L}$ and $\text{Ni}(\text{NO}_3)_2 \cdot \text{L} \cdot 2\text{H}_2\text{O}$. The Ni(II) sulphato complex exhibits bands at 3926, 8418, 14964 and $\sim 29000 \text{cm}^{-1}$, which may be assigned to ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$, ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{A}_2(\text{F})$, ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ and charge transfer transition respectively suggesting tetrahedral geometry around Ni(II). This is further supported by the magnetic moment value observed at 4.12 BM.

The calculated ligand field parameters of Ni(II) complexes also support the proposed structures. The v_2/v_1 ratios for the chloro and nitrate complexes are 1.649 and 1.658 respectively indicating octahedral geometry. But for the sulphato complex the v_2/v_1 ratio is 2.144 suggesting tetrahedral stereochemistry of Ni(II). The order of Dq values among the octahedral complexes is $\text{NiCl}_2 \cdot 2\text{L} > \text{Ni}(\text{NO}_3)_2 \cdot \text{L} \cdot 2\text{H}_2\text{O}$. The

percentage covalency is found in the order: $\text{NiCl}_2 \cdot 2\text{L} > \text{Ni}(\text{NO}_3)_2 \cdot \text{L} \cdot 2\text{H}_2\text{O} > 2\text{NiSO}_4 \cdot \text{L} \cdot \text{H}_2\text{O}$.

Thermal Study

Thermal studies (TG/DTA) have been carried out to understand the thermal stabilities and thermal decomposition patterns of the ligand and a selected few metal complexes. The TG/DTG and TG/DTA patterns of $2\text{CoSO}_4 \cdot \text{L} \cdot \text{H}_2\text{O}$ shown as representative cases in Figures 3 and 4. The thermal data are furnished in Table 5.

The ligand L is thermally stable upto 139.4°C at which it melts. It undergoes rapid decomposition and weight loss with three different rates as shown by the DTG peaks centered at 140.28, 198.38 and 313.15°C and also the two endothermic DTA peaks found at 139.37 and 206.24°C signifying the melting of the compound and breaking of bonds in the ligand molecule.

The $2\text{CoSO}_4 \cdot \text{L} \cdot \text{H}_2\text{O}$ complex is stable upto 90°C . An endotherm observed at $\sim 100^\circ\text{C}$ shows the loss of coordinated water to give the anhydrous complex. Decomposition of the anhydrous complex occurs in the temperature range $120\text{--}400^\circ\text{C}$ to form an intermediate of CoSO_4 . When heated above 500°C the decomposition of CoSO_4 to form the final residue of CoO is observed. The same is indicated by an exotherm at 450.4°C .

The $\text{NiCl}_2 \cdot 2\text{L}$ complex is stable upto 185°C . The weight loss between $185\text{--}300^\circ\text{C}$ signifies the elimination of two molecules of the organic ligand to give the intermediate of NiCl_2 . The NiCl_2 intermediate undergoes a slow decomposition above 500°C to form the final residue of NiO . The elimination of the organic molecule is supported by the appearance of an endothermic DTA peak at 233.6°C and the DTG peak centered at 231.9°C .

TABLE- 5 TG/DTG/DTA Data for L and its Metal Complexes

Compound	Stable upto (°C)	Stage	Decomposition Temperature		Nature of Transformation/ Intermediate Formed % mass found(calc.)	Nature of DTA peak and Temp. (°C)	DTG peak Temp. (°C)
			Initial (°C)	Final (°C)			
L (C ₁₃ H ₁₆ N ₂ O ₂)	127.2				Melting	139.4 Endo	-
		I	139	360	Continuous decomposition of DEID	206.2 Endo	140.3 198.4 313.2
2CoSO ₄ .L.H ₂ O	90.0	I	90	120	Elimination of water to form anhydrous complex 2CoSO ₄ .DEID (R) 88(95)	99.5 Endo	93.19
		II	120	400	Elimination of DEID to form CoSO ₄ as an intermediate (G) 53(55)	-	200.9 310.0 380.0
		III	425	720	Partial decomposition of CoSO ₄ to give CoO and CoSO ₄ mixture(S) 36(39)	450.4 Exo	531.6
NiCl ₂ .2L	185.0				Phase transformation	103.5 Endo	-
		I	185	300	Elimination of organic ligands to give intermediate of NiCl ₂ (R) 22.0(21.84)	233.61 Endo	231.9 299.48
		II	500	700	Conversion of NiCl ₂ into NiO (S) 10.5(11.58)	-	-

Note: (R) = rapid, (G) = gradual and (S) = slow decomposition

Exo = exothermic, Endo = endothermic, Temp = Temperature

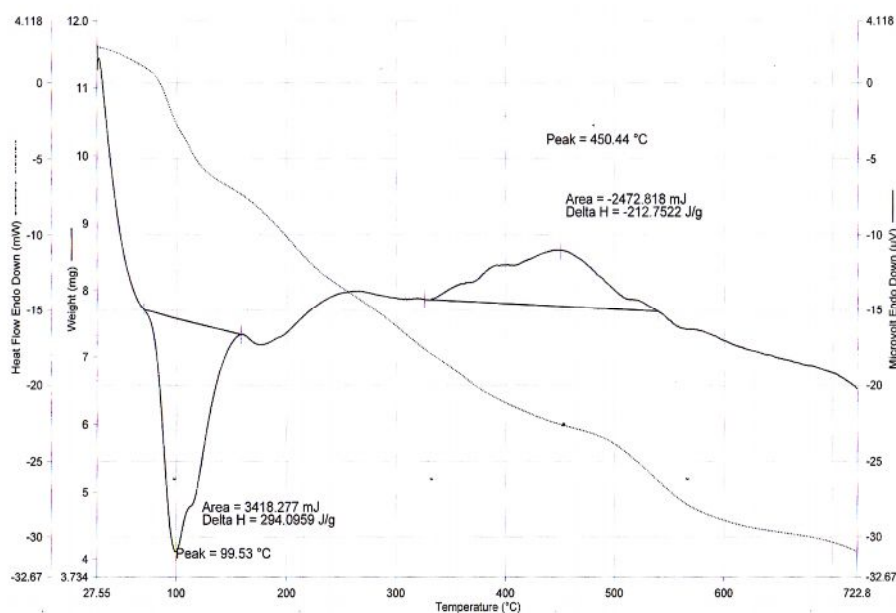
Figure 3: TG/DTA Patterns of 2CoSO₄.DEID.H₂O

Figure 4: TG/DTG Pattern of 2CoSO₄.DEID.H₂O

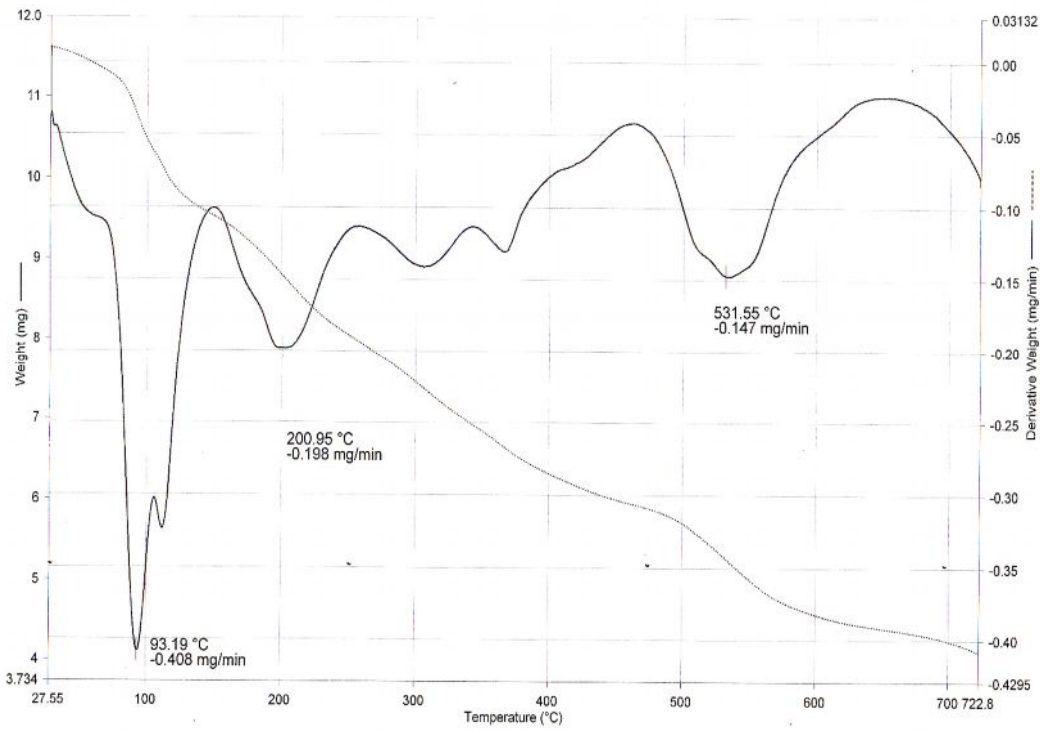


Figure 5: Cyclic Voltammogram of CoCl₂.L.2H₂O at the Scan Rate of 500 mVs⁻¹

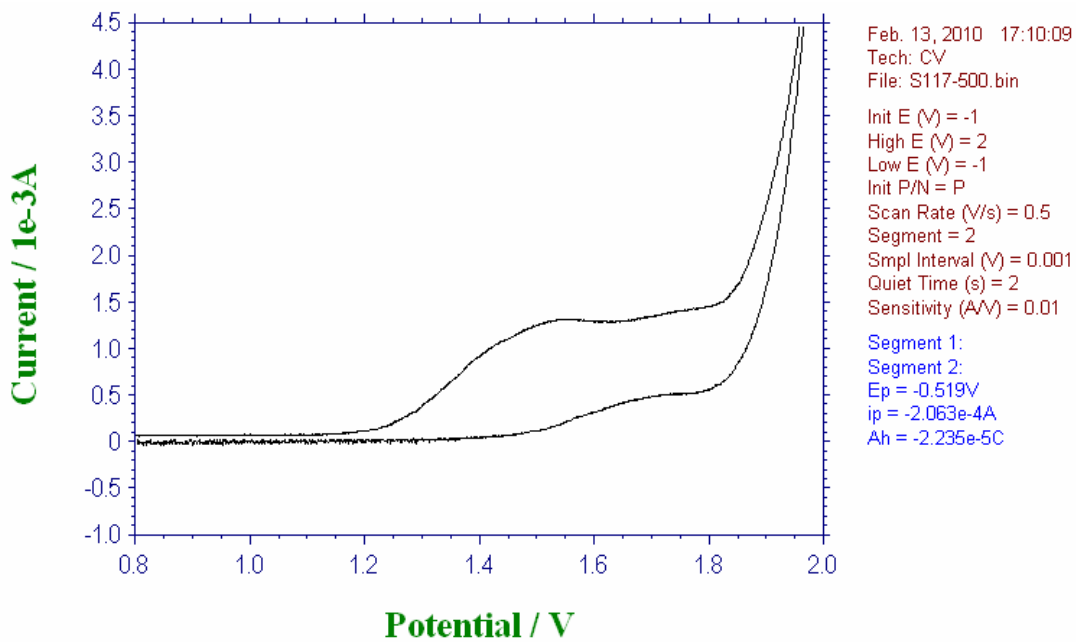


TABLE-6: Redox Properties of CoCl₂.L.2H₂O at Various Scan Rates

Scan rate	E _{pa} (V)	E _{pc} (V)	ΔE _p (mV)	E _{1/2} (V)	i _{pa} (μA)	i _{pc} (μA)	i _{pa} /i _{pc}
50	1.4677	1.4414	26	1.4545	116.7	20.0	5.835
250	1.4569	1.4150	42	1.4359	356.4	23.64	15.076
500	1.5426	1.5126	30	1.5276	1311	124.0	10.572

Electrochemical study on CoCl₂.L.H₂O

The cyclic voltammograms of this cobalt(II) chloro complex have been measured at different scan rates (50, 250 and 500mVs⁻¹). The typical voltammogram of CoCl₂.L.H₂O at scan rate 500mVs⁻¹ is shown in Figure 5. The redox properties are listed in Table 6. The plot of cathodic peak current versus $v^{1/2}$ reveals a diffusion controlled redox process and it is expected to involve cobalt(II)/cobalt(I) redox couple[33,34]. At $v = 50, 250$ and 500mVs^{-1} , the reduction of cobalt(II) to cobalt(I) occurs at the cathodic peak potentials of 1.4414, 1.4150 and 1.5126V respectively versus Ag/Ag⁺. The separations between the anodic and cathodic peak potentials (ΔE_p) are 26, 42 and 30mV at 50, 250 and 500mVs⁻¹ respectively. These values of ΔE_p indicate reversible one-electron redox process. The voltammetric E_{1/2} (or the formal E⁰) taken as the average of E_{pc} and E_{pa} at the scan rates of 50, 250 and 500mVs⁻¹ are 1.4545, 1.4359 and 1.5276V indicating that the present complex can not undergo reduction easily at a positive potential as the σ-donating ability of the chelating (N,O) Mannich base would tend to stabilize cobalt(II) ion in the complex. The peak current ratios i_{pa}/i_{pc} (5.835, 15.076 and 10.572) are greater than unity at all scan rates. The peak current increases with increase in $v^{1/2}$. This

establishes the electrode process as diffusion controlled.

Antimicrobial activity

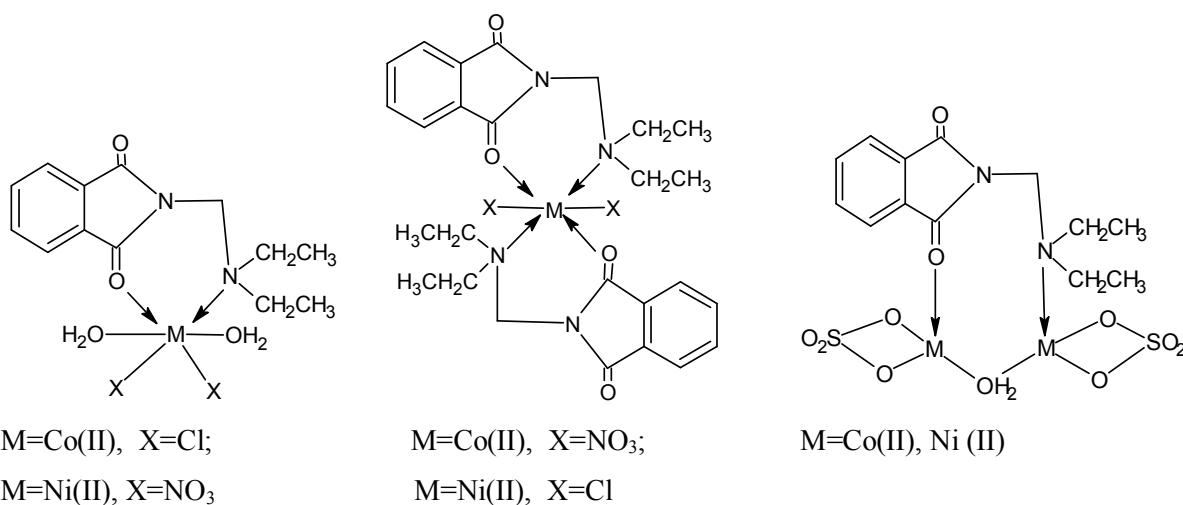
The Mannich base ligand (L) and its cobalt(II) and nickel(II) complexes have been screened for their *in vitro* antibacterial activity against *S.aureus* and *E.coli* and for antifungal activity against *C.albicans* and *A.niger*. The zones of inhibition produced by the test compounds are presented in Tables 7 and 8. It is seen that antimicrobial activity of the test samples increases with increase of their concentrations. It is observed that the test compounds exhibit activity comparable to that of standard drugs. It is known that cyclic imide derivatives possess a structural feature –CO-N(R)-CO- and an imide ring which confer on them potent biological activities [35]. It is also observed that the metal complexes are more active than the free organic ligand. The increased activity of the metal complexes may be explained on the basis of chelation theory [36]. Chelation reduces the polarity of the metal ion and enhances the lipophilic or hydrophobic character of the metal chelate which favours its permeation through microbial cell wall. The metal chelates may also disturb the respiration process of the microbial cells and thereby hinder the protein synthesis and further growth of the microorganism [37].

TABLE-7: Antibacterial Activity of L and its Metal Complexes

Compound	Zone of Inhibition (mm)							
	<i>S.aureus</i>				<i>E.coli</i>			
	Conc. of Compound (μg/mL)				Conc. of Compound (μg/mL)			
	25	50	75	100	25	50	75	100
L(C ₁₃ H ₁₆ N ₂ O ₂)	8	10	12	13	10	12	13	14
CoCl ₂ .L.2H ₂ O	12	15	17	20	10	12	15	19
2CoSO ₄ .L. H ₂ O	12	14	16	16	10	12	13	16
NiCl ₂ .2L	11	16	17	18	9	11	14	18
2NiSO ₄ .L. H ₂ O	14	16	18	20	10	11	14	17
Kanamycin	9	-	-	-	-	-	-	-
Tetracyclin	-	-	-	-	10	-	-	-

TABLE- 8: Antifungal Activity of L and its Metal Complexes

Compound	Zone of Inhibition (mm)							
	<i>A.niger</i>				<i>C.albicans</i>			
	Conc. of Compound ($\mu\text{g/mL}$)				Conc. of Compound ($\mu\text{g/mL}$)			
	25	50	75	100	25	50	75	100
L($\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_2$)	6	8	9	12	10	12	13	15
$\text{CoCl}_2 \cdot \text{L} \cdot 2\text{H}_2\text{O}$	8	11	15	18	11	14	17	20
$2\text{CoSO}_4 \cdot \text{L} \cdot \text{H}_2\text{O}$	9	12	15	19	10	14	16	18
$\text{NiCl}_2 \cdot 2\text{L}$	7	10	14	17	10	13	16	19
$2\text{NiSO}_4 \cdot \text{L} \cdot \text{H}_2\text{O}$	8	11	14	17	8	12	14	17
Amphotericin	10	-	-	-	-	-	-	-
Nystatin	-	-	-	-	9	-	-	-

Figure 6: Proposed Structures of the Metal complexes**ACKNOWLEDGEMENT**

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