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### Synthesis, characterization and antimicrobial activity studies on manganese(II) and cobalt(II) complexes of a new Mannich base 2-(morpholin-4-ylmethyl)isoindole-1,3-dione

M. Ramesh<sup>1\*</sup> and A. Sabastiyam<sup>2</sup>

<sup>1</sup>Department of Chemistry, J. J. College of Engineering and Technology, Tiruchirappalli, Tamil Nadu, India

<sup>2</sup>Department of Chemistry, Urumu Dhanalakshmi College, Tiruchirappalli, Tamil Nadu, India

#### ABSTRACT

In the present study a new Mannich base 2-(morpholin-4-ylmethyl)isoindole-1,3-dione and its coordination complexes with manganese(II) and cobalt(II) ions have been synthesized and characterized. The structural features of the complexes are investigated by elemental analysis, IR, UV-Vis, <sup>1</sup>H and <sup>13</sup>C NMR, mass, magnetic, conductance, TG/ DTA and cyclic voltammetric data. 2-(Morpholin-4-ylmethyl)isoindole-1,3-dione is found to act as a neutral bidentate chelating ligand binding to the metal ion through a carbonyl oxygen and tertiary amino nitrogen atoms. The non-electrolytic nature of the complexes are evidenced by their very low molar conductance values. On the basis of magnetic moments and electronic spectral data, the Mn(II) and Co(II) complexes are assigned an octahedral geometry excepting and the Co(II) chloro complex which is assigned a tetrahedral geometry. The antimicrobial activity of the ligand and a selected few complexes has been studied by 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, chelates, thermogravimetry, voltammetry, antimicrobial activity.

#### INTRODUCTION

Interest in the study of Mannich bases of phthalimide has been growing because of their antimicrobial, antituberculosis and antitumour activity. Mannich bases play an important role in inorganic chemistry, as they easily form stable complexes with most transition metal ions. The developments in the field of bioinorganic chemistry have increased interest in Mannich base complexes, since it has been recognized that these complexes may serve as models for biologically important molecules [1-4]. Metal ions play a vital role in a vast number of biological processes. The antimicrobial properties of metals have been recognized for centuries and have represented some of the most fundamental breakthrough in medicinal chemistry [5]. The inorganic pharmacology has emerged as an important field with more than 25 inorganic compounds, being used in therapy as antibacterial, antiviral, antitumor, anxiolytic and anticancer drugs [6,7]. Recently Mannich bases of phthalimide and succinimide and their metal complexes have been synthesized, characterized and screened for their biological activities [8-9]. In view of these facts, we report herein the synthesis, characterization and antimicrobial screening of the new Mannich base 2-(morpholin-4-ylmethyl)isoindole-1,3-dione and its Mn(II) and Co(II) complexes.

## MATERIALS AND METHODS

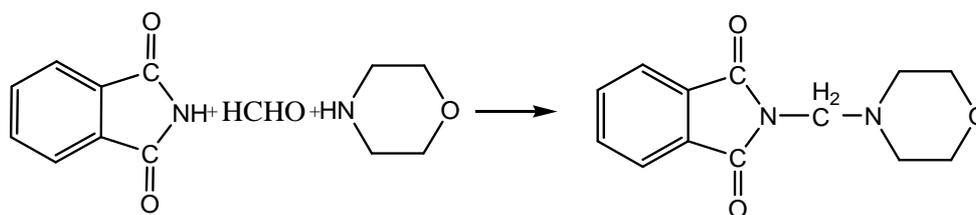
All the reagents used were of A.R. grade and the solvents used were commercial products of the highest available purity. Elemental analysis (C, H and N) was performed using Carlo Erba 1108 elemental analyzer. The metal and anion contents of the complexes were estimated by standard literature procedures [10]. The conductance data of the complexes were obtained in  $\sim 10^{-3}$  M DMF solutions at room temperature using Systronics Direct Reading Conductivity Meter 304 with a dip type conductivity cell. Infrared spectral measurements were made as KBr pellets using Perkin Elmer Spectrum-1 FT IR spectrometer. The far IR spectra were taken using Ratio Recording Bruker 3000 Hyperion Microscope with Vertex 80 FTIR spectrometer. The electronic spectra of Mn(II) and Co(II) complexes in the UV-visible region were measured in DMF solutions using a double beam UV-visible spectrometer, Perkin Elmer EZ 301. The mass spectral study of the ligand was carried out using JEOL-GC MATE II GC-MS (EI/CI) mass spectrometer. The  $^1\text{H}$  NMR spectra were recorded on JEOL GSX-400 FT NMR spectrometer (400 MHz) employing TMS as internal reference and DMSO- $d_6$  as solvent at ambient temperature. The  $^{13}\text{C}$  NMR spectrum of the ligand was recorded using JEOL GSK-400 spectrometer in  $\text{CDCl}_3$  solution at ambient temperature. Cyclic voltammograms were recorded in acetonitrile solution at 300 K using a three-electrode cell comprising reference Ag/AgCl, auxiliary Pt and working glassy carbon electrodes. Room temperature magnetic measurements of the complexes were carried out using a Gouy magnetic balance, calibrated using mercury(II) tetrathiocyanatocobaltate(II). The thermal studies (TG/DTA) were carried out on a Du Pont 910 DSC system with the 1090 programmer/data analyser in an atmosphere of air at a linear heating rate of  $10^\circ\text{C min}^{-1}$  from ambient to  $1000^\circ\text{C}$  using alumina as the standard reference material. Antimicrobial screening of the test compounds was carried out using agar-well diffusion method.

**Synthesis of the Ligand (L)**

2-(Morpholin-4-ylmethyl)isoindole-1,3-dione was synthesized by Mannich condensation reaction of morpholine, formaldehyde and phthalimide in 1:1:1 mol ratio (Scheme 1). Phthalimide (29.42 g, 0.1 mol) was mixed with aqueous formaldehyde (15 mL, 0.1 mol) followed by adding then morpholine (17.6 mL, 0.1 mol) was added into the mixture at room temperature with constant stirring. After 2 days the colourless solid mass obtained was filtered, washed with water and dried at  $100^\circ\text{C}$  in an air oven and recrystallised from ethanol. The yield of the compound was 85 % (melting point:  $116^\circ\text{C}$ ). The synthetic route of the synthesized compound L is shown in **Scheme-1**

**The analytical and spectral data obtained for the ligand are summarized below:**

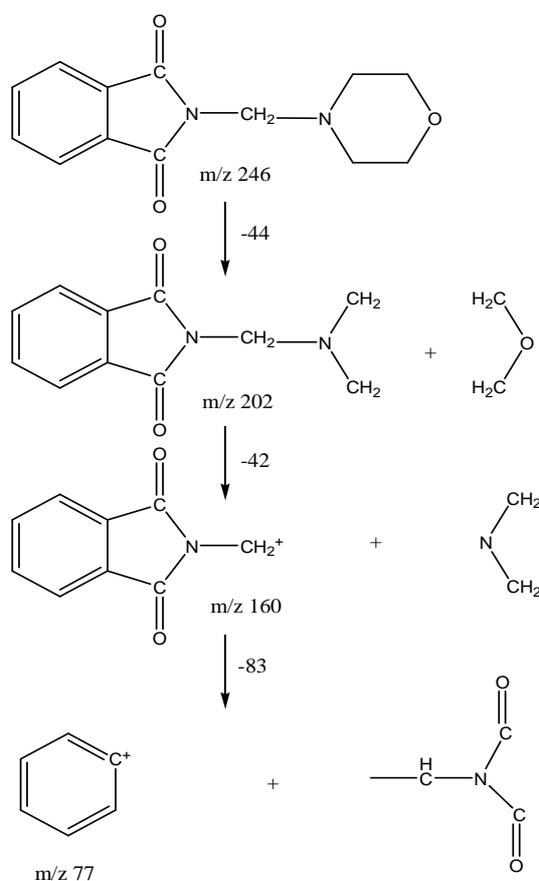
**Analysis:** Calculated for  $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_3$ : C 63.41, H 5.69, N 11.38 %, Found: C 63.55, H 5.65, N 11.50 %; **FT-IR** ( $\text{KBr}$ ,  $\text{cm}^{-1}$ ): 2962(aromatic C-H), 2853(aliphatic C-H), 1771, 1704, 1640( $\text{C}=\text{O}$ ), 1640-1413(aromatic  $\text{C}=\text{C}$ ), 1267, 1152( $\text{C}-\text{N}-\text{C}$ ), 1112 ( $\text{C}-\text{O}-\text{C}$ );  **$^1\text{H}$  NMR** (DMSO- $d_6$ ,  $\delta$ ppm): 7.85(4H, aromatic), 4.43(2H,  $\text{N}-\text{CH}_2-\text{N}$ ), 2.50(4H,  $\text{N}(\text{CH}_2)_2$ ), 3.54(4H,  $\text{O}(\text{CH}_2)_2$ );  **$^{13}\text{C}$ -NMR** (DMSO- $d_6$ ,  $\delta$ ppm): 134.50 – 123.13(aromatic carbons), 134.50(Bridgehead carbons) 168.68( $\text{C}=\text{O}$  carbons), 65.94( $\text{O}(\text{CH}_2)_2$  carbons), 50.34( $\text{N}(\text{CH}_2)_2$  carbons); **Mass** ( $m/z$ ): 246 ( $\text{M}^+$  peak), 202, 160, 77 (Fig.1) the fragmentation pattern of the ligand is shown in **Scheme-2**.



Scheme-1

**Synthesis of the Metal Complexes**

All the complexes of L were isolated from non-aqueous medium using ethanol. In each case, the hot ethanolic solution of the metal salt was added slowly with constant stirring to the hot ethanolic solution of the ligand either in 1:1 or 1:2 mol ratio. The insoluble complexes formed were filtered, washed with ethanol and then dried in an air oven at  $85^\circ\text{C}$ .



**Scheme-2** Mass spectral fragmentation pattern of **L**  
**RESULTS AND DISCUSSION**

The analytical and molar conductance data of the Mn(II) and Co(II) complexes of **L** are provided in **Table 1**. The analytical and conductance data 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. The manganese (II) and cobalt(II) chloro, nitrate complexes have 1:1 stoichiometry while cobalt(II) sulphato complex shows 1:2 stoichiometry. The 1:1 stoichiometry of the Co(II) chloro complex is also evidenced by the mass spectrum of the complex ie by the existence of molecular ion peak at  $m/z = 375.93$ . (Fig. 2).

**Table 1.** Analytical and conductance data for **L** and its metal complexes

Compound	% C		% H		% N		% Metal		% Anion		$\Omega^{-1}\text{cm}^2\ \text{mol}^{-1}$
	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.	
L ( $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_3$ )	63.55	63.41	5.65	5.69	11.50	11.38	-	-	-	-	-
$\text{MnCl}_2 \cdot \text{L} \cdot 2\text{H}_2\text{O}$	38.41	38.24	4.47	4.41	6.90	6.86	13.52	13.46	17.48	17.40	11.20
$\text{MnSO}_4 \cdot \text{L} \cdot 2\text{H}_2\text{O}$	36.29	36.03	4.26	4.15	6.57	6.46	12.77	12.68	22.30	22.17	20.45
$\text{CoCl}_2 \cdot \text{L}$	41.15	41.49	3.72	3.72	7.45	7.44	15.68	15.67	18.89	18.88	22.32
$\text{Co}(\text{NO}_3)_2 \cdot \text{L}$	36.65	36.36	3.48	3.26	13.26	13.06	13.84	13.73	-	28.90	28.15
$\text{CoSO}_4 \cdot 2\text{L} \cdot \text{H}_2\text{O}$	47.05	46.92	4.82	4.58	8.64	8.42	8.98	8.86	14.67	14.43	10.50

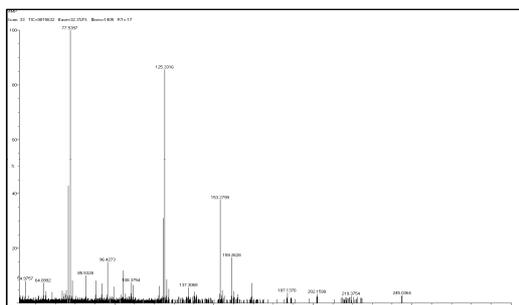
**IR Spectra**

The characteristic IR absorption bands of the Mn(II) and Co(II) complexes have been compared with the free ligand bands (Table 2) in order to get meaningful information regarding the bonding sites. The ligand exhibits absorption bands at 1771, 1704 and 1640  $\text{cm}^{-1}$  which are assigned to  $\nu_{\text{C=O}}$  of phthalimide moiety [11,12]. But in the IR spectra of metal complexes the ligand at band 1704  $\text{cm}^{-1}$  has split into two bands one at a higher position (1740-1700  $\text{cm}^{-1}$ ) and another at lower position (1611-1595  $\text{cm}^{-1}$ ) in the spectra of the metal complexes indicating the coordination of one of the two carbonyl oxygen atoms of the phthalimide moiety to the metal ion. This coordination tendency of the MMP ligand is consistent with the observations of Adams *et al* [11] and Fairlamb *et al* [12]. The binding of the carbonyl oxygen to the metal ion has also been confirmed by the appearance of new bands due to  $\nu_{\text{M-O}}$  in the far IR region at 524-535  $\text{cm}^{-1}$ . The ligand L exhibits vibrational bands at 1267 and 1152  $\text{cm}^{-1}$  which are assigned to  $\gamma_{\text{C-N-C}}$  [13, 14] of the morpholine moiety. These bands have shifted to lower region (1153-1050  $\text{cm}^{-1}$ ) in the complexes indicating the coordination of the tertiary amino nitrogen atom to the metal ion. The appearance of bands due to  $\nu_{\text{M-N}}$  in the far IR region at 458-463  $\text{cm}^{-1}$  is also an indication of metal-nitrogen bonding in the metal complexes. In the case of Co(II) chloro complex, observation of absorption band at 357  $\text{cm}^{-1}$  points to the binding of chloro group to the metal ion. Though the coordination of aliphatic tertiary amino nitrogen is not sterically favoured, the high electron density available on tertiary amino nitrogen favours its coordination to a metal ion where there is a possibility for chelation [9,15,16].

The Co(II) nitrate complex have shown IR absorptions in the regions of 1590( $\nu_5$ ), 1315( $\nu_1$ ), 1109( $\nu_2$ ) and 851( $\nu_6$ )  $\text{cm}^{-1}$ . The difference between  $\nu_5$  and  $\nu_1$  bands is 275  $\text{cm}^{-1}$  suggesting the bidentate coordination of the nitrate group to the metal in the complex. The Mn(II) sulphato complex absorbs at 1152, 1107 and 967  $\text{cm}^{-1}$  ( $\nu_3$ ); 897  $\text{cm}^{-1}$  ( $\nu_1$ ), 729, 678 and 606  $\text{cm}^{-1}$  ( $\nu_4$ ) and 525  $\text{cm}^{-1}$  ( $\nu_2$ ) suggesting chelating bidentate coordination. But the Co(II) sulphato complex absorbs at 1112 ( $\nu_3$ ), 715 and 622 ( $\nu_4$ ), 860 ( $\nu_1$ ) and 535  $\text{cm}^{-1}$  ( $\nu_2$ ) suggesting the presence of monodentate sulphato group. The presence of coordinated water molecules in Mn(II) chloro and sulphato and Co(II) sulphato complexes is supported by the appearance of absorption bands at 3407-3456 ( $\nu_{\text{OH}}$ ), 1596-1605 ( $\delta_{\text{HOH}}$ ), 851-860 ( $\rho_{\text{rHOH}}$ ) and 605-622  $\text{cm}^{-1}$  ( $\rho_{\text{wHOH}}$ ).

**Table 2. Infrared spectral data of L and its Mn (II) and Co (II) complexes**

Compound	$\nu_{\text{C=O}}$	$\nu_{\text{CNC}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-X}}$
L ( $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_3$ )	1771, 1704, 1640	1267	-	-	-
$\text{MnCl}_2 \cdot \text{L} \cdot 2\text{H}_2\text{O}$	1771, 1703, 1596	1154	529	463	-
$\text{MnSO}_4 \cdot \text{L} \cdot 2\text{H}_2\text{O}$	1773, 1702, 1605	1151	524	458	-
$\text{CoCl}_2 \cdot \text{L}$	1771, 1703, 1598	1153	531	460	357
$\text{Co}(\text{NO}_3)_2 \cdot \text{L}$	1771, 1705, 1590	1153	527	459	-
$\text{CoSO}_4 \cdot 2\text{L} \cdot \text{H}_2\text{O}$	1708(s)	1112	535	-	-



${}^4T_{2g}$  respectively. These spectral features [18-24] indicate octahedral stereochemistry of Mn(II) in its complexes and it is further supported by the observed magnetic moment values [17-21] in the range 5.28-5.36 BM. The Co(II) nitrate and sulphate complexes exhibit bands in the regions 6738-6712, 14430-14432, 18416-18248 and ~34211  $\text{cm}^{-1}$ , which may be assigned to  ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$ ,  ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{F})$ ,  ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$  and charge transfer transition respectively, which indicate octahedral geometry of Co(II). The observed magnetic moment values of Co(II) nitrate and sulphate complexes at 4.78 and 5.20 B.M respectively also supports the high spin octahedral stereochemistry of Co(II). The Co(II) chloro complex exhibits absorptions at 3905, 6716, 15152 and 27473  $\text{cm}^{-1}$  which are assigned to  ${}^4A_2(\text{F}) \rightarrow {}^4T_2(\text{F})$ ,  ${}^4A_2(\text{F}) \rightarrow {}^4T_1(\text{F})$ ,  ${}^4A_2(\text{F}) \rightarrow {}^4T_1(\text{P})$  and charge transfer transition respectively, which indicate tetrahedral geometry of Co(II). This is further supported by the measured magnetic moment at 4.51 BM.

The ligand field parameters for the cobalt(II) complexes have been computed and presented in **Table 4**. For the Co(II) chloro complex the measured  $\nu_2/\nu_1$  ratio 1.72 is much lower than 1.80 indicating the tetrahedral geometry of Co(II). For Co(II) nitrate and sulphate complexes the  $\nu_2/\nu_1$  ratios 2.09 and 2.15 are indicating octahedral geometry of the metal ion. The order of Dq values (0.79-0.81) among the octahedral Co(II) complexes is found to be  $\text{Co}(\text{NO}_3)_2 \cdot \text{L} > \text{CoSO}_4 \cdot 2\text{L} \cdot \text{H}_2\text{O}$ . This trend is in accordance with the position of anions in the spectrochemical series. From the calculated  $\beta$  % values (13-30) covalent character of the Co(II) complexes has been established.

**Table 3. Colours, electronic spectral bands, transition assignments and magnetic moment values of complexes**

Compound	Colour	Magnetic moment B.M	Absorption maxima( $\text{cm}^{-1}$ )	Transition Assignment
$\text{MnCl}_2 \cdot \text{L} \cdot 2\text{H}_2\text{O}$	Light pink	5.28	13193	${}^6A_{1g} \rightarrow {}^4T_{1g}$
			22780	${}^6A_{1g} \rightarrow {}^4A_{1g} + {}^4E_g$
			25213	${}^6A_{1g} \rightarrow {}^4T_{2g}$
$\text{MnSO}_4 \cdot \text{L} \cdot 2\text{H}_2\text{O}$	Light pink	5.36	12640	${}^6A_{1g} \rightarrow {}^4T_{1g}$
			22490	${}^6A_{1g} \rightarrow {}^4A_{1g} + {}^4E_g$
			25455	${}^6A_{1g} \rightarrow {}^4T_{2g}$
$\text{CoCl}_2 \cdot \text{L}$	Blue	4.51	3905	${}^4A_2(\text{F}) \rightarrow {}^4T_2(\text{F})$
			6716	${}^4A_2(\text{F}) \rightarrow {}^4T_1(\text{F})$
			15152	$A_2(\text{F}) \rightarrow {}^4T_1(\text{P})$
			27473	CT
$\text{Co}(\text{NO}_3)_2 \cdot \text{L}$	Pale brown	4.78	6738	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$
			14432	${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{F})$
			18248	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$
			34211	CT
$\text{CoSO}_4 \cdot 2\text{L} \cdot \text{H}_2\text{O}$	Brownish red	5.20	6712	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$
			14430	${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{F})$
			18416	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$
			27100	CT

**Table 4. Ligand field parameters of Co(II) Complexes**

Compound	$\nu_2/\nu_1$	B $\text{cm}^{-1}$	Dq $\text{cm}^{-1}$	$\beta$	$\beta$ %	LFSE $\text{kcal.mol}^{-1}$
$\text{CoCl}_2 \cdot \text{L}$	1.72	676.8	390.5	0.70	30	13.39
$\text{Co}(\text{NO}_3)_2 \cdot \text{L}$	2.09	831.0	673.8	0.86	14	23.10
$\text{CoSO}_4 \cdot 2\text{L} \cdot \text{H}_2\text{O}$	2.15	847.3	671.2	0.87	13	23.01

Note: Free ion  $B_0$  value for  $\text{Co}^{II} = 971 \text{ cm}^{-1}$ ,  $\text{LFSE} = 12Dq \text{ kcal.mol}^{-1} = 350 \text{ cm}^{-1}$

### Thermal decomposition studies

The TG/DTA and TG/DTG patterns obtained for the representative metal complexes of L are shown in Fig. 3 and 4. The TG/DTG/DTA data obtained for L and its complexes are summarized in Table 5.

The compound L melts at 116.48°C as revealed by a sharp endotherm involving absorption of heat of 92.159 J/g as there is no weight loss. The organic compound is stable up to 211.92°C. It undergoes rapid decomposition and weight loss in the range 211.9-291.5°C. This first stage of decomposition is evidenced by the DTG peak centered at 255.76°C occurring at a rate of 2.129 mg/min and also by the endothermic DTA peak seen at 267.25°C. There is a gradual weight loss at the rate of 0.161mg/min from 300 to 520°C (II stage) as indicated by the DTG peak centered at 494.51°C. The gradual decomposition of the intermediate in the 300-520°C range is also marked by two

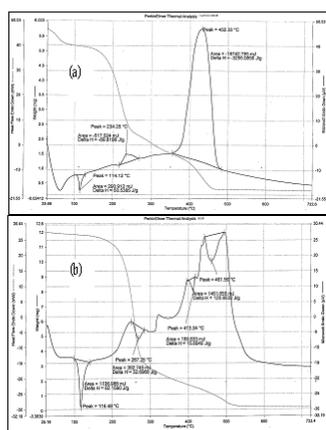
endothermic DTA peaks observed at 413°C and 461.56°C [27]. The intermediate may be a lower polymer of formaldehyde which is a decomposition product of L. The weight of the final residue which is stable above 530°C is only 4% of the initial weight taken (2.012 mg). The final residue may be a higher polymer of formaldehyde.

The thermal study of  $\text{Co}(\text{NO}_3)_2 \cdot \text{L}$  shows a two stage decomposition pattern. The compound experiences a weight loss up to 86°C due to loss of water of hydration/adsorbed water. The onset of decomposition of the dry complex begins at 177.5°C. There is a rapid loss of weight to the extent of 57% due to elimination of the organic ligand L to form the metal nitrate. The elimination of L takes place in the temperature range of 177.5-288°C. This first stage of decomposition of the complex takes place at the rate of 0.580 mg/min as indicated by the DTG peak centered at 223.16°C. The cobalt nitrate intermediate formed undergoes gradual decomposition at two different rates 0.092 mg/min (DTG peak at 296.5°C) and 0.171 mg/min (DTG peak at 422.59°C) to produce the oxide of cobalt as the final residue. The observed weight of the final residue (0.29 mg) is slightly less than that expected [22].

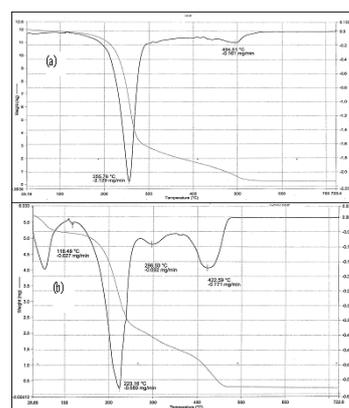
The differential thermal analysis of the complex exhibits one endothermic peak at 61°C showing the elimination of adsorbed water. The sharp endothermic peak at 114.12°C may indicate the melting of the anhydrous complex compound. The exothermic peak found at 234.25°C may indicate slow oxidation process, while the exotherm seen at 432.33°C may indicate rapid oxidative decomposition and sublimation.

**Table 5. TG/ DTG / DTA Data for L and its Co(II) nitrate Complex**

Compound	Stable up to (°C)	Decomposition Temperature range (°C)			Probable change / Intermediate formed with % mass Found(Calc.)	DTA Peak (°C) and its nature	DTG Peak (°C)
		Stage	Initial	Final			
L ( $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_3$ )	211.9	I	211.9	291.5	Melting process	116.5 endo	-
		II	300	520	Oxidative degradation (R) 25	267.3 endo	255.8
						Polymer of formaldehyde (G) 4(12)	461.5 endo
$\text{Co}(\text{NO}_3)_2 \cdot \text{L}$	177.5	I	177.0	288	Melting	114.1 endo	-
		II	382	465	Elimination of L and formation of intermediate $\text{Co}(\text{NO}_3)_2$ . (R) 43 (35)	234.3 exo	223.2
				Decomposition of $\text{Co}(\text{NO}_3)_2$ to form CoO and possible sublimation of residue 5 (20.4)	432.3 exo	422.6	



**Fig. 3 TG /DTA Pattern of L and  $\text{Co}(\text{NO}_3)_2 \cdot \text{L}$**   
Cyclic voltammetric study of  $\text{CoCl}_2 \cdot \text{L}$



**Fig. 4 TG /DTG Pattern of L and  $\text{Co}(\text{NO}_3)_2 \cdot \text{L}$**

The cyclic voltammogram of  $\text{CoCl}_2 \cdot \text{L}$  at  $250 \text{ mVs}^{-1}$  is reproduced in Fig. 5. The cyclic voltammograms of  $\text{CoCl}_2 \cdot \text{L}$  at the three different scan rates feature the reduction of Co(II) to Co(I) form at cathodic peak potential values of 1.4484, 1.4346 and 1.4110 V at 50, 250 and 500  $\text{mVs}^{-1}$  respectively. Reoxidation of cobalt (I) species has occurred

at the anodic peak potential values of 1.4875, 1.4807 and 1.4770 V at scan rates of 50, 250 and 500 mVs<sup>-1</sup> respectively. The separations between the anodic and cathodic peak potential ( $\Delta E_p$ ) are observed at 39.1, 46.1 and 66.0 mV, when scanned at 50, 250 and 500 mVs<sup>-1</sup> respectively. In this case  $\Delta E_p$  increases with scan rate and is less than 60 at 50, 250 and 500 mVs<sup>-1</sup> scan rates and around 60 at 500 mVs<sup>-1</sup> scan rate. This trend indicates a reversible Co<sup>II</sup>/Co<sup>I</sup> redox couple. The ratios of  $i_{pa}/i_{pc}$  at 50, 250 and 500 mVs<sup>-1</sup> scan rates are 2.50, 6.31 and 9.62 respectively. These peak current ratios are higher than unity, suggesting that the electron transfer is not followed by a chemical reaction. In other words EC mechanism is not followed. The peak current values have increased with the square roots of scan rates showing diffusion controlled electrode process [23]. The calculated values of  $E_{1/2}$  or ( $E^0$ ) at the three different scan rates 50, 250 and 500 mVs<sup>-1</sup> are found to be positive values viz. 1.4679, 1.4576 and 1.4440 V. These positive values of  $E_{1/2}$  show that the present Co(II) complex cannot undergo an easy reduction. As the  $\sigma$ -donating ability of the chelating Mannich base L would tend to stabilize Co<sup>II</sup> ion in the chelate complex, reduction becomes difficult.

**Table 6. Redox Properties of Co(II) chloro Complex at Various Scan Rates**

Complex	Scan rate mVs <sup>-1</sup>	$E_{pa}$ V	$E_{pc}$ V	$\Delta E_p$ mV	$E_{1/2}$ V	$i_{pa}$ $\mu$ A	$i_{pc}$ $\mu$ A	$i_{pa}/i_{pc}$
CoCl <sub>2</sub> .L	50	1.487	1.448	39.1	1.467	169.6	67.73	2.504
	250	1.480	1.434	46.1	1.457	507.4	80.4	6.310
	500	1.477	1.411	66.0	1.444	806.2	83.84	9.615

**Table 7. Antibacterial activity of L and its metal complexes**

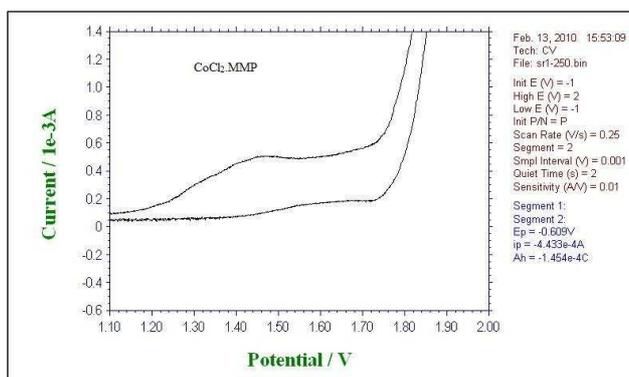
Compound	Zone of Inhibition (mm)							
	<i>E.coli</i>				<i>S.aureus</i>			
	Conc. of Compound ( $\mu$ g/mL)				Conc. of Compound ( $\mu$ g/mL)			
	25	50	75	100	25	50	75	100
L (C <sub>13</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> )	6	7	10	12	5	7	10	11
MnCl <sub>2</sub> .L.2H <sub>2</sub> O	16	17	19	20	10	12	13	15
MnSO <sub>4</sub> .L.2H <sub>2</sub> O	16	19	20	23	10	11	12	17
CoCl <sub>2</sub> .L	21	22	23	25	12	13	15	17
CoSO <sub>4</sub> .2L.H <sub>2</sub> O	13	16	18	20	11	12	14	18
Kanamycin	<b>10</b>							
Tetracyclin	-	-	-	-	<b>13</b>	-	-	-

**Antimicrobial activity**

The Mannich base ligand (L) and its manganese (II) and cobalt(II) complexes were screened for their in vitro antibacterial activity against *S.aureus* and *E.coli* and for antifungal activity against *C. albicans* and *A.niger* [24,25] at four different concentrations of 25, 50, 75 and 100  $\mu$ g/mL in DMF by agar-well diffusion method. Standard drugs kanamycin, tetracycline, amphotericin and nystatin were screened against *S.aureus*, *E.Coli*, *C. albicans* and *A.niger* respectively under identical conditions for comparison. The zones of inhibition which are the measures of antimicrobial activities produced by the test compounds are presented in **Table 6** and **7**. 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 the standard drugs and 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 and overtone's concept of cell permeability. Chelation reduces the polarity of the metal ion and enhances the lipophilic or hydrophobic character of the metal chelate which favours the permeation through microbial cell wall. According to overtone's concept liposolubility of the compounds is an important factor which control the antimicrobial activity[26, 27].

**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 ( $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_3$ )	5	6	7	8	6	8	9	10
$\text{MnCl}_2 \cdot \text{L} \cdot 2\text{H}_2\text{O}$	10	12	13	14	9	10	11	12
$\text{MnSO}_4 \cdot \text{L} \cdot 2\text{H}_2\text{O}$	10	11	12	14	10	11	12	14
$\text{CoCl}_2 \cdot \text{L}$	12	14	16	19	12	14	15	17
$\text{CoSO}_4 \cdot 2\text{L} \cdot \text{H}_2\text{O}$	9	11	12	13	8	9	12	14
Amphotericin	<b>12</b>	-	-	-	-	-	-	-
Nystatin	-	-	-	-	<b>14</b>	-	-	-

**Fig. 5 Cyclic Voltammogram of  $\text{CoCl}_2 \cdot \text{L}$  at  $250 \text{ mVs}^{-1}$  Scan Rate**

### CONCLUSION

The Mannich base ligand (L) and its metal complexes have been newly synthesized and characterized by elemental analysis, IR, NMR, electronic and mass spectra, TG/DTA, cyclic voltammetry, conductivity and magnetic measurements. The IR and far IR studies indicate that the ligand (L) involves in bidentate coordination through the morpholine ring nitrogen atom and one of the two carbonyl oxygen atoms. On the basis of electronic and magnetic data, octahedral geometry is assigned to all the manganese (II) complexes and to the nitrate and sulphato complexes of cobalt (II). Tetrahedral geometry is proposed to the chloro complex of cobalt (II). Thermal decomposition studies on the Mannich and its Co(II) nitrate complex show that they undergo two stage decompositions. The study on redox properties of Co(II)/Co(I) redox couple and that the chelation of  $\sigma$ -donating organic ligand stabilizes the Co(II) ion very much stable in its complexes. The ligand and its metal complexes show significant antimicrobial activity. The complexes are found to be more effective than the free ligand. The antimicrobial activity of the test compounds are comparable to that of the standard drugs used.

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