



## **Synthesis, Characterization and Biological Studies of Copper(II) Complexes of 2-(Piperidin-4-ylmethyl)isoindoline-1,3-dione**

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**Abstract :** A new Mannich base, 2-(piperidin-4-ylmethyl)isoindoline-1,3-dione (L), formed by the condensation of piperidine, formaldehyde and phthalimide, and its Cu(II) complexes have been synthesized. Their structures have been elucidated on the basis of elemental analysis, molar conductance, IR, UV-visible, mass, <sup>1</sup>H NMR and <sup>13</sup>C NMR, EPR, magnetic, thermal and electrochemical studies. The complexes exhibit octahedral or tetrahedral geometry. Infrared spectral data show that the organic ligand is bidentate, binding through one of the two carbonyl oxygen atoms of the phthalimide moiety and the piperidine ring nitrogen and also the existence of coordinated water molecules. The X band EPR spectra of Cu(II) complexes in DMSO at room temperature were recorded and their salient features are reported. The electrochemical behaviour of Cu(II) chloro complex indicates that there exists Cu(II)/Cu(I) redox couple and that the organic ligand can stabilize the unusual oxidation state of Cu(I). Thermal data of some of the compounds show that the thermal decompositions take place mostly in two steps to produce metal oxides as final residues. Antimicrobial activities of the newly synthesized compounds were also investigated.

**Keywords:** Mannich base, thermal analysis, electrochemical behaviour, biological studies.

### **1. Introduction**

Mannich base ligands and their metal complexes have attracted great interest in chemistry and biology due to their facile synthesis and wide applications<sup>1-3</sup>. Considerable attention has been focused on the syntheses of new copper(II) complexes of ligands containing bulky groups because of their role in the development of coordination chemistry, and in inorganic biochemistry<sup>4</sup>, catalysis<sup>5</sup>, optical materials<sup>6</sup>, antibacterial, antifungal, analgesic, anxiolytic, antitumor<sup>7</sup> activities and so on. Metal complexes of Mannich bases have been studied<sup>8-13</sup> extensively in recent years due to their selectivity and sensitivity towards various metal ions. A search through the literature reveals that no work has been done on the Mannich base of piperidine and phthalimide. It is well known from the literature that phthalimide compounds containing the imido moiety have a strong ability to form metal complexes. Therefore, it was thought worthwhile to synthesise some metal complexes of this type of Mannich base and investigate its bonding characteristics<sup>17-29</sup>. We herein report a new Mannich base, 2-(piperidin-4-ylmethyl)isoindoline-1,3-dione and its coordination chemistry.

### **2. Experimental**

#### **2.1 Materials and methods**

All the reagents used for synthesizing the ligand and its complexes were of A.R. grade. The solvents used were commercial products of the highest available purity and were further purified by distillation. Micro

elemental data were obtained with Carlo Erba 1108 elemental analyzer. Metal contents were estimated by usual procedure<sup>14</sup>, after digesting the complexes with con.HNO<sub>3</sub>. Conductance data were obtained in ~10<sup>-3</sup> M DMF solution of the complexes using digital conductivity meter. IR spectra were recorded using Perkin Elmer FT-IR spectrometer by using KBr pellets. Absorbance in UV-Visible region was recorded in DMF solution using UV-Visible spectrometer. The <sup>1</sup>H and <sup>13</sup>C NMR of the ligand were recorded on a Bruker instrument employing TMS as internal reference and DMSO-d<sub>6</sub> as solvent. The FAB mass for the ligand was carried out using Mass spectrometer. The room temperature magnetic susceptibility measurements of the complexes were made by using a Gouy Magnetic Balance. Electrochemical study on Cu(II) chloro complex was carried out using Electrochemical analyser CHI- 620A, USA. The three electrode assembly of the cell consists of the glassy carbon working electrode, Pt foil auxiliary electrode and Ag/ AgCl reference electrode. A solution of 0.1 M NaClO<sub>4</sub> was the supporting electrolyte. The DMF solution of the sample was purged with N<sub>2</sub> gas. Thermal studies were carried out on a Perkin Elmer Diamond TG/DTA thermal analyzer in an atmosphere of air/N<sub>2</sub> at a linear heating rate of 10° C/min from ambient to 900° C using alumina as the reference material. The TG was derivatized to get DTG by the software associated with the instrument. The antimicrobial activity was determined the agar well diffusion method.

## 2.2 Synthesis of the Mannich base ligand (L)

A new Mannich base 2-(piperidin-4-ylmethyl)isoindoline-1,3-dione (L) was synthesized by employing Mannich condensation reaction<sup>14</sup> between piperidine, formaldehyde and phthalimide in 1:1:1 mole ratio. It was recrystallized from ethanol (yield: 82 %, melting point: 115° C).

## 2.3. Synthesis of Mannich base metal complexes

Metal complexes of the Mannich base ligand (L) were isolated from alcoholic medium. 2-(piperidin-4-ylmethyl)isoindoline-1,3-dione ligand was dissolved in hot ethanol. Hot ethanolic solution of Cu (II) salt was added drop wise to the ligand solution with constant stirring. The insoluble complex precipitated in each case was filtered, washed repeatedly with ethanol and with minimum quantity of acetone, and then dried in a vacuum desiccator.

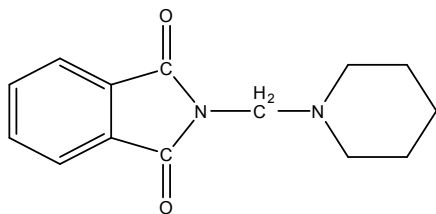
## 2.4. Antimicrobial Screening

Antibacterial and antifungal activities of the organic ligand and its selected few metal complexes were screened *in vitro* against the bacterial strains viz. *E.coli* and *S.aureus* and the fungal species *C.albicans* and *A.niger* employing agar well diffusion technique. Nutrient agar medium was used for culturing bacteria and Rose Bengal Chloramphenicol agar medium was used for culturing fungal species. *Kanamycin* and *tetracyclin* were used as standard antibacterial drugs and *amphotericin* and *nystatin* were used as the standard antifungal agents. Wells were made on the previously seeded agar plate with a metallic borer and various concentrations of the test solutions in DMF were transferred into the wells. The concentrations tested were 25, 50, 75 and 100 µg/mL. The nutrient agar plates inoculated with the bacterial organisms under test were incubated at 35 - 37°C for 24 h, but the plates streaked with fungal species were incubated at 35 - 37°C for 48 h and then the diameters of inhibition zones (in mm) were measured.

## 3. Results and Discussion

### 3.1 Synthesis and Characterization of the Mannich base ligand (L)

**Analysis:** Calculated for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C 68.85, H 6.55, N 11.48%; Found: C 68.23, H 6.87, N 11.22%; Uv (DMF nm): 292, 272; IR (KBr cm<sup>-1</sup>): 1763,1718 (C=O), 1256,1174 (CNC); <sup>1</sup>HNMR (CDCl<sub>3</sub> δppm): 7.85(aromatic H), 2.47(NCH<sub>2</sub>), 1.45 (CH<sub>2</sub> piperidine), 4.43 (NCH<sub>2</sub>N); <sup>13</sup>CNMR (CDCl<sub>3</sub> δppm): 168.76, 134.44, 131.4, 123.06, 52.14, 51.19, 25.38, 23.25, 59.85; Mass (m/z): 244 (M<sup>+</sup> peak). Thus based on the data obtained from various physical and chemical studies, the molecular structure of L is confirmed as shown below.



### 2-(piperidin-4-ylmethyl)isoindoline-1,3-dione (L)

### 3.2. Characterization of metal complexes

The analytical data and the stoichiometries of the metal complexes are shown in Table 1. The molar conductivity values of the metal complexes establish the fact that they are non-ionic due to the inclusion of anions within the coordination sphere.<sup>15</sup>

**Table 1 Analytical and physical data of the metal complexes of L.**

Compound	Colour	Analytical (%) found (calculated)					$\Lambda_M (\Omega^{-1} \text{cm}^2 \text{mol}^{-1})$
		C	H	N	M	A	
CuCl <sub>2</sub> .L	greenish brown	39.98 (39.38)	4.89 (4.27)	7.83 (7.39)	16.21 (16.79)	18.98 (18.75)	29.32
CuBr <sub>2</sub> .L.2H <sub>2</sub> O	pale green	33.14 (33.38)	4.02 (3.97)	5.26 (5.56)	12.14 (12.62)	31.22 (31.75)	14.75

**Table 2 IR spectral assignments of the ligand L and its complexes**

Compound	$\nu_{\text{C=O}}$	$\nu_{\text{CNC}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-X}}$	$\nu_{\text{OH}}$
L (C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )	1644	1174	-	-	-	-
CuCl <sub>2</sub> .L	1600	1137	535	409	359	
CuBr <sub>2</sub> .L.2H <sub>2</sub> O	1597	1138	535	-	360	347

**Table 3. Magnetic and electronic spectral data of the metal complexes**

Complex	Magnetic moment (B.M)	Coordination Environment	Absorption maxima	Transition Assignment
CuCl <sub>2</sub> .L	2.24	N, O, 2Cl	8328 10324 12645 26435	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> A <sub>1g</sub> <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub> <sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub> (F) CT
CuBr <sub>2</sub> .L.2H <sub>2</sub> O	0.78	N, 3O, 2Br	9394 11448 13605 26039	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> A <sub>1g</sub> <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub> <sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub> (F) CT

Analytical and conductance data (Table 1) indicate the stoichiometry of the complexes as CuCl<sub>2</sub>.L and CuBr<sub>2</sub>.L.2H<sub>2</sub>O. The IR spectrum of the complexes registered lower frequency values for the C=O by about 44 and 47 cm<sup>-1</sup> respectively. The CNC of the ligand shifted to lower frequency of 37 and 36 cm<sup>-1</sup> respectively, which suggests bidentate coordination of the ligand (Table 2). Thus the Mannich base ligand (L) in all the complexes studied behaves as a chelating or bridging bidentate one and the binding sites are one carbonyl oxygen atom and the piperidine ring nitrogen atom. The bromo complex of Cu(II) also exhibits bands at 3485 (ν<sub>OH</sub>) due to the presence of coordinated water in the aqua complexes. This fact is also supported by the thermal data.

The chloro complex of Cu(II) shows ligand field transitions at 8328, 10324 and 12645  $\text{cm}^{-1}$  which may be assigned  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  ${}^2E_g \rightarrow {}^2T_{2g}$  (F) transitions respectively, while the band at 26435  $\text{cm}^{-1}$  may be due to charge transfer transition. Thus based on the spectral features, the Cu(II) chloro complex is proposed to have 4-coordinate geometry. The effective magnetic moment of chloro complex of Cu(II) is 2.24 B.M. which is expected for a pseudo-tetrahedral Cu(II) complex.

The bromo complex of Cu(II) exhibit electronic absorption bands at 9394, 11448 and 13605  $\text{cm}^{-1}$  which may be assigned  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  ${}^2E_g \rightarrow {}^2T_{2g}$  (F) transitions respectively, The bands observed at 26039  $\text{cm}^{-1}$  may be due to respective charge transfer transitions (Table 3). The band positions suggest a tetragonally distorted octahedral geometry for these complexes. The effective magnetic moments of 6-coordinated Cu(II) bromo complex is measured at 0.78 B.M. which are much less than the spin only value indicating the interaction between unpaired spins in the solid state.

### EPR spectrum of Cu(II) complex

The X band EPR spectra of polycrystalline chloro and bromo complexes of Cu(II) with L recorded at room temperature (Table 4) using DPPH as a reference standard. The EPR spectra of chloro and bromo complex of  $\text{Cu}^{\text{II}}$  ion show only a single line ie. g is isotropic, which indicate that the symmetry of Cu(II) complexes are cubic.

**Table 4.** EPR Spectral Parameters for Cu(II) Complexes at Room Temperature

Complex	$g_{\text{iso}}$	$g_{\perp}$	$g_{\parallel}$	G	$g_{\text{av}}$
CuCl <sub>2</sub> .L	2.2519	-	-	-	-
CuBr <sub>2</sub> .L.2H <sub>2</sub> O	2.2842	-	-	-	-

### Electrochemical studies of CuCl<sub>2</sub>.L

The cyclic voltammograms of CuCl<sub>2</sub>.L measured at 50, 250 and 500  $\text{mVs}^{-1}$  scan rates feature the reduction of Cu(II) to Cu(I) at cathodic peak potentials of -0.035, -0.0908 and -0.1178 V Vs Ag / Ag<sup>+</sup>. The  $\Delta E_p$  values are measured at 578.6, 651.2 and 659.2 mV at the respective scan rates. Very large values of  $\Delta E_p$  above 200 mV give evidence for the reduction process to be irreversible in nature and chemical change to occur with electron transfer. The  $E_{1/2}$  values measured at three different scan rates are 0.3201, 0.2772 and 0.2706 V indicating that the present complex may not undergo easy reduction at positive potentials due to stabilization of Cu(II) ion in the complex by the chelating L ligand.

The peak current ratio  $i_{pa}/i_{pc}$  is greater than unity at scan rate of 50  $\text{mVs}^{-1}$  and it is less than unity at the scan rate of 250 and 500  $\text{mVs}^{-1}$ . These values at higher scan rate show that EC mechanism is followed. The peak current values increase with increase of square roots of the scan rates to show that the electrode process is diffusion controlled.

### Thermal decomposition studies

**Table 5** Thermal decomposition data for the Mannich base L

Compound	Stable up to (°C)	Decomposition Temperatur range (°C)			Probable change Intermediate	DTA Peak (°C) and its nature	DTG Peak (°C)
		Stage	Intial	Final			
L (C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> )	174.5				Melting	113.9 endo	
		I	174.5	310	Oxidative degradation polymer of HCHO.	304.9 exo	251.3
		II	484	540	Decomposition of polymer of HCHO to form more stable higher polymer	524.2 exo	522.43

The TG/DTA and TG/DTG patterns are shown in Fig. 2 and 3 respectively. The TG/DTG curves of the (L) show that it is thermally stable up to 174.55°C. It melts at 113.92°C as shown by a sharp endotherm at 113.92°C. Rapid decomposition and weight loss occur in the temperature range 174.55-310°C. The rapid oxidative decomposition of the organic compound in the presence of air is supported by the existence of an exothermic DTA peak at 304.92°C. There is a rapid decomposition of the residue in the range of 484-540°C as indicated by the endotherm at 524.20°C and by the DTG peak centered at 522.43°C. The presence of 10% weight as the final residue in the temperature range 530-706°C may indicate the formation of some stable polymeric product of formaldehyde, the composition of which is not known.

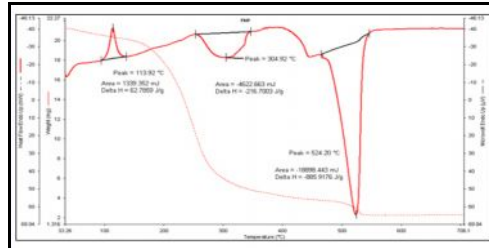


Fig. 1 Cyclic Voltammogram of  $\text{CuCl}_2 \cdot \text{L}$  N-(Piperidinomethyl)phthalimide (L)

Fig. 2 TG /DTA Pattern of at  $250 \text{ mVs}^{-1}$  Scan Rate

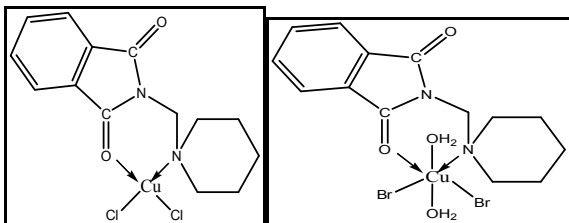
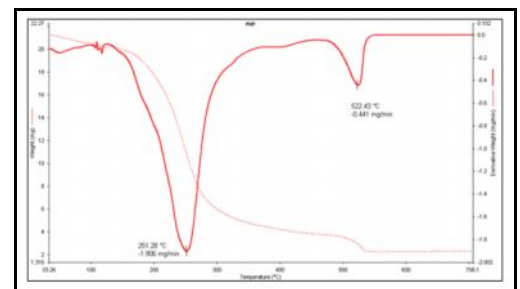
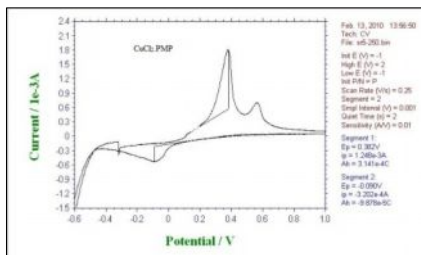


Fig. 3 TG /DTG Pattern of Structures of  $\text{CuCl}_2 \cdot \text{PMP}$   $\text{CuBr}_2 \cdot \text{PMP} \cdot 2\text{H}_2\text{O}$  N-(Piperidinomethyl)phthalimide (L)

### Evaluation of antimicrobial activities

The antibacterial and antifungal activities of the (L) and its Cu(II) complexes studied *in vitro* are provided in Table 6. The metal complexes are more active than the Mannich base ligand. The Cu(II) bromo complex is more toxic than Cu(II) chloro complex against both bacterial and fungal strains tested. The higher activity of the metal complexes is ascribed to the increase in the lipophilic nature of the complexes arising from chelation<sup>16</sup>. The mode of action of the complexes may also involve formation of hydrogen bonds with the imidato carbonyl groups by the active sites leading to interference in the process of cell wall synthesis.

**Table 6 Antibacterial and Antifungal activities of the ligand L and its metal complexes**

Compound	Antibacterial activity( Zone of Inhibition in mm)						Antifungal Activity ( Zone of Inhibition in mm)					
	<i>E.coli</i>			<i>S.aureus</i>			<i>A. niger</i>			<i>C. albicans</i>		
	Conc. of Compound			Conc. of Compound			Conc. of Compound			Conc. of Compound		
	50	75	100	50	75	100	50	75	100	50	75	100
CuCl <sub>2</sub> .L	3	5	12	7	9	11	18	20	23	19	21	24
CuBr <sub>2</sub> .L.2H <sub>2</sub> O	20	21	22	11	13	15	13	14	16	12	15	17
Kanamycin	15	-	-	-	-	-						
Tetracyclin	-	-	-	13	-	-						
Amphotericin							12	-	-	-	-	-
Nystatin							-	-	-	14	-	-

## Conclusions

The new Mannich base (L) and its metal complexes with Cu(II) have been synthesized and characterized. The Mannich base ligand is bidentate, binding through one of the two carbonyl oxygens and the morpholine ring nitrogen. Most of the metal complexes contain aqua ligand except the Cu(II) chloro complex. The metal complexes studied display either octahedral or tetrahedral geometry. The results on antibacterial and antifungal screening of the ligand and its complexes indicate that the metal complexes are more active than the free L.

## Acknowledgement

The authors express their sincere thanks to the Management, President, Secretary and Principal, Nehru Memorial College, Tiruchirapalli for providing facilities and motivating them with constant encouragement. The authors are grateful to Dr. K Ruckmani, Director, Centre for Excellence in Nanobio Translational Research Centre, Anna University, BIT Campus, Trichy, for helping them to carry out antimicrobial studies at her laboratory. The author also thank CECRI-Karaikudi for the use of their instrumentation facilities.

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