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## SYNTHESIS, SPECTRAL STUDIES OF TRANSITION METAL COMPLEXES DERIVED FROM DEHYDROACETIC ACID

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### ABSTRACT

The solid complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) with bidentate Schiff base ligands derived from Dehydroacetic acid and 2,4 dibromoaniline were synthesized and characterized by elemental analysis, molar conductance, magnetic, uv-visible and  $^1\text{H-NMR}$  spectroscopy. The magnetic moment and spectral data suggest the square planar geometry Cu(II) complex, octahedral geometry for Ni(II), Co (II), Mn(II), Fe(III) .

**KEY WORDS:** Dehydroacetic acid, Schiff base, transition metal complexes.

### INTRODUCTION:

The Schiff bases and their metal complexes play an important role in modern coordination chemistry. Schiff bases are capable of forming coordinate bonds with many of metal ions through both azomethine group and phenolic group or via its azomethine or phenolic groups. Schiff bases are one of the most widely used as chelating ligands in coordination chemistry. Literature survey reveals that though some work has been done on the metal complexes of Schiff bases derived from dehydroacetic acid with aliphatic amines and aromatic amines have been prepared and studied intensively. However, much less attention has been focused on the metal complexes of Schiff bases derived from dehydroacetic acid and disubstituted aniline. In the view of the above fact, we report here the synthesis and characterization of the Schiff bases derived from biologically active dehydroacetic acid and 2,4 dibromoaniline. The complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) metal ions with this ligand were also prepared. The structure of the complexes has been established using analytical, magnetic, IR and electronic spectral data.

### MATERIAL AND METHODS:-

Dehydroacetic acid for synthesis is obtained from E-merk, Gemaney. and 2,4 dibromoaniline of AR Grade are obtained from Across Organics chemicals are used for the synthesis of ligands. The AR Grade metal chlorides from E-Merck and Qualigens were used for the synthesis of metal complexes. C, H and N analysis were determined on CHN Analyzer flash model EA-1112. Magnetic measurements were carried out by using Gouy's balance at room temperature using  $\text{HgCo}(\text{CNS})_4$  as calibrant. The IR spectra of the ligands and their metal complexes were recorded on a Perkin Elmer spectrum 11b No.- 75430 nujol spectrophotometer in the range 4000-400  $\text{cm}^{-1}$ . The electronic spectral measurements were made on Shimadzu UV- Visible spectrophotometer uv-1601. The NMR spectra of the ligands were recorded on Bruker FT 200 mhz NMR spectrophotometer in  $\text{CDCl}_3$  solvent using TMS as a reference sample.

## SYNTHESIS OF LIGANDS

The unsymmetrical Schiff base ligands {1-(2,6-dibromophenylimino)ethyl}-4-hydroxy -6-methyl-2H-pyran-2-one. Synthesized by refluxing equimolar solution of dehydroacetic acid and 2,5 dimethyl aniline in 50 ml ethanol on 1 RML Rotamantale for about 4-5 h. The thus formed schiff base was cooled at room temperature and collected by filtration, followed by recrystallization in ethanol. The purity of the ligands were checked by TLC technique.

## SYNTHESIS OF METAL COMPLEXES.

To a hot methanolic solution (25 ml) containing 2.0 mmol of the ligand, a methanolic solution (25 ml) of a metal chloride (1.0 mmol) was added drop wise with constant stirring. The pH of the reaction mixture was maintained around 7.5 by adding 10 % alcoholic ammonia solution and refluxed for about 2 hrs. The precipitated solid metal complex was filtered off under hot conditions and washed with hot methanol, petroleum ether (40-60 °C) and dried over anhydrous CaCl<sub>2</sub> in vacuum desiccators.

## RESULTS AND DISCUSSION

All the metal complexes are colored solids, stable to air and nonhygroscopic. They are insoluble in water but soluble in DMF, DMSO. The physical characteristics, analytical and molar conductance data of the ligand and metal complexes are given in Table 1. The molar conductance values of all the metal complexes in DMSO at the concentration of 10<sup>-4</sup> M are very low indicating their non electrolytic nature. The analytical data indicate 1:2 metal:ligand stoichiometry for the Cu(II), Ni(II), Co(II), Mn(II), Fe(III) complexes.

**Table 1. Analytical, molar conductance data of the Ligand and its Metal Complexes.**

Compound	Color	Found (Calculated) %				F. Wt.	M.P Oc	$\lambda_m$ Mho cm <sup>2</sup> mol <sup>-1</sup>
		C	H	N	Br/M			
Ligand- L [C <sub>14</sub> H <sub>11</sub> Br <sub>2</sub> NO <sub>3</sub> ]	white	41.97 (41.93)	2.96 (2.76)	3.50 (3.49)	38.90 (38.85)	401	150	-
[Cu(C <sub>14</sub> H <sub>11</sub> Br <sub>2</sub> NO <sub>3</sub> ) <sub>2</sub> ] complex	brown	38.36 (38.83)	2.32 (2.54)	3.00 (3.23)	7.11 (7.34)	805	267	6.3
[Ni(C <sub>14</sub> H <sub>11</sub> Br <sub>2</sub> NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] complex	brown	45.06 (45.62)	3.12 (3.53)	3.31 (3.80)	7.49 (7.97)	736	261	4.2
[Co(C <sub>14</sub> H <sub>11</sub> Br <sub>2</sub> NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] complex	pink	37.01 (37.47)	2.00 (2.33)	2.07 (2.51)	6.14 (6.57)	896	268	8.8
[Mn(C <sub>14</sub> H <sub>11</sub> Br <sub>2</sub> NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] complex	brown	37.19 (37.64)	2.13 (2.68)	2.97 (3.13)	6.19 (6.60)	892	284	10.2
[Fe(C <sub>14</sub> H <sub>14</sub> N <sub>2</sub> O <sub>5</sub> S) <sub>2</sub> (Cl) (H <sub>2</sub> O)] complex	brown	35.08 (35.48)	2.49 (2.95)	2.70 (2.95)	5.57 (5.89)	947	300	4.3

### **1H-NMR spectrum of the Schiff Base**

The 1H-NMR spectra of the free ligand in CDCl<sub>3</sub> at room temperature showed the following signals at  $\delta$ (ppm): 2.16 (3H,s,C6-CH<sub>3</sub>), 2.52 (3H,s,N=CH<sub>3</sub>), 5.79(1H,s,C5-H), for DHA moiety. 7.12(1H,d,C6-H), 7.30(1H,dd,C5-H), 7.88(1H,d,C3-H) for phenyl moiety. 15.92 (1H,S(hump),C4 -OH) for DHA moiety.

### **IR Spectra:**

The Characteristic IR frequencies (cm<sup>-1</sup>) of the ligands and their complexes are shown in Table 2. The IR spectrum of the free ligands show a broad weak band ~2600-2400 cm<sup>-1</sup> attributed to intramolecular bonding  $\nu$ (OH). The bands 1700, 1667, 1350, 1271 cm<sup>-1</sup> are assigned to  $\nu$ (C=O) (Lactone carbonyl),  $\nu$ (C=N) (azomethine),  $\nu$ (C-N) (aryl azomethine) and  $\nu$ (C-O) (enolic) stretching modes, respectively. The disappearance of IR band at 2600 cm<sup>-1</sup> (intramolecular hydrogen bonding) in the spectra of all the

complexes indicates deprotonation of enolic oxygen and azomethine nitrogen in coordination to the metal ion. It is further supported by an upward shift in  $\nu(\text{C-O})$  by 20-30  $\text{cm}^{-1}$  in all complexes. A downward shift in  $\nu(\text{C=N})$  by 15-20  $\text{cm}^{-1}$  indicates participation of azomethine nitrogen in complex formation. The IR spectra of the metal complexes showed new bands in the 512-542  $\text{cm}^{-1}$  and 405-485  $\text{cm}^{-1}$  region, which can be assigned to  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$  vibrations respectively.

**Table 2. Characteristic IR frequencies ( $\text{cm}^{-1}$ ) of the Ligands and their Complexes**

Compound	$\nu(\text{C=O})$	$\nu(\text{C=C})$	$\nu(\text{C=N})$	$\nu(\text{C-N})$	$\nu(\text{C-O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
Ligand- L [C <sub>14</sub> H <sub>11</sub> Br <sub>2</sub> NO <sub>3</sub> ]	1700	1562	1667	1350	1261	-	-
[Cu(C <sub>14</sub> H <sub>11</sub> Br <sub>2</sub> NO <sub>3</sub> ) <sub>2</sub> ] complex	1742	1566	1649	1369	1271	542	485
[Ni(C <sub>14</sub> H <sub>11</sub> Br <sub>2</sub> NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] complex	1698	1580	1660	1346	1288	528	460
[Co(C <sub>14</sub> H <sub>11</sub> Br <sub>2</sub> NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] complex	1692	1581	1658	1342	1288	530	455
[Mn(C <sub>14</sub> H <sub>11</sub> Br <sub>2</sub> NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] complex	1708	1577	1631	1357	1270	512	405
[Fe(C <sub>14</sub> H <sub>14</sub> N <sub>2</sub> O <sub>5</sub> S) <sub>2</sub> (Cl)(H <sub>2</sub> O)] complex	1708	1585	1637	1355	1265	505	405

#### Magnetic Measurements and Electronic Absorption Spectra:

The magnetic and electronic spectral data are given in Table 3. The data is of relevance for the proposed structure of the complexes. The Cu(II) complexes showed magnetic moment 1.77 B.M. and three electronic absorption bands in the range 14104, 24096, 31545  $\text{cm}^{-1}$  assigned to  $2B_{1g} \rightarrow 2A_{1g}$  and two charge transfer transitions respectively, reported square-planar geometry. The Ni(II) complex shows the magnetic moment 3.16 B.M. suggesting the octahedral geometry. The electronic spectral data showed three bands at 9633, 17730 and 23148  $\text{cm}^{-1}$  assignable ( $\nu_1$ )  ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ , ( $\nu_2$ )  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  and ( $\nu_3$ )  ${}^3A_{2g} \rightarrow T_{1g}(p)$  transitions respectively. The Co(II) complex shows the magnetic moment 4.77 B.M. suggesting the octahedral geometry. The electronic spectral data showed three bands at 9842, 19011 and 25000  $\text{cm}^{-1}$  assigned to the transitions  ${}^4T_{1g} \rightarrow {}^4T_{2g}(P)$ ,  ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$  and  ${}^4T_{1g} \rightarrow {}^4T_{2g}(P)$  respectively. The Mn(II) complex shows the magnetic moment 5.78 B.M. suggesting the octahedral geometry. The electronic spectral data showed bands at 15698, 22935, 24691  $\text{cm}^{-1}$  assigned to the transitions  ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$ ,  ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$  and  ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$  respectively. Fe(III) complex shows the magnetic moment 5.99 B.M. suggesting the octahedral geometry. The electronic spectral data showed bands at 16447, 22026 and 24967  $\text{cm}^{-1}$  assigned to the transitions  ${}^6A_{1g} \rightarrow {}^4T_{2g}(F)$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}(F)$  and  ${}^6A_{1g} \rightarrow {}^4T_{2g}(F)$  respectively.

**Table 3. Magnetic and Electronic Absorption Spectral data (in DMSO) of the Complexes**

Complex	$\mu_{\text{eff}} / \mu_{\text{B}}$	$\nu / \text{cm}^{-1}$	Geometry
[Cu(C <sub>14</sub> H <sub>11</sub> Br <sub>2</sub> NO <sub>3</sub> ) <sub>2</sub> ] complex	1.77	15151 28735 31446	Square Planar
[Ni(C <sub>14</sub> H <sub>11</sub> Br <sub>2</sub> NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] complex	3.16	9633 17730 23148	Octahedral
[Co(C <sub>14</sub> H <sub>11</sub> Br <sub>2</sub> NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] complex	4.77	9842 19011 25000	Octahedral
[Mn(C <sub>14</sub> H <sub>11</sub> Br <sub>2</sub> NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] complex	5.78	15698 22935 24691	Octahedral
[Fe(C <sub>14</sub> H <sub>14</sub> N <sub>2</sub> O <sub>5</sub> S) <sub>2</sub> (Cl) (H <sub>2</sub> O)] complex	5.99	16447 22026 24967	Octahedral

### CANCLUSION

On the basis of physicochemical and spectral data discussed above, the square planar geometry Cu(II) complex, and octahedral geometry for Ni(II), Co(II), Mn(II) and Fe(III) complexes are proposed. The ligands behave as bidentate, coordinating through carbonyl oxygen and the imino nitrogen of dehydroacetic acid moiety. Figure 1,2,3 shows the proposed structure of Schiff base metal complexes.

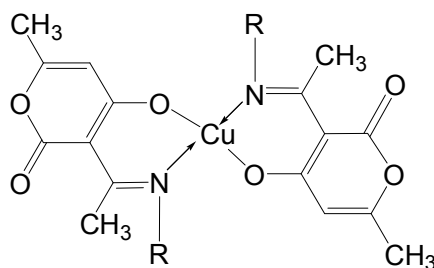


Fig.1 . structure of Cu(II) complex

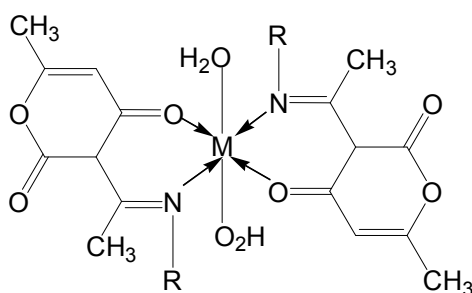


Fig.2. structure of Ni(II), Co(II), Mn(II) complexes.

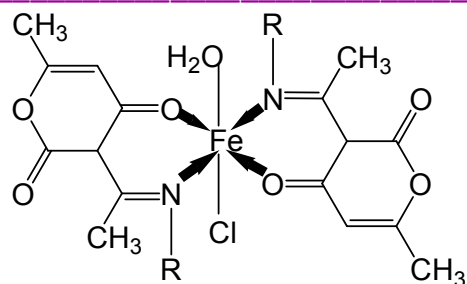


Fig.3. structure of Iron complex.

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