

## Spectral, Magnetic and Biocidal Studies of Mn(II), Ni(II), Co(II) and Cu(II) Mixed Ligand Complexes

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Some bivalent transition metal complexes have been prepared with tinidazole as primary ligand and 4-amino benzoic acid as secondary ligand. The crystalline metal complexes have been characterized by spectral, magnetic studies. The fungicidal behaviour of both ligands with their metal complexes have also been studied against *A. niger* and *A. flavus*.

**Key Words:** Mixed ligand complexes, Tinidazole drug, Amino acid, Fungicidal activity.

### INTRODUCTION

The introduction of oxygen and nitrogen atoms in the structure of organic compounds has often resulted in important consequences in their behaviour towards metal ions. Many investigations have been undertaken of the interaction of metal ions with ligands containing oxygen and nitrogen as donor atoms<sup>1-4</sup>. Although, in many cases the stereochemistry and electronic structures are reasonably understood. A number of papers dealing with the studies of mixed ligand complexes of bivalent metal ions have appeared in the literature<sup>5-7</sup>. The present study aims with the synthesis and characterization of coordination compounds of mixed ligand complexes with tinidazole and 4-amino benzoic acid. Emphasis is centered on the correlation of molecular structure and tinidazole acts as a monodentate ligand whereas the amino acid act as bidentate ligand co-ordinating through carboxylate oxygen and amino nitrogen. An octahedral geometry of M(II) mixed ligand complexes was proposed.

### EXPERIMENTAL

All the chemicals used were BDH reagents and Pfizer Pharmaceuticals Ltd. melting point were determined in open capillaries and are uncorrected. IR spectra (KBr) were recorded on a Perkin-Elmer-577 grating IR spectrometer in the range 4000-200 cm<sup>-1</sup>. The conductivity measurements were made on systronic conductometer model-303 using DMF. Magnetic moment

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were measured by Guoy method using mercury tetrathiothiocyanato cobaltate as the calibrant. The metal contents were determined using standard<sup>8</sup> method. All the analytical data have been recorded in Table-1.

**Preparation of mixed ligand complexes:** A general method was used for the preparation of bivalent metal complexes. The metal chloride dihydrate (10 mmol) was added to tinidazole drug (10 mmol) in 20 mL ethanol and few drops of NaOH solution to adjust pH at 5-7. The mixture was digested for 20 minutes with constant stirring. Both clear solution was added in further ethanolic solution of 4-amino benzoic acid was refluxed on water bath for 5-6 h. The contents were cooled and the volume of solution was reduced to one third. The resulting solution was kept over night at room temperature. A coloured complex separated out, which was filtered and washed with water-ethanol mixture, ether and dried in air.

## RESULTS AND DISCUSSION

The analytical results, melting points, colour and magnetic moments of the compounds are presented in Table-1. All the compounds are stable in air and non-hygroscopic at room temperature. They are slightly soluble in acetone, dioxane and fairly soluble in DMF and DMSO and insoluble in water. The elements analysis of metal complexes suggests 1:1 [M(T)(L)(H<sub>2</sub>O)Cl] metal to tinidazole and 4-amino benzoic acid stoichiometry.

TABLE-1  
PHYSICAL CHARACTERISTICS AND ANALYTICAL DATA OF  
MIXED LIGANDS COMPLEXES

Compounds/ (Refluxing in h)	Colour/ (state)	m.p. (°C)/ Yield (%)	Elemental analysis %: Found (Calcd.)				$\mu_{\text{eff}}$ (BM)	Molar cond. (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
			M	C	H	N		
[Mn(T)(L)(H <sub>2</sub> O) <sub>2</sub> Cl] (> 5)	Greenish brown (amorphous)	> 180 (55)	10.62 (10.75)	35.18 (35.26)	4.62 (4.73)	10.80 (10.96)	5.30	12.6
[Ni(T)(L)(H <sub>2</sub> O) <sub>2</sub> Cl] (5-6)	Pista (amorphous)	< 250 (65)	11.35 (11.40)	34.60 (35.00)	4.55 (4.70)	10.61 (10.88)	3.00	19.3
[Co(T)(L)(H <sub>2</sub> O) <sub>2</sub> Cl] (> 6)	Chocolati brown (crystalline)	> 190 (62)	11.22 (11.44)	34.80 (34.99)	4.58 (4.69)	10.67 (10.88)	4.30	21.6
[Cu(T)(L)(H <sub>2</sub> O) <sub>2</sub> Cl] (6)	Dark grey (amorphous)	189 (55)	12.12 (12.23)	34.62 (34.68)	4.61 (4.65)	10.70 (10.78)	3.06	23.2

T = Tinidazole; L = 4-Amino benzoic acid.

The magnetic moment data are presented in Table-1. Mn(II) complexes showed a value of magnetic moment in the range of 5.30 BM, which is slightly lower than spin only value of 5.92 BM for high spin octahedral, Mn(II) complexes<sup>9</sup>. The Co(II) complexes (4.30 BM) is much higher than the spin-only value of 3.87 BM. This can be explained on the basis of

octahedral symmetry involving a high degree of orbital contribution due to the three fold degeneracy of the  $^4t_{1g}$  ground state<sup>10</sup>. The observed values of Ni(II) complexes (3.00 BM) is in good agreement with spin free octahedral geometry<sup>11</sup>. The  $\mu_{\text{eff}}$  value 3.06 BM, Cu(II) complexes is suggesting an octahedral geometry.

The electronic spectra of the complexes were recorded in solution state. The electronic spectrum of the Mn(II) complexes shows four weak bands at  $\cong 15900 \cong 19800 \cong 20600$  and  $\cong 26800 \text{ cm}^{-1}$  which have been assigned to transitions  $^6A_{1g} \rightarrow ^6T_{1g}$ ,  $^6A_{1g} \rightarrow ^4T_{2g}$ ,  $^6A_{1g} \rightarrow ^4E_g$  (4D) and  $^6A_{1g} \rightarrow ^4T_{1g}$ , respectively in an octahedral field of Mn(II) ion<sup>12</sup>. The electronic spectra of isolated Co(II) complexes shows three clear bands at  $\cong 8400$ -8320,  $\cong 17700$ -17550 and  $\cong 20000$ -21000  $\text{cm}^{-1}$ , which may be assigned to the transition  $^4T_{1g} \rightarrow ^4T_{2g}(\text{F})$  ( $\nu_1$ ),  $^4T_{1g}(\text{F}) \rightarrow ^4A_{1g}$  ( $\nu_2$ ) and  $^4T_{1g}(\text{F}) \rightarrow ^4T_{1g}(\text{P})$  ( $\nu_3$ ) in order of increasing energy. The increased intensity of these bands indicates some tetragonal distortion and the position of the bands closely resemble with the spectra of the other distorted octahedral cobalt(II) complexes<sup>13</sup>. For the present series of Ni(II) and Cu(II) complexes, pronounced tetragonal splitting for the excited level  $^3T_{2g}(\text{F})$  and  $^3T_{1g}(\text{F})$  have been observed. The split components for  $^3T_{2g}(\text{F})$  are observed near 8100-8410 and 10700-11000  $\text{cm}^{-1}$ . The split components of  $^3T_{1g}(\text{F})$  located near 14300-14600 and 16950-17150  $\text{cm}^{-1}$ .

The infrared spectral data and their tentative assignments for the ligands tinidazole and 4-amino benzoic acid when compared with those of its Mn(II), Co(II), Ni(II) and Cu(II) mixed ligand complexes provide meaningful information regarding the bonding sites of the ligands. Metal binding through water molecules and chloride is also evidenced by the IR spectra<sup>14,15</sup>. The characteristics of IR bands of tinidazole corresponding to  $\nu(\text{NO}_2)$  anti-sym and sym and  $\nu(\text{NH}_2)$  are shown in the spectra of the complexes without any negative shifts, thus ruling out their participation in coordination.

IR spectra of metal complexes a bands (1555-1440  $\text{cm}^{-1}$ ) having lower shifting than the ligand (tinidazole) *ca.* 1603  $\text{cm}^{-1}$  indicates that the azomethine nitrogen is participating in chelation<sup>16</sup>. As regards chelation through amino acid the IR spectra exhibit significant features in  $\nu(\text{NH}_2)$  and  $\nu(\text{COO})$  regions in the present complexes, the IR spectra show characteristic bands in the region 3157-2922  $\text{cm}^{-1}$  which is lower in comparison with free  $\nu(\text{NH}_2)$ . Hence, it can be concluded nitrogen of the amino group is involved in coordination. The IR spectra show strong evidences in support of the involvement of carboxylate group in coordination. In comparison with amino acid, the  $\nu(\text{COO})$  (asy) shows positive shift and  $\nu(\text{COO})$  (sym) record negative shifts, which are confirmatory evidences in support of monodenticity<sup>17</sup>. Thus, it may be concluded that amino acid behave as monobasic bidentates in these complexes involving amino nitrogen and carboxylate oxygen in coordination<sup>18</sup>.

The free ligands (tinidazole and 4-amino benzoic acid) and their M(II) chelates were screened against two fungi (*A. niger* and *A. flavus*) to assess their potentially as antifungal agents by radial growth method. The amount of growth inhibition was calculated by the equation given by Vincent<sup>19</sup> at the compounds of 250, 500 and 1000 ppm concentrations. The results are presented in the Table-2. These results indicate that the growth is completely inhibited at 1000 ppm in all the cases. The microbial is considerably inhibited as compared to free ligands against fungal organisms. The increase in activity in these metal complexes may be attributed to the combined bioactive effect of metal and ligands present in the complexes and trace elements present in fungi species.

TABLE-2  
ANTIFUNGAL ACTIVITY OF MIXED LIGAND COMPLEXES  
(Inhibition of radial growth percentage)

Complexes	Inhibition zone (%)					
	<i>A. niger</i> (conc. ppm)			<i>A. flavus</i> (conc. ppm)		
	250	500	1000	250	500	1000
[Mn(T)(L)(H <sub>2</sub> O) <sub>2</sub> Cl]	74	92	100	72	78	100
[Ni(T)(L)(H <sub>2</sub> O) <sub>2</sub> Cl]	78	95	100	76	80	100
[Co(T)(L)(H <sub>2</sub> O) <sub>2</sub> Cl]	54	85	100	50	82	100
[Cu(T)(L)(H <sub>2</sub> O) <sub>2</sub> Cl]	56	87	100	52	80	100

T = Tinidazole; L = 4-amino benzoic acid.

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