

# Synthesis and Characterization of Manganese (II), Nickel (II) and Zinc (II) Complexes of Uramido Benzoic Acid

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**Abstract-** The Manganese (II), Nickel (II) and Zinc (II) complexes of Uramido Benzoic acid were prepared and characterized by magnetic studies, molar conductance studies, thermal analysis and spectroscopic techniques (FTIR and UV). The IR spectral studies revealed that the Uramido Benzoic acid behaves as a tridentate ligand. Electronic spectral studies and magnetic studies suggest that the complexes are in octahedral geometry. The thermal study explained the stability of complexes and their decomposition.

**Index Terms-** Metal salts, ligand, thermal analysis.

## I. INTRODUCTION

Newly synthesized organic ligand Uramido benzoic acid consisting of a benzene ring with two functional groups at ortho position namely carboxylic acid and NH-CO-NH<sub>2</sub> group is derived from anthranilic acid. There are many reports regarding metal- anthranilate complexes. A literature survey revealed the characterization of complexes of anthranilate ligands in which carboxylate anion and nitrogen or both involved in coordination,<sup>[1-4]</sup> and oxygen of carbonyl and nitrogen of amino group of anthranilic acid bonded to the metal atom of the Terpolymer ligand.<sup>5</sup>

The present paper reports the synthesis and characterization of Mn(II), Ni (II) and Zn(II) complexes with unionized Uramido benzoic acid. The Uramido benzoic acid is also involved in coordination through the acid group and the NH-CO-NH<sub>2</sub>

substituents. The TGA and DTA of Manganese (II) and Nickel (II) complexes were characterized.

## II. EXPERIMENTAL METHOD

The FTIR spectra were recorded as KBr pellets using Fourier transform infrared spectrometer Shimadzu 24 FTIR 8400S. Electronic spectra of the prepared complexes were taken in the region (300 – 1100) nm for 10<sup>-3</sup> M solution in ethanol at 25 °C using Shimadzu UV – 160 A Ultra-violet visible spectrometer with 1.000 ± 0.001 cm matched quartz cell. The magnetic susceptibility measurements were measured using Gouy apparatus using Gouy's method.

### 2.1 Preparation of Metal (II) perchlorate Complexes

Manganese, Nickel and Copper complexes of Uramido benzoic acid was prepared by the refluxion of Manganese(II) chloride, Nickel (II) chloride, Zinc (II) chloride and Uramido benzoic acid in ethanol taking 1: 2 molar ratio for six hours. The solutions were concentrated and cooled, to crystallize out the complexes and washed with ether to remove the excess ligand.

## III. RESULTS AND DISCUSSION

### 3.1 Conductance Studies:

The molar conductance of the complexes in DMF is suggested that the complexes are of 1: 2 electrolytic nature.

**Table 1. Characterization of metal complexes**

Complex	Conductance Ohm <sup>1</sup> cm <sup>2</sup> mol <sup>-1</sup>	Electrolytic nature	$\mu_{eff}$ B.M.	Colour
[MnL <sub>2</sub> ]Cl <sub>2</sub>	122.18	1:2	6.05	Light ash
[NiL <sub>2</sub> ] Cl <sub>2</sub>	138	1:2	2.9	Light green
[ZnL <sub>2</sub> ] Cl <sub>2</sub>	126	1:2	-	Dark ash

L= Uramido benzoic acid

### 3.2 IR Spectroscopy:

The IR spectrum of ligand Uramido benzoic acid showed a band at  $3448\text{cm}^{-1}$  which is assigned to the hydroxyl group of carboxylic acid<sup>6</sup> and band at  $3336\text{cm}^{-1}$  is assigned to asymmetric stretching of  $\text{NH}_2$  group of the ligand. The peak found at  $3222\text{cm}^{-1}$  is assigned to the NH stretching of secondary amine<sup>7</sup> group, which may be merged with the symmetric stretching of amide. The stretch found at  $1689\text{cm}^{-1}$  is assigned to the C=O of acid group.  $1323\text{cm}^{-1}$  is assigned to the C-N stretch of the secondary amine. The stretch found at  $1658\text{cm}^{-1}$  is assigned to the C=O of amide group of the ligand.

The comparison of the IR spectra of the ligand and its complexes confirmed the complex formation and it is a tool to find out the mode of coordination. There were expected shifts in the IR spectra of the complexes. The presence of anion in the complex and the absence of symmetric and asymmetric stretch of the carboxylate anion suggest that the acid group of the ligand is not ionized and the shift of C=O stretch found at  $1689\text{cm}^{-1}$  in the spectra of the ligand to lower wave number of about  $20\text{cm}^{-1}$

suggest that the carbonyl oxygen of the unionized carboxylic acid group is coordinated with metal ion<sup>8</sup>. The shift of the band of secondary amine NH group and the C-N stretch to the lower wave number suggest that the nitrogen of secondary amine is coordinated to the metal ion. The asymmetric stretch of  $\text{NH}_2$  increasing in the spectra of the complexes is not involved in coordination. The stretch found at  $1658\text{cm}^{-1}$  assigned to C=O of the amide group is also shifted to lower wave number by about  $40\text{cm}^{-1}$  suggesting that the carbonyl oxygen of the amide group is also coordinated to the metal ion. The bands found at  $528\text{--}523\text{cm}^{-1}$ ,  $491\text{cm}^{-1}$  in the spectra of the complexes alone are assigned to M-O stretch and the band at  $464\text{--}462\text{cm}^{-1}$  which is also absent in the spectrum of the ligand is assigned to the M-N stretch of the complexes. The other peaks are not much affected in the complexes including the stretch found at  $1581\text{cm}^{-1}$  is assigned to the C=C of the benzene ring. Thus it is concluded that the Uramido Benzoic acid acts as a tridentate ligand from which the two carbonyl oxygen and secondary amine nitrogen is coordinated to the metal atom.

**Table 2. FTIR spectra of metal complexes**

Compound	$\nu_{\text{O-H}}$ Stretching for acid $\text{cm}^{-1}$	$\nu_{\text{C=O}}$ Acid $\text{cm}^{-1}$	$\nu_{\text{C=O}}$ Amide $\text{cm}^{-1}$	$\nu_{\text{C=C}}$ ring $\text{cm}^{-1}$	$\nu_{\text{C-N}}$ stretching $\text{cm}^{-1}$	$\nu_{\text{N-H}}$ stretching $\text{cm}^{-1}$	$\nu_{\text{M-O}}$ $\text{cm}^{-1}$	$\nu_{\text{M-N}}$ $\text{cm}^{-1}$
Ligand	3448	1689	1658	1581	1323	3224	-	-
$[\text{MnL}_2]\text{Cl}_2$	3776	1663	1616	1587	1299	3192	523, 491	464
$[\text{NiL}_2]\text{Cl}_2$	3780	1668	1616	1589	1295	3213	528, 491	462
$[\text{ZnL}_2]\text{Cl}_2$	3774	1665	1613	1594	1293	3147	525, 491	462

### 3.3 Magnetic susceptibility measurements:

The strong and weak field complexes of several transition metal ions differ in the number of unpaired electrons in the complex. When this number can be ascertained readily from a comparison of the measured magnetic moment and that calculated from the spin paired and spin free complexes. Determination of the number of unpaired electrons can also give information regarding the oxidation state of a metal ion in a complex. It is also useful in establishing a structure of many complexes. The Manganese (II) chloride complex exhibits a moment of 6.05 B.M, Nickel (II) chloride complex exhibits a moment of 2.9 B.M suggesting octahedral geometry Zinc(II)chloride complex is diamagnetic in nature .

### 3.4 Electronic Spectra:

In the electronic spectra of octahedral Nickel (II) complex should expect three bands corresponding to  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$  at  $10,000\text{cm}^{-1}$ ,  $14,000\text{cm}^{-1}$

to  $18,000\text{cm}^{-1}$  and  $25000\text{ to }30000\text{cm}^{-1}$  respectively<sup>9</sup>. Ni (II) chloride complex exhibits the band at  $27,382\text{cm}^{-1}$  ( $365\text{nm}$ ) which is assigned to  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$  transition suggesting octahedral geometry.

### 3.6 Thermal analysis

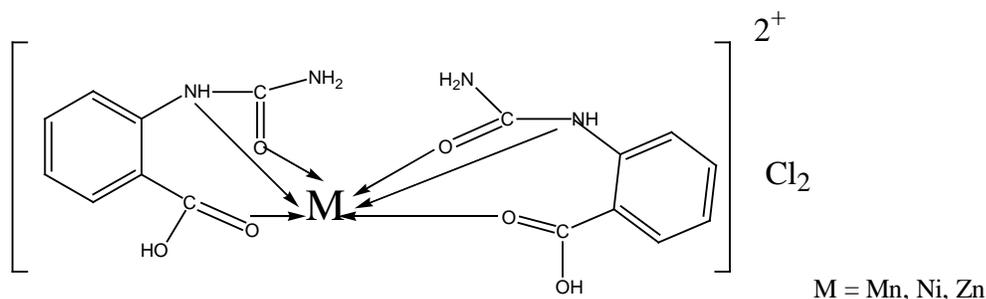
The TGA and DTA of Manganese (II) complex is stable up to  $250^\circ\text{C}$ , and no weight loss is observed before this temperature therefore, the complex has no coordinated water molecule. The first stage degradation was observed at above  $250^\circ\text{C}$  with loss of chloride and part of the ligand with experimental weight about 35.3% (calc 33.5%) accompanied by an endothermic peak with  $182.3^\circ\text{C}$  and  $250.7^\circ\text{C}$  on the DTA curve showed that the complex melts before decomposition. The TGA curve exhibits slow decomposition of ligand with an exothermic peak  $534^\circ\text{C}$  on DTA which may be attributed to the decomposition of the ligand. The



mass of the final residue obtained with 33% corresponds to metal with remaining part of the coordinated ligand.

TGA and DTA of Nickel (II) complex shows 79.9 °C on DTA endothermic peak which is not corresponding to any water

molecule in the complex with mass loss of about 1.5% and then the ligand decomposes completely with an exothermic peak at 414.4 °C and 510.2 °C on DTA which may be attributed to the decomposition of the ligand, so it has no final residue.



**Fig 1. Structure of Uramido Benzoic acid Metal Complex**

#### IV. CONCLUSION

The Uramido Benzoic acid act as a tridentate ligand in which carbonyl oxygen of the acid group, carbonyl oxygen of the amide part and nitrogen of the secondary amine group is coordinated to the metal ion. Conductance studies show that, the complexes are of 1:2 electrolytic nature. Electronic spectra and magnetic moment of the complexes confirmed the octahedral geometry for the complexes. A thermal study revealed that the complexes are thermally stable.

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