

Synthesis and Characterization of Nickel (II) and Copper (II) Complexes of Uramido Benzoic Acid

S. Prema¹, Dr. A. Pasupathy² and Dr.S.R. Bheeter³

¹Asst. Professor, Dept of Chemistry, Urumu Dhanalakshmi College, Tiruchirappalli

²Head, Associate Professor, Dept of Chemistry, Urumu Dhanalakshmi College, Tiruchirappalli

³Head, Associate Professor, Dept of Chemistry, St.Joseph's College, Tiruchirappalli

Abstract- The Nickel(II) and Copper(II) complexes of Uramido Benzoic acid were prepared and characterized by magnetic studies, molar conductance studies, thermal analysis and spectroscopic techniques (FTIR, UV and ESR). 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 complex and its 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-NH₂ 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.^[1-4]

The present paper reports the synthesis and characterization of Ni (II) and Cu (II) complexes with unionized Uramido benzoic acid. The Uramido benzoic acid is also involved in coordination through the acid group and the NH-CO-NH₂ substituents. The TGA and DTA of Nickel (II) complex was characterized.

Table 1. Characterization of metal complexes

Complex	Conductance Ohm ¹ cm ² mol ⁻¹	Electrolytic nature	μ_{eff} B.M.	Colour
[NiL ₂](ClO ₄) ₂	136	1:2	3.1	Light green
[CuL ₂](ClO ₄) ₂	127	1:2	1.8	Dark green

L= Uramido benzoic acid

The molar conductance of the complexes in DMF is suggested that the complexes are of 1: 2 electrolytic nature, indicating that the perchlorate groups are ionic in nature.

3.2 IR Spectroscopy:

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 10⁻³ M solution in ethanol at 25 °C using Shimadzu UV – 160 A Ultraviolet visible spectrometer with 1.000 ± 0.001 cm matched quartz cell. The magnetic susceptibility measurements were measured using Gouy apparatus using Gouy's method. ESR spectra were recorded on a JOEL ESR spectrometer at liquid nitrogen temperature operating at X-band frequency (9.1GHz).

2.1 Preparation of Metal (II) perchlorate Complexes

Nickel and Copper complexes of Uramido benzoic acid was prepared by the refluxion of Nickel (II) perchlorate, Copper (II) perchlorate 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 IR spectrum of ligand Uramido benzoic acid showed a band at 3448cm⁻¹ which is assigned to the hydroxyl group of carboxylic acid⁵ and band at 3336cm⁻¹ is assigned to asymmetric stretching of NH₂ group of the ligand. The peak found at

3222cm⁻¹ is assigned to the NH stretching of secondary amine⁶ group, which may be merged with the symmetric stretching of amide. The stretch found at 1689cm⁻¹ is assigned to the C=O of acid group. 1323cm⁻¹ is assigned to the C-N stretch of the secondary amine. The stretch found at 1658cm⁻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 1689cm⁻¹ in the spectra of the ligand to lower wave number of about 20cm⁻¹ suggest that the carbonyl oxygen of the unionized carboxylic acid group is coordinated with metal ion. 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 NH₂ increasing in the spectra of the complexes is not involved in coordination. The stretch found at 1658cm⁻¹ assigned to C=O of the amide group is also shifted to lower wave number by about 50cm⁻¹ suggesting that the carbonyl oxygen of the amide group is also coordinated to the metal ion. The band found at 1084cm⁻¹ in the spectra of the complexes alone is assigned to the perchlorate ion, which is not coordinated to metal ion as it appears as single peak without splitting. The bands found at 534cm⁻¹, 490cm⁻¹ in the spectra of the complexes alone are assigned to M-O stretch and the band at 460cm⁻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 1581cm⁻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	ν_{O-H} Stretching for acid cm ⁻¹	$\nu_{C=O}$ Acid cm ⁻¹	$\nu_{C=O}$ Amide cm ⁻¹	$\nu_{C=C}$ ring cm ⁻¹	ν_{C-N} stretching cm ⁻¹	ν_{N-H} stretching cm ⁻¹	ν_{M-O} cm ⁻¹	ν_{M-N} cm ⁻¹
Ligand	3448	1689	1658	1581	1323	3224	-	-
[NiL ₂](ClO ₄) ₂	3795	1672	1614	1592	1295	3125	526, 490	460
[CuL ₂](ClO ₄) ₂	3782	1675	1609	1591	1274	3117	534, 486	458

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 Nickel (II) perchlorate complex exhibits a moment of 3.1B.M and Copper (II) perchlorate complex exhibits a moment of 1.8 B.M. suggesting octahedral geometry.

3.4 Electronic Spectra:

In the electronic spectra of octahedral Ni(II) complex should expect three bands corresponding to ³A_{2g}, ³T_{2g}, ³A_{2g} ³T_{1g}(F), ³A_{2g} ³T_{1g}(P) at 10,000 cm⁻¹, 14,000 cm⁻¹ to 18,000 cm⁻¹ and 25000 to 30000 cm⁻¹ respectively. Ni (II) perchlorate complex exhibits the band at 29,498 cm⁻¹ (339nm) →

which is assigned to ³A_{2g} ³T_{1g}(P) transition suggesting octahedral geometry.

The Copper complexes show absorption band in 600-900nm regions. They are blue or green in colour⁸. The octahedral complexes show a unique band due to ²E_g ²T_{2g} transition. The Cu(II) perchlorate complex shows a broad band found at 15,037 cm⁻¹ (665nm) suggesting distorted octahedral geometry.

3.5 ESR:

The X-band ESR spectrum of copper perchlorate complex was recorded in DMSO at liquid nitrogen temperature showing five peaks on the parallel component which is due to the interaction of unpaired electron of Cu(II) ion. The g_{||} and g_⊥ values found to be 2.42 and 2.08 respectively. (g_{||} > g_⊥) suggesting that the system is axial. The value of exchange interaction term G=5.25. The g value (g_{||} > g_⊥ > 2.0023) and the exchange interaction term (G > 4) suggest that the unpaired electron of Cu(II)ion is present in d_{x²-y²} orbital. Thus the

results suggested that the Cu(II) complex possess the distorted octahedral geometry.

3.6 Thermal analysis

The TGA and DTA of Ni(II) complex is stable up to 200 °C, the complex has no coordinated water molecule. The first stage degradation was observed at above 250 °C with loss of two perchlorate anion at 31.1% (calc 32%). The TGA curve exhibits slow decomposition of ligand with an exothermic peak at 350 °C on DTA which may be attributed to the decomposition of the ligand. The mass of the final residue obtained with 28%.

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, both the complexes are of 1 : 2 electrolytic nature. Electronic spectra of the complexes confirmed the octahedral geometry for the complexes. The ESR studies revealed that the Copper (II) complex exhibits a distorted octahedral geometry.

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AUTHORS

First Author – S. Prema, Asst. Professor, Dept of Chemistry, Urumu Dhanalakshmi College, Tiruchirappalli

Second Author – Dr. A. Pasupathy, Head, Associate Professor, Dept of Chemistry, Urumu Dhanalakshmi College, Tiruchirappalli

Third Author – Dr.S.R. Bheeter, Head, Associate Professor, Dept of Chemistry, St.Joseph's College, Tiruchirappalli