

Synthesis and Characterization of Manganese (II), Cobalt (II) and Nickel (II) Complexes of Phenyl glycine-o-Carboxylic 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 Manganese (II), Cobalt (II) and Nickel (II) complexes of phenyl glycine-o-carboxylic 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 phenyl glycine-o-carboxylic acid behaves as a bidentate 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 phenyl glycine -o-carboxylic acid consisting of a benzene ring with two functional groups at ortho position namely carboxylic acid and NH-CH₂-COOH 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] and oxygen of carbonyl and nitrogen of amino group of anthranilic acid bonded to the metal atom of the Terpolymer ligand.⁵

The present paper reports the synthesis and characterization of Mn(II), Co(II) and Ni(II) complexes with unionized phenyl glycine -o-carboxylic acid. The phenyl glycine -o-carboxylic acid is also involved in coordination through the acid group and nitrogen of the secondary amine. The TGA and DTA of

Manganese (II), Cobalt (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 10⁻³ 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, Cobalt and Nickel complexes of phenyl glycine - o - carboxylic acid was prepared by the refluxion of Manganese (II) perchlorate, Cobalt(II) perchlorate, Nickel (II) perchlorate and phenyl glycine-o-carboxylic acid in ethanol taking 1: 3 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 Acetonitrile is suggested that the complexes are of 1:2 electrolytic nature, indicating that the perchlorate groups are ionic in nature

Table 1. Characterization of metal complexes

Complex	Conductance Ohm ¹ cm ² mol ⁻¹	Electrolytic nature	μ_{eff} B.M.	Colour
[MnL ₃](ClO ₄) ₂	167.87	1:2	6.01	Light yellow
[CoL ₃](ClO ₄) ₂	170.6	1:2	5.1	Brown
[NiL ₃](ClO ₄) ₂	196.19	1:2	3.05	Light brown

L= Phenyl glycine-o-carboxylic acid

3.2 IR Spectroscopy:

The IR spectrum of ligand phenyl glycine-o-carboxylic acid showed a band at 3373cm^{-1} which is assigned to the hydroxyl group of carboxylic acid groups⁶. The band for NH stretching vibration is merged with the former band. The strong band appeared at 1662cm^{-1} is attributed to the NH bending vibration.⁷ The band at 1398cm^{-1} is assigned to the C-N stretching. The stretch found at 1726cm^{-1} is assigned to the C=O of aliphatic acid group. The stretch found at 1705cm^{-1} is assigned to the C=O of aromatic carboxylic acid 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 1705cm^{-1} in the spectra of the ligand to lower wave number of about 30cm^{-1}

suggest that the carbonyl oxygen of the unionized aromatic carboxylic acid group is coordinated with metal ion⁸. 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 stretch found at 1726cm^{-1} assigned to C=O of the aliphatic acid group is also shifted to higher wave number suggesting that the carbonyl oxygen of the aliphatic acid group is not coordinated to the metal ion. The bands found at the range of $569-539\text{cm}^{-1}$ in the spectra of the complexes alone are assigned to M-O stretch and the band at the range of $497 - 490\text{cm}^{-1}$ 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 1573cm^{-1} is assigned to the C=C of the benzene ring. Thus it is concluded that the phenyl glycine-o-carboxylic acid acts as a bidentate ligand from which 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 cm^{-1}	$\nu_{\text{C=O}}$ Acid Aliphatic cm^{-1}	$\nu_{\text{C=O}}$ Aromatic acid cm^{-1}	$\nu_{\text{C=C}}$ ring cm^{-1}	$\nu_{\text{C-N}}$ stretching cm^{-1}	$\nu_{\text{N-H}}$ bending cm^{-1}	$\nu_{\text{M-O}}$ cm^{-1}	$\nu_{\text{M-N}}$ cm^{-1}
Ligand	3373	1726	1705	1573	1398	1662	-	-
$[\text{MnL}_3](\text{ClO}_4)_2$	3787	1736	1672	1581	1384	1620	539	490
$[\text{CoL}_3](\text{ClO}_4)_2$	3786	1733	1673	1577	1380	1624	567	496
$[\text{NiL}_3](\text{ClO}_4)_2$	3783	1740	1671	1575	1379	1593	569	497

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) perchlorate complex exhibits a moment of 6.05 B.M, Cobalt (II) perchlorate complex exhibits a moment of 5.1 B.M, Nickel (II) perchlorate complex exhibits a moment of 3.05 B.M. suggesting octahedral geometry.

3.4 Electronic Spectra:

The Cobalt (II) perchlorate complex shows the characteristic band of octahedral geometry having a band at $19,445\text{cm}^{-1}$ due to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ Transition. 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 $25,000$ to $30,000\text{cm}^{-1}$ respectively⁹. Ni(II) perchlorate complex exhibits the band at $27,822\text{cm}^{-1}$ which is assigned to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ transition suggesting octahedral geometry.

3.6 Thermal analysis

$[\text{Mn}(\text{PGC})_3](\text{ClO}_4)_2$

TGA and DTA curves of Manganese (II) complex showed that the complex is stable up to 200°C and no weight loss is observed before this temperature. The first stage of degradation occurred at 200°C with the loss of one perchlorate ion with a moisture experimental weight 16.7% (Cal 11.8%). The complex



further decomposes in the second step from 400-600 °C, with weight loss 67.3% (cal 69.7%) corresponds to the decomposition of the coordinated part of the ligand accompanied by an exothermic peak with 443.3 °C on DTA curve was observed. The mass of the final residue corresponds to stable Manganese oxalate (16%) calculated (17%).

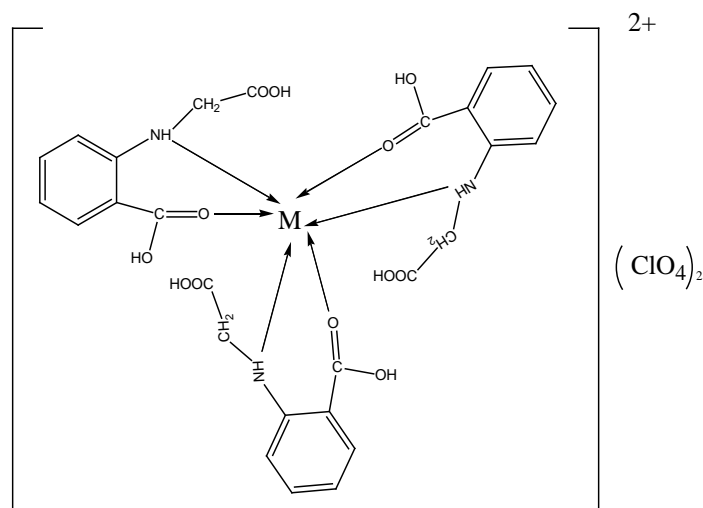
[Co(PGC)₃](ClO₄)₂

TGA and DTA curve of Cobalt (II) perchlorate complex showed that the complex is stable upto 200 °C and no weight loss is observed before this temperature. The first stage of degradation occurred at 200-250 °C decomposition of perchlorate ion with a mass loss 10.2% (Cal 11.8%) accompanied by an exothermic peak with 265 °C on the DTA curve was observed. Slowly decompose the perchlorate and ligand from 320-640 °C with 79.9% (cal 76.3%) mass loss and an exothermic peak with

468.3 °C and 614.5 °C on DTA which may be attributed to the decomposition of the non-coordinated and coordinated part of the ligand. The mass of the final residue corresponds to stable Cobalt oxide 9.9% calculated (8.9%)

[Ni(PGC)₃](ClO₄)₂

TGA and DTA curve of Nickel (II) complex showed that the complex is stable up to 200 °C, no mass loss is observed before the temperature. First step from 200-310 °C decomposition of perchlorate ion with a mass loss of 9.8% (cal 11.8%) accompanied by an exothermic peak with 248.8 °C and 301.1 °C on DTA curve was observed, The second step from 400-650 °C with a mass loss of 47.1% (cal 46.7%) corresponds to removal of the ligand. The mass of the final residue 9.95% (calculated 8.85%) corresponds to stable nickel oxide



Structure of phenylglycine-o-carboxylic acid complex

M = Mn, Co, Ni

IV. CONCLUSION

The phenyl glycine-o-carboxylic acid act as a bidentate ligand in which carbonyl oxygen of the acid group 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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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