Synthesis and Characterization of Manganese (II) and Cobalt (II) Complexes of O – Benzoyl Benzoic Acid

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Abstract- The Manganese (II) and Cobalt (II) complexes of o-benzoyl benzoic acid were prepared and characterised by magnetic susceptibility, molar conductivity, thermal analysis and spectroscopic Techniques (FTIR and UV). The IR spectral studies revealed that o-benzoyl benzoic acid behaves as a bidendate ligand and coordinate to the metal ions via; the two carbonyl oxygen. Electronic spectral studies and magnetic studies suggest that Manganese (II) complex is in octahedral geometry except the cobalt complex. The conductance studies show that, cobalt complex is electrolytic in nature. The thermal study explained the stability of the complexes and decomposition.

Index Terms- o-benzoyl benzoic acid, metal salts and Thermal studies.

I. INTRODUCTION

There is a widespread interest in the identification and development of transition metal based compounds for biological applications. Metal ions play enormous important roles in biological chemistry in about one third of enzymes[1].Benzoic acid and some of its salts are used in medicine as urinary antiseptics. A literature survey of the reported mixed ligand containing o-benzoyl benzoic acid with metal ions indicates o-benzoyl benzoic acid exhibits different bonding modes through oxygen of benzoyl group and oxygen of the hydroxyl group of the o-benzoyl benzoic acid ligand [2-3]. 4 - Nitro benzoic acid with metal ions is also bonding through oxygen of carboxylate anion[4].

In this paper, we report the synthesis and characterization of Manganese (II) and Cobalt (II) complexes of unionized o-benzoyl benzoic acid. o-benzoyl benzoic acid is involved in coordination through two carbonyl oxygen.

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 measured in the region (300 – 1100) nm for 10^{-3} M solution in ethanol and methanol at 25℃ using Shimadzu UV – 160.A – Ultraviolet – visible spectrometer with 1.000 ± 0.001 cm matched quartz cell. The electrical conductivity of the complexes was recorded at the room temperature for 10^{-3} M solution of the samples in acetonitrile using digital conductivity meter. The magnetic susceptibility measurements were measured using Gouy apparatus using Gouy's method.

2.1 Preparation of the Manganese (II) and Cobalt (II) complexes

Manganese, Cobalt complexes of o- benzoyl benzoic acid were prepared by the refluxion of Manganese (II) chloride, Cobalt (II) chloride and o-benzoyl benzoic acid in ethanol taking 1:3molar ratio was 6 hours. The solutions were concentrated and cooled, to crystallize out the complexes and complexes were washed with ether to remove the excess ligand. The prepared complexes were characterized by conductance, magnetic behaviour, IR, and Electronic spectral studies.

III. RESULTS AND DISCUSSION

3.1 IR Spectra :

In the spectrum of ligand the sharp peak found at 3324 cm^{-1} assigned to the OH stretching of Carboxylic acid. The band found at 1710 cm-^{1} and 1668 cm^{-1} are assigned to C=O group of Carboxylic acid and C=O of the benzoyl group of the ligand respectively[5]. The band found at 1594 cm^{-1} is assigned to the C=C group of benzene ring.

In the spectra of the complexes, the C=O stretching of the carboxylic acid group found at 1710 cm^{-1} in the spectra of the ligand is shifted to the lower wave number by about 40 cm^{-1} in the spectra of the complexes suggesting that the carbonyl oxygen of carboxylic acid is coordinated to the metal ion. The OH-stretch of the acid group is present in the spectra of complexes are shifted to higher frequency. The presence of anion such as chloride in the complex and absence of symmetric and asymmetric stretches of carboxylate ion, indicating that the acid group is not ionised. Suggest that the carbonyl oxygen of the benzoic acid group is coordinated with metal ion[6].

The stretch found at 1668 cm^{-1} is assigned to C=O stretch of benzoyl group which is shifted to the lower wave number by about 40 cm^{-1} in the spectra of complexes , suggesting that the carbonyl oxygen of benzoyl group is also coordinated to the metal ion. The new peaks at the range of 503-456 cm^{-1} which is found in the spectra of the complexes and those which are absent in the spectrum of the ligand have been assigned to M-O stretch of the complexes[7].

Table 1. FTIR spectra of the metal complexes

Compound	γ_{O-H} cm^{-1}	$\gamma_{C=O}$ acid cm^{-1}	$\gamma_{C=O}$ benzoyl cm^{-1}	γ_{M-O} acid cm^{-1}	γ_{M-O} benzoyl cm^{-1}	γ_{C-C-C} bending mode cm^{-1}
Ligand	3324	1710	1668	-	-	1278
$[Mn(BBA)_2Cl_2]2H_2O$	3369	1670	1622	503	476	1297
$[Co(BBA)_3]^{2+}[CoCl_4]^{2-}$	3393	1671	1624	477	456	1287

3.2 Electronic Spectra of Metal Complexes:

The electronic spectra of Cobalt (II) chloride complex displays the bands at 19,193 cm^{-1} and 15,068 cm^{-1}. The first band is assigned to $^4T_1g(F) \rightarrow {}^4T_1g$ (P) transition of octahedral geometry and the other band is assigned to $^4A_2(F) \rightarrow {}^4T_1(F)$ transition of tetrahedral geometry[8]. This suggests that this complex is the mixture of octahedral and tetrahedral geometries with the composition of the type $[Co(BBA)_3]^{2+}[CoCl_4]^{2-}$ which is supported by the conductance data

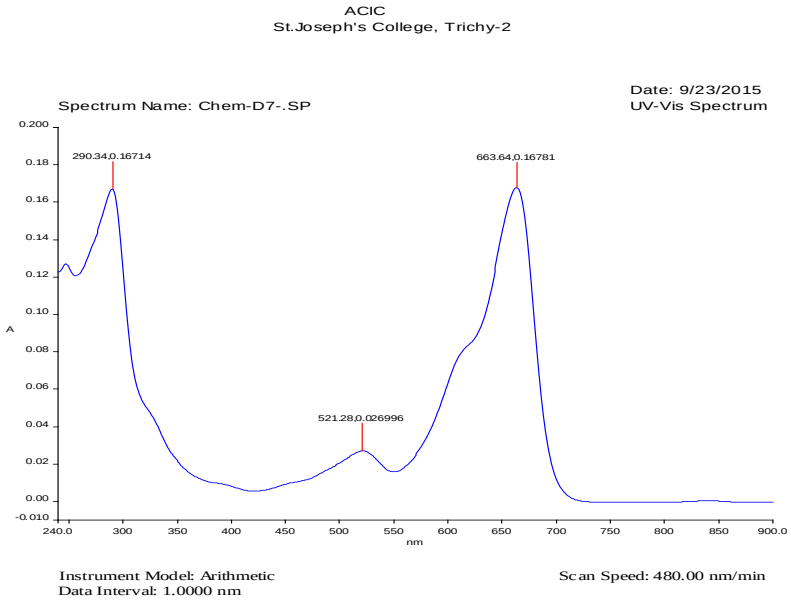

Table 2. Physical properties, conductance and magnetic studies of metal complexes

S.No	Complexes	Colour	Conductance $Ohm^{-1}cm^2\,mol^{-1}$	Electrolytic nature	μ_{eff} B.M

1	$[Mn(BBA)_2Cl_2]2H_2O$	White	42.65	1:0	5.96
2	$[Co(BBA)_3]^{2+}[CoCl_4]^{2-}$	Pink	145.01	1:1	4.4

1:0 electrolytic nature, in which anions are inside the coordination .The cobalt complex exhibits 1:1 electrolytic nature.

3.5 Thermal Analysis:

The TGA curve of Manganese (II) complex which shows loss of 6.2% (Calc 6.4%) at around 100$^{\circ}C$ which suggests that the complex is a dihydrate and two water molecules are lost at that range.

On DTA, it shows the melting of complex at about 131.9$^{\circ}C$ and 204.4$^{\circ}C$. The TGA curve 131 – 204 $^{\circ}C$ with release of chloride molecule of 11.1% (calc 12.7%). Above 204.4$^{\circ}C$ of TGA curve exhibits the slow decomposition of the ligand with 17.8% (calc 18.6%) and further decomposition of another ligand with 19.5% (calc 18.7%). Finally above 550 $^{\circ}C$ of TGA curve, 33% of residue is present.

The TGA and DTA curve of Cobalt (II) complex shows the endothermic peak of DTA at about 176.6$^{\circ}C$ and 210$^{\circ}C$ which indicate that the cationic and anionic complex melts. The TGA of the complex at about 200$^{\circ}C$, the first degradation occurs with the decomposition of the anionic complex and slow decomposition of ligand of the cationic complex. The experimental weight of the final residue of both the oxides of cobalt is 25% (calc 24.4%)

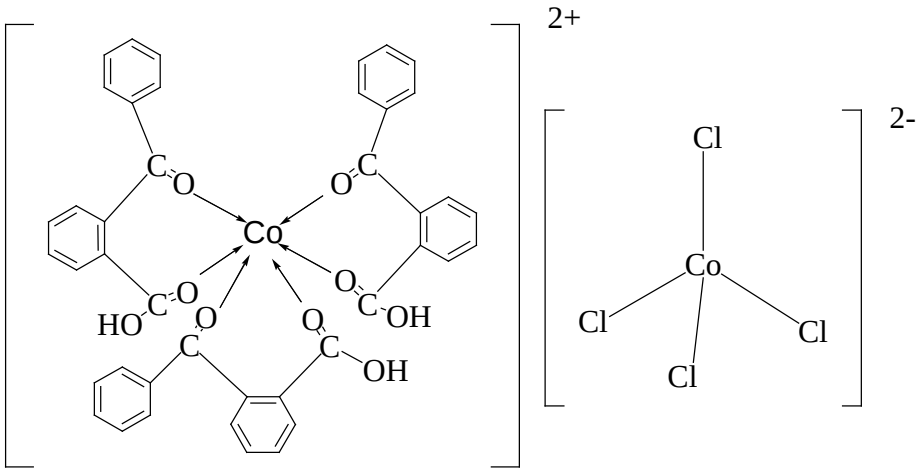

Fig 3. Structure of metal complex $[Co(BBA)_3]^{2+}[CoCl_4]^{2-}$

IV. CONCLUSION

The o – benzoyl benzoic acid acts as a bidendate ligand in which the carbonyl of the acid group and carbonyl of the benzoyl group is coordinated to the metal ion. The mode of coordination has been confirmed by the negative shift of the carbonyls of acid group and the benzoyl group by the stretching frequency in the spectra of the complexes. The electronic spectra of the complexes confirmed the geometry of the complex. A thermal study revealed that the complexes are thermally stable.

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