Volume : 5 | Issue : 8 | August 2016 • ISSN No 2277 - 8179 | IF : 3.508 | IC Value : 69.48

Original Research Paper

Synthesis and Study of Cobalt Complexes of Benzilic Acid

Chemistry

KEYWORDS : benzilic acid, cobalt complexes, Coordination Chemistry

Dr. M. JEROME ROZARIO Associate Professor, Dept., of Chemistry, PRIST University, Thanjavur

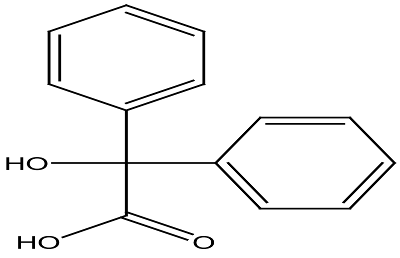
Dr. A. JOHN MERINA Principal, Govt., Arts College for Women (Autonomous), Kumbakonam

ABSTRACT

Benzilic acid complexes with Co(II) metal ions have been systhesised and characterised by electrical conductance, analysis of cation, magnetic susceptibility, electronic and infrared spectral studies. The analytical data show that the Chloride complexes of Co(II) have the general formula [ML4Cl2]. The PerChloride complexes of Co(II) have the general formula [ML6][ClO4].The conductance measurements show that the chloride complexes behave as a 1:2 nonelectrolyte. The magnetic moment measurement indicates paramagnetic behavior for the complex and the electronic spectral data suggest octahedral geometry for the complexes. The infrared spectral studies clearly indicate that the carbonyl group is coordinated to the metal ion and benzilic acid acts as monodentate.

INTRODUCTION

Benzilic acid is soluble in hot water and in ordinary organic solvents. The structure of benzilic acid is



Benzilic acid

Since carbonyl group serves as a donor of electrons, Benzilic acid acts as a ligand. Hence it is of immense importance to study the coordinating ability of this ligand with the metal cobalt. The transition metal cobalt is chosen to study the coordination tendency. This work deals with the Synthesis and characterization of Cobalt complexes of benzilic acid.

EXPERIMENTAL TECHNIQUES

1.Preparation of Cobalt (II) Chloride complex:[1]

Cobalt(II) chloride and benzilic acid were mixed in the molar ratio of 1:6 in ethanol and refluxed for five hours. The solution was concentrated to half of the volume and cooled to crystallize out the complex. It was washed with ether to remove excess ligand and dried in a designator over anhydrous calcium chloride.

2.Preparation of Cobalt (II) Perchlorate complex:

About 10gm of the cobalt carbonate was made into a paste by adding water. About 14ml of Perchloric acid was added and the mixture was concentrated on a water bath to obtain the crystals of cobalt Perchlorate. It was treated again with water and concentrated. The crystals were dried over anhydrous calcium chloride in a desiccator. Cobalt (II) Perchlorate and benzilic acid were mixed in 1:6 ratio in ethanol and the mixture was refluxed for five hours. The solution was concentrated and cooled. Coloured crystals of complex were obtained. They were washed with ether to remove excess ligand, filtered and dried in a desiccator over anhydrous calcium chloride.

Analysis of the complexes:

Estimation of Metals:

Preparation of the complex solution[2]

About 0.5gm of the complex was weighed accurately and 10ml of concentrated nitric acid was added. The solution was evaporated and concentrated almost to dryness. Then few ml of nitric acid was added and concentrated to 1ml. Then the solution was made upto 100ml in standard flask.

Estimation of cobalt

The percentage of cobalt was estimated complexometrically by titration with EDTA using muroxide as indicator. 20ml of the test solution was taken in a conical flask and neutralised to about pH=6. The solution was orange yellow coloured. The cobalt muroxide complex $(CoH_4D)^+$ served as acid base indicator for the subsequent neutralization which was carried out by adding ammonia until there was a colour change to yellow $(CoH_2D(-))$. Titration with EDTA was conducted until there was sharp change of colour from yellow to violet. The percentage of metal ion was calculated then.

General properties of the complexes[3,4]

All complexes were coloured solids, soluble in ethanol, stable at room temperature and nonhygroscopic in nature.

INSTRUMENTAL METHODS

1.Electrical Conductivity

Conductance measurements of the complexes in solution were made to verify the ionic formulation of complexes. Conductivity bridge with dip-type platinized platinum electrodes were employed for measurements. The cell constant was determined by measuring the resistance of 0.1N KCL whose specific conductivities were known at various temperature from literature. The solution used for conductivity measurements has concentration around 10-3M. All the measurements were corrected for the conductance of the solvent subtracting the conductance of t pure solvent from that of the solution.

Molar conductance calculated by using the relation.

Specific conductance (K) = Conductance × Cell constant

$$\text{Molar conductance} = \frac{1000 \times \text{Specific conductance}}{\text{Molar concentration}}$$

$\Lambda m = 1000K/C$

The value in Acetonitrile are given in Table II.

2.Magnetic Susceptibility Measurements

Magnetic susceptibility and hence magnetic moments of various complexes can be determined using the Gouy balance. The magnetic susceptibility of the complexes were calculated using the relation

$$106\ X = \frac{\alpha + \beta F'}{W}$$

Where F′ = corrected force = F in mg, β = calibration constant, $\alpha = 0.029 \times 10^{-6}$ × volume of the tube, W = Weight of substance in gm, X = gram susceptibility.

To find out the effective magnetic moment the following relation was used.

μ_{eff} = 2.84

X′M = Molar susceptibility, T = Absolute temperature.

The weights of the gouy tube were taken in the absence and in the presence of the magnetic field. To evaluate the value of calibrant constant the tube filled with Hg $[Co(CNS)_4]$ up to the mark and the weight was taken in the absence or in the presence of the magnetic field. The calibration was removed and the gouy tube was filled with various complexes and the weight were taken. Finally the weight of the gouy tube with water, filled upto the mark was noted in order to find out the volume of the sample, using the formula, magnetic susceptibility and effective magnetic moment were calculated after making proper diamagnetic corrections. Using Pascal's constant[5]. The magnetic susceptibility values are given in Table III.

3.Electronic Spectra

The electronic spectra of the complexes were taken in the ethanol medium for various wavelengths ranging from 300–700nm. Absorbance values were plotted against the corresponding wavelengths (nm). The maximum values corresponding to the peaks were noted.

4.Infrared Spectra

The infrared spectra of the free ligand and the complexes were taken in KBr pellets in the range of 4000-200cm^{-1} by infrared spectrometer (pellet technique). The percentage transmission was recorded against wavelength(cm^{-1}). The infrared spectral bands along with their probable assignments are given below.

RESULTS AND DISCUSSION

1.Behavior of Complexes in Solution[6]

The electrical conductance of these complexes in ethanol were measured. Molar conductance values (Table II), expected for 1:0, 1:1, 1:1, 1:2, 1:3, 1:4 in Electrolyte in Acetonitrile are given below.

Conductance values (Ohm^{-1}cm^{2}mole^{-1})	Type of electrolyte
<80	1:0
80-115	1:1
160 -220	1:2
290-350	1:3
>450	1:4

The molar conductance of the Perchlorate complexes of the divalent metals correspond to those of 1:2 electrolytes indicating that the Perchlorate groups are ionic in nature[7]. The low electrical conductance values of chloride complexes show that all of them are 1:0 nonelectrolytes. Based on the analytical and the molarconductance data of the complexes, the prepared complexes may be assigned the following compositions.

$[Co(BENZ)_4Cl_2]$

$[Co(BENZ)_6\ (ClO_4)]_2$

(BENZ=Benzilic acid)

2.MagneticSusceptibility[8]

The strong and weak field complexes of several transition metal ions differ in the number of unpaired electrons in the complex. This number can be found readily by a comparison between the measured magnetic moment and that calculated from the spinonly moment. Hence it is possible to distinguish spin paired and spin free complexes. Determination of the number of unpaired electron can also give information regarding the oxidation state of a metalion in a complex. It is also useful in establishing the structure of many complexes[9]. The magnetic moments, μ_{eff} of the complexes are given in Table III. The values indicate that they are all of high spin type. The μ_{eff} of Co(II) chloride and Perchlorate complexes are 4.85 and 4.9B.M. respectively suggesting octahedral coordination for the metal ion. The magnetic moment of Co(II) chloride and Perchlorate complex are 5.92B.M and 5.96B.M respectively indicating octahedral geometry. The $CuCl_2$ has the magnetic moment 1.9 indicating octahedral geometry.

3.InfraRed Spectra[10]

The IRspectra of the complexes are very useful in determining the coordinating groups of the ligand. The shifts in the bands indicate mode of linkage in the complexes. The comparison of IRspectrum of Benzili cacid and its complex confirmed the formation of their complex. There were expected shifts in the IRspectrum of the complexes especially in the C=O stretching frequencies of the acid group of the benzilic acid. The C=0 stretching frequency of the ligand are shifted to the lower frequency in the spectrum of the complex. The peak at 1720cm^{-1} which is due to C=O stretching of the carboxyli cacid group in the spectrum of ligand is shifted to 1690cm^{-1} in the spectrum of the complex, the peak at 1230cm^{-1} which may be to C=O or OH deformation of the carboxylic acid group in the ligand spectrum shipped to 1170cm^{-1} in the complex spectrum. The absence of symmetric and asymmetric C=O stretching frequencies and the presence of anions indicate that the acid group of benzilic acid is not ionized and the carbonyl oxygen is coordinated to metal ion. Vandorne and Hannik[11] reported that the unionized acetic acid is coordinated to metal atom through carbonyl oxygen. The band at 3380cm^{-1} which is due to OH stretching of alcoholic group is not affected in the complex spectrum. Hence it may be concluded that the hydroxyl group is not coordinated with the metal ion and the carbonyl oxygen is coordinated with the metal ion.

4.Elecctonic spectra[12]

In the electronic spectra of high spin octahedral complexes of Co(II) one should expect three bands corresponding to the transitions.

${}^4T_{1g}$ ------------------------ ${}^4T_{Zg}$

${}^4T_{1g}$ ------------------------- ${}^4A^{Zg}$

${}^4T_{1g}$ ------------------------- ${}^4T_{1g}$

The cobalt(II)perchlorate complexes of benzilic acid exhibited the band at 485nm suggesting octahedral geometry

5.Structure of the complexes:

The analytical data suggest that benzilic acid is a Mono dentate ligand in which C=O group is coordinated to the metal atom. The analytical and magnetic moment data suggested octahedral geometry for both cobalt (II) chloride and Perchlorate complexes (Table I).

Table I Analytical data and colour of benzilic acid complexes

No	Complex	Colour of the Complex	Percentage of Metal	
			Calculated	Observed
01	$Co(BENZ)_4Cl_2$	Rose	5.64	5.35
02	$[Co(BENZ)_6](ClO_4)_2$	Light Rose	3.61	3.55

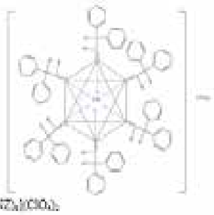
Table II. Molarconductance in acetonitrle

No	Complex	Molar conductance	Nature of the electrolyte
01	$Co(BENZ)_4Cl_2$	58.5	1:0
02	$[Co(BENZ)_6](ClO_4)_2$	205.3	1:2

Table III. Magneticmoments of complexes

No	Complex	μ_{eff}	Magnetic behavior
01	$Co(BENZ)_4Cl_2$	4.85	Para
02	$[Co(BENZ)_6](ClO_4)_2$	4.9	Para

$Co(BENZ)_4Cl_2$



$[Co(BENZ)_6](ClO_4)_2$

CONCLUSION

Benzilic acid complexes with Co(II) metal ions have been prepared and characterised by electrical conductance, analysis of cation, magnetic susceptibility, electronic and infrared spectral studies. The analytical data show that the CO have the general formula $[ML_4Cl_2]$. The perchloride complex have the general formula $[ML_6]$ $(ClO_4)_2$. The conductance measurements show that the chloride and perchlorate complexes behave as a 1:2 nonelectrolyte and 1:2 electrolyte respectively. The magnetic moment measurement indicates paramagnetic behavior for the complexes and the octahedral geometry. The electronic spectral data suggest octahedral geometry for the complexes. The infrared spectral studies clearly indicate that the carbonyl group is coordinated to the metalion and benzilic acid acts as monodentate ligand.

REFERENCES

[1] Eggleston, D.S. and Jackels, S.C., "Tetrasubstituted [14]-1,3,8,10-Tetraene N4 Macrocyclic Complexes: Synthesis, Organic Precursor, and Template Reaction Mechanism". Inorg.Chem.,vol.19, pp.1593-1599,1980.

[2] Malik, W.U; Bembi, R & Singh, R.(1983). Preparation and Characterization of Copper, Cobalt and Nickel Complexes of Tetradentate N6 Macrocyclic Ligand. Polyhedron,2,369-373.

[3] Eggleston,D.S and Jackels,S.C.(1980). Tetrasubstituted [14]-1,3,8,10-Tetraene N4 Macrocyclic Complexes: Synthesis, Organic Precursor, and Template Reaction Mechanism. Inorg.Chem.,19,1593-1599.

[4] Hathaway, B.J., and Billing, D.E., Coord. Chem.Rev.,vol.5, pp.143,1970.

[5] Hathaway, B.J., Duggan, M., Murphy, A., Mullane, J., Power, C., Walsh, A., and Wahsh, B., Coord.Chem. Rev., vol.36, pp.267,1981.

[6] Figgis,B.N and Lewis.J., "Mordrencoordination chemistry" (Interscience,1960).

[7] Parekh, J., Inamdhar, P., Nair, R., Baluja, S., and Chanda, S., J. Serb. Chem.Soc., vol.70,pp.1161,2005.

[8] Geary,W.J Coord.chem.Rewiew,7(1971),81.

[9] Bersuker,I. B., Coord.Chem.Rev., vol.14, pp.367,1975.

[10] Nyholm,R.S.J.CoordChem.Rewiew,1958,8,401.

[11] Vandoorne,W and Hanni K.M. signth, React inorganic met.org.chemistry 11 (I),1981,15.

[12] Sutton,D. "Electronic spectra of transition metal complexes" McGrawHill, London,1968,186-192.