SYNTHESIS OF CO(II) METAL COMPLEXES WITH N4 MACROCYCLIC LIGANDS

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Abstract: Family of tetra aza macrocylic Co (II) complex (CoLX₂) ligands where $L = N_4$ donor macrocylc ligands) and $X = (Cl^-, NO^-_3)$ have been synthesized. Characterization has been done on the basis of elemental analysis, molar conductance I.R. & XPS data. These analysis shows that the ligands behave as tetra dentate through four N- atoms. The binding energies suggest the square planar geometry for Co (II).

Key WORDS; Tetra aza, macrocyclic ligands, square planar

INTRODUCTION :

Cobalt is the 7th element of 3d transition series. Cobalt shows +2 oxidation state in simple salt & +3 in complex. It is the only metal present in vitamin. Vitamin B_{12}^{1-3} contains cobalt as a central metal atom. Complexes of cobalt with macrocylic ligands continue to be actively studied. Although a large no. of macrocylic complex of Cobalt (II) have been reported, only spectra have appeared. Cobalt & its compounds are widely used in analytical chemistry, metallurgical process & pigment industry. The play excellent role in catalytic property.⁴

REVIEW OF LITERATURE

A brief review on this complex forming character is presented.

The coordination chemistry of cobalt (II) ion has been less extensively investigated. Most of the working laid emphasis on the preparation & synthesis of complex of Co (II) macrocyclic ligand.

Kandar *et al.*,⁵ reported a new generation of solution of melalloph thalocyanine derivatives.

Rai *et al.*,⁶ reported the spectral & electro chemistry studied on some dinuclear cobalt (II) macrocylic complex.

Kang et al.,⁷ synthesized four new metal complex with octahedral macrocylic ligands.

Chandra *et al.*,⁸ reported a novel macrocylic scihff base ligands. The transition metal complex Co (II) with macrocylic ligands were synthesized and characterized by elemental, IR, mass, HNMR studied.

The Cobalt (II) metal ion forms a broad range of complexes.

AIM OF THE STUDY

The aim of the study is to deal with synthesize & characterization of Cobalt (II) complexes with macrocylic ligands (L).

EXPERIMENTAL

Material :

All the solvent used were of E. Merck (LR grade & ranbaxy) solvent were used after purification and drying by conventional methods.

The IR spectra of the complexes and ligands were recorded on perkin elmer 457 spectrometer at room temperature in KBr. X-ray photoelectron spectra were recorded in a VG scientific ESCA - 3 MK-II electron spectrometer.

The elemental analysis for C, H & N, were determined on a semi microscale.

Synthesis of ligands :-

A solution of 3,4 hexandione, 2,3 hexandione or furil (2mmol) was added drop wise with constant string in cyclohexane diamine or 2,3 phenylene diamine (2 mmol) in ethanol (20 ml) solution & refluxed for 5 hrs. A white solid product appeared which was filtered washed with C_2H_5OH & dried under vacuum. The L⁻ macrocyclic ligands was characterized by elemental analysis and IR spectra.

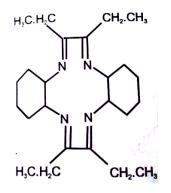


Fig.-1: Ligand = L

Synthesis of complex :-

The complex of the Co (II) with L ligands is done by using Co (II) salts such as [CoCl₂. 2H₂O], Co (NO₃)₂ 6H₂O.

A warm ethanolic suspension (20 ml) of ligands L (1 mmol) & hot ethanolic solution (20 ml) of corresponding Co (II) salts (1 mmol) were mixed together with constant stirring. The mixture was refluxed for 6-8 hrs at 80° C . on cooling a colored complex was precipitated art. It was filtered, washed with cold ETOH & dried under vacuum over P₄O_{1 0}

RESULT AND DISCUSSION

On the basis of elemental analysis the complexes were found to have general composition [Co (L) X₂]

 $X = Cl^{-}, NO_{3}^{-}$

Molar conductance :

The molar conductance indicates that the complex with L having composition $CoLX_2$ are non electrolyte in nature and may be formulated as [Co (L) X_2].

Magnetic moment :

The complexes of Co (II) in octahedral field the ground state $({}^{4}T_{1})$ is orbitally degenerate. The moments would lie between the μ eff= 3.38 BM to 5.2 BM, which account for electron delocalization and a low symmetry ligands field component.

IR spectra :

IR spectra of all ligands and their complexes show that all the ligands behave as tetra dentate⁹.

The IT spectra consist of three absorption bonds at 1390, 830 & 720 cm⁻¹ justifies that free nitrate ions has relatively high symmetry D_3h .

Electronic spectra

Electronic spectra of present complexes having composition [Co (L) X_2] (X = Cl⁻, NO₃⁻). They display bonds at 9541 – 10752 cm⁻¹, 18260 – 20634 (V₃) Cm⁻¹ along with 142792 – 15267 (V₂) cm⁻¹.¹⁰

The position of bonds indicate that these complexes have distorted octahedral geometry & posses D₄h symmetry.

Table-1: Molar conductance & Elemental analysis of Co (II) complexes: -

S. No.	Complexes	Elemental analysis for (Calc. %)			Molar conductance
		С	Н	Ν	$\Omega^{-1}\mathrm{cm}^2\mathrm{mol}^{-1}$
1.	[Co L Cl ₂]	56.4 (56.6)	7.0 (7.0)	11.2 (11.0)	10

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Ī	2.	$[Co L (NO_3)_2]$	51.0 (51.1)	6.2 (6.3)	14.8 (14.9)	22	

Table-2: Magnetic moment & electronic spectra data of Co (II) complex.

S. No.	Complex	µeff B.M.	λmax, cm ⁻¹
1.	[Co L Cl ₂]	5.00	10030, 14792, 18260
2.	[Co L (NO ₃) ₂]	4.88	10550, 15621, 27460

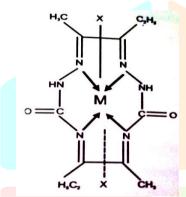
Table-3: Co 2 p_{1/2}, _{3/2} binding energies in CoCl₂.2H₂O and their metal complex.

S. No.	Salt & their metal complexes	2 p _{1/2}	2 p _{3/2}
1.	Co.Cl ₂ . 2 H ₂ O	795.6	780.6
2.	Co L Cl ₂	794.6	779.6
3.	[Co (NO ₃) ₂ . 6 H ₂ o	795.8	780.8
4.	[Co L (NO ₃) ₂]	794.8	779.8

CONCLUSION :

On the basis of elemental analysis, magnetic susceptibility, molar conductance measurement, IR, electron & XPS spectral studies give the below results that these complexes shows the (MLX_2) geometry, where M = Co (II)

 $X = Cl^{-}, NO_{3}^{-}$



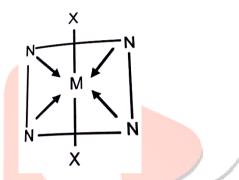


Fig-2: Structure of complex, where,

Fig-3: [Mn (L) X₂] square planar geometry

[M=Co(II)] (X=Cl, NO₃) [Co (L) X₂]

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