

Studies of the physico – chemical properties of complex compounds of divalent Cobalt, Nickel, Copper and Zinc with multidentate organic ligand N-[4-methyl phenyl]–pyridine–2–thiocarboamide

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Abstract : Complexes of Cobalt (II), Ni(II), Cu(II) and Zn(II) were synthesized with N- (4-methyl phenyl)–pyridine–2–carbothioamide ligand. These complexes were characterized by their elemental analysis, magnetic moment, intra-red and electronic spectra. This ligand works in above complexes as divalent ligand having nitrogen and sulphur as donor atom.

(Keywords : Electronic spectra, Intra-red, Magnetic moments, Crystal field parameter)

Introduction

A lot of complexes of cobalt, nickel, copper and zinc have been reported in their divalent state with various organic multidentate or bidentate ligands. They are highly stable being chelated complex compounds¹. Various complexes of transition metal ions have been reported with bivalent organic ligands coordinating with oxygen and sulphur donor atoms. In this present work, complexes are five membered chelate. The study of complexes containing nitrogen and oxygen as donor atoms

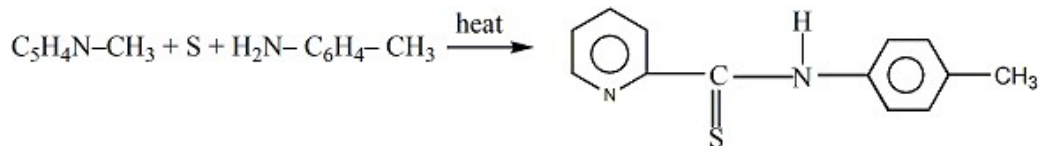
of ligands has received great impetus attribute to their remarkable potential of inhibiting ribonucleotide reductase an obligatory enzyme in DNA synthesis.

Ligands of Azo-dyes² have also been used for complexation with transition metal ion² as they exhibit both chemo-therapeutic and antiseptic properties.

Experimental

This ligand N- (4-methyl-phenyl) pyridine – 2 – carbothioanilide was prepared by will-gerodt synthesis.

For preparing this ligand equal volume (100 ml) - α - picoline, 100 ml p-methylaniline and 50 gram pure sulphur powder were refluxed in a round bottom flask adjusting the apparatus with air condenser and heated upto 150 – 165°C. Again this reaction mixture was cooled and then dissolved in pure ethanol. Again this ligand was crystallized. The dull red coloured crystals of ligand was obtained.



After that the alcoholic solution of this ligand was mixed with 0.01 molar solution of Copper (II), Cobalt(II), Nickel(II) and Zinc (II) separately and refluxing the content for 6 – 7 hours, the change in colour of the reaction mixture indicated the formation of complex compounds.

In case of copper (II) deep bluish complex was obtained, which was washed thoroughly with water and then small portion of ethanol. After that the complex was dried over CaCl_2 in desiccator. The process of the synthesis of all complexes was similar. In all the cases chlorides of transition metals were taken in (0.01 M) solution. The colour of the cobalt complexes was light yellowish and the colour of nickel complexes was deep blue, whereas the complexes of zinc (II) was sand like crystal.

The melting point and conductivity were also measured. The melting point of all complexes were above 250°C .

The high melting point indicated that all these complexes are thermally stable.

Results and Discussion

The molar conductivity of all the complexes found were too low except copper (II) and zinc complexes. These low values of molar conductivity account for non – electrolytic nature of cobalt and nickel complexes. These lower conductivity values may be due to impurities. The molar conductivities of CuL_2Cl_2 and ZnCl_2 are $210 \text{ S cm}^2 \text{ mole}^{-1}$ and $185 \text{ S cm}^2 \text{ mole}^{-1}$ respectively indicating their electrolytic nature.

Table No. - 2

Complex (CoL_2Cl_2)	NiL_2Cl_2	CuL_2Cl_2	ZnL_2Cl_2
% Co = 10.05	% Ni = 10.02	% Cu = 32.8	Zn = 65.38 %
% C = 53.24	% C = 53.27	% C = 52.98	C = 52.66 %
% H = 4.09	% H = 4.10	% H = 4.06	H = 4.05 %
% N = 9.55	% N = 9.56	% N = 9.48	N = 9.45 %
% S = 10.92	% S = 10.93	% S = 10.80	S = 10.80 %
Cl = 12.11	% Cl = 12.12	% Cl = 10.02	Cl $\pm$ 11.98 %

Table No. 03

Colour of complexes
 CuL_2Cl_2 - Dark blue
 CoL_2Cl_2 - light yellowish
 NiL_2Cl_2 - Deep blue
 ZnL_2Cl_2 - Sand colour

Magnetic moments – CuL_2Cl_2 = 1.721 B.M
 CoL_2Cl_2 = 3.7 B.M
 ZnL_2Cl_2 = 0 B.M
 NiL_2Cl_2 = 2.6 B.M

The magnetic moments and conductivity measurements helped to determine the structure

of the complexes. Their magnetic moments values are in good agreement with the number of d-electrons. This indicates that all complexes are outer orbital complexes and high spin complexes. The magnetic moment value of Cu (II) complex with the above prepared ligand indicates the square planar geometry of the CuL_2X_2 complex. It is good a electrolyte also because its molar conductivity is high.

The Pauling valence bond theory assumed that the tetrahedral complex of copper (II), owing to their own symmetry have a greater orbital contribution to the magnetic moment than the square one.

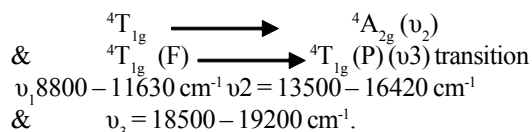
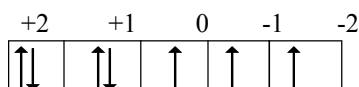
The orbital contribution to the magnetic moment is greater in case of tetrahedral copper (II) complexes⁴. Since the ground state is orbitally triply degenerate. The nine 3d – electrons of the copper (II) ions are distorted⁵ among the five 3d – orbitals in such a way that the energy of the system be minimum. Therefore, the stabilization energy due to the crystal field will be greater for a square planar than for a tetrahedral structure. The complexes of ZnL_2Cl_2 is tetrahedral with sp^3 hybridisation.

Complexes of Co(II) i.e. CoL_2Cl_2 and Ni (II) i.e. NiL_2Cl_2 are octahedral because their magnetic moments values are in favour of outer orbital complexes⁵ and non-electrolytic nature indicate that both chlorides are also coordinated with central atom and hence are non – ionisable. On the basis of I.R. and electronic spectral studies and octahedral geometry⁶ was assigned of Co(II) and Ni(II) complexes. The decrease in – C = S frequency indicated the linkage with S of thiocarbonyl group and N-atom of pyridine ring⁷. $(CuL_2)Cl_2$ show one broad band at about 16500 cm^{-1} to 1700 cm^{-1} , which is in good agreement with those generally absorbed for square planar copper (II) complex⁸.

The peak around 3200 cm^{-1} to 3300 cm^{-1} indicates the non- involvement of – NH group⁹ in complexation^{10,11}.

The electronic spectra of the octahedral complexes exhibit absorption assigned.

To ${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)(\nu_1)$
Co⁺²



The decrease in the value of B is related to the extent of metal – ligand covalency. The metal ligand becomes partially covalent when the d – orbitals overlap with the ligand orbitals. As a result the inter electronic repulsion within the d – orbitals decreases and B value is lowered.

The ${}^4T_1$ ground level of Co (II) is splitting in octahedral field because of spin – orbit coupling and Zerman effects.

The absorption spectra of Ni (II) octahedral complex, reported the first bands of the spectra of NiL_2X_2 split into two components with same intensity approx, the split is about 1000 cm^{-1} .

It is well know that octahedral nickel (II) complexes exhibit splitting absorption bonds. The explanation for the splitting for the splitting are probably due to the split of ${}^3T_2$ and the ${}^3T_1$ states due to spin orbit – coupling.

The splitting of these states due to some ligand field with low symmetry. The polarized crystal spectra of ZnL_2Cl_2 shows that the trigonal distortion is very small¹².

Ballhausen and Leihir assigned the double bond of NiL_2Cl_2 to the spin – orbit component of the $3T_1$ level¹³⁻¹⁴.

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