

Synthesis, Spectral and Structural Studies of Binuclear Cobalt (II) Complexes With Aryl Schiff Bases.



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ABSTRACT

Binuclear Cobalt (II) Complexes with Schiff Bases have been reported. Author have synthesized similar complexes with Schiff bases derived from 2-hydroxy-1-naphthaldehyde and aryl amines. The red to orange red coloured Binuclear Cobalt (II) complexes have general formula $[(ML)_2 Cl_2]$, where 'L' is a Schiff base molecule. IR spectra, electrical conductance and magnetic susceptibility of the complexes are measured. Magnetic moments of the complexes at room temperature were found to be lower than that expected for one unpaired electron on each Cobalt (II) ion indicating antiferromagnetic spin exchange interaction. The super exchange must be taking place through '6' interaction of Cobalt (II) d-orbitals with 's' and 'p' orbitals of bridging diamagnetic 'O-' of the Schiff bases

Keywords : Schiff bases, Binuclear complexes, Cobalt (II) Complexes.

Introduction:

The Schiff base complexes have more importance (1-3) because of their applications in various biological systems, polymers, dyes and catalysis. Schiff bases play an important role in both synthetic and structural research. Binuclear complexes with Schiff bases of various aldehydes with aromatic amines are known (6 - 8). The Oxygen bridged homo and hetero binuclear and trinuclear complexes have attracted much attention due to their interesting spectral and magnetic properties and their use in biochemical processes and homogeneous catalysis. Jonassen and Haris (9, 10) Bhattacharya (11), Khanolkar (8, 12) prepared mononuclear and binuclear complexes of Copper (II) ions. In this paper the author reports synthesis, spectral and structural studies of Binuclear Cobalt (II) complexes with Aryl Schiff bases.

Structure - 1

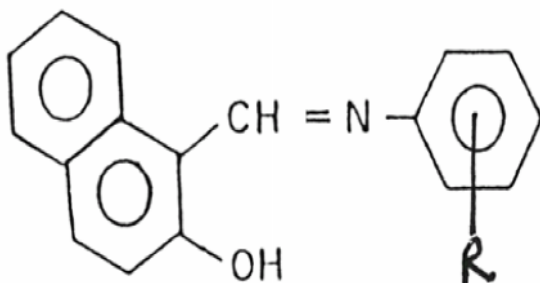


TABLE - 1

No.	R	Symbol	No.	R	Symbol
1.	Hydrogen	SB1	4	4 ¹ - Methyl	SB4
2.	2 ¹ - Methyl	SB2	5	1-Naphthyl	SB5
3.	3 ¹ - Methyl	SB3	6	2-Naphthyl	SB6

2. Experimental:

2.1 Materials :

The Aldehyde, 2-Hydroxy-1-naphthaldehyde used in the synthesis of complexes was of Fluka make (extra pure). All the aromatic amines used were of L.R. grade, which were purified by conventional methods. The metal salt Cobalt (II) Chloride used was of B.D.H. -A. R. Grade.

2.2 Preparation of Schiff Bases :

Schiff bases were prepared (13) by mixing calculated amount of aldehyde and the corresponding amines in ethanolic medium for 2 hrs. On cooling solidification occurred rapidly. All the ligands crystallized as light yellow to orange yellow coloured crystals.

2.3 Preparation of complexes :

The Binuclear Cobalt (II) complexes were prepared by refluxing ethanolic solution of metal chloride and the ligands in 1:2 ratio for half an hour on water bath. The pH was adjusted to 11.0 by adding excess of ammonium hydroxide. The precipitate obtained was filtered, washed with hot ethanol and dried in vacuum. The metal complexes obtained were red to orange red coloured compounds.

2.4 Elemental Analysis :

The purity of complexes was ascertained by elemental analysis. Cobalt in the complexes was estimated by using complexometric titration method using a standard EDTA solution of disodium salt of ethylene diamine tetra-acetic acid of E-Merc-A.R. quality.

2.5 Physical Measurements :

The conductance measurements of all the complexes in DMF were recorded on a systronic direct reading conductivity meter, having cell constant of 1.10 cm⁻¹. Infra red spectra of all the ligands and their complexes were recorded on Perkin Elmer IR spectropho-

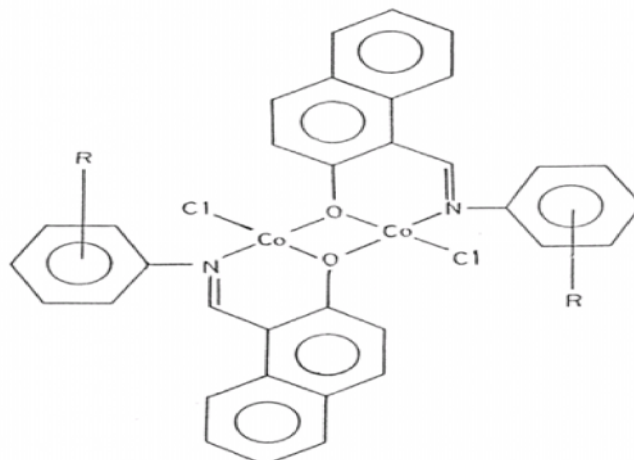


TABLE-2 Colour, Elemental Analysis, Conductance Data and Magnetic Moments of Cobalt Complexes of Schiff Bases.

Cobalt (II) Complex of	Colour	Elemental Analysis				Conductance Ohm-1, Cm2, Mol-1	Magnetic Moments
		%C Obs (Cal)	%H Obs (Cal)	%N Obs (Cal)	%Co Obs (Cal)		
SB ₁	Red	60.30 (59.71)	3.2 (3.8)	4.20 (4.10)	12.50 (12.74)	9.60	2.04
SB ₂	Dark-Red	61.20 (60.72)	4.52 (4.22)	4.30 (3.94)	15.50 (16.57)	12.31	1.90
SB ₃	Brown	59.42 (60.72)	4.52 (4.22)	3.90 (3.94)	15.80 (16.57)	14.21	1.93
SB ₄	Red	60.30 (60.72)	4.00 (4.22)	3.80 (3.94)	16.90 (16.57)	12.13	1.88
SB ₅	Orange – Red	65.20 (64.33)	3.67 (3.83)	3.60 (3.57)	15.60 (15.04)	20.45	2.26
SB ₆	Red	65.00 (64.33)	3.90 (3.83)	4.20 (3.57)	14.80 (15.04)	22.61	2.28

tometer, in the region 4000 - 600 cm⁻¹. The magnetic measurements of all the complexes at room temperature were carried out on Gouy Balance (15).

3 Results and Discussions :

3.1 Analytical data and conductance measurements: The analytical data of the compounds is reported in table 2. The elemental analysis indicated that the complexes are binuclear in nature and are represented by the general formula [(CoL)₂Cl₂] (8). The molar conductance values fall in the range 9.00 to 24.00 Ohm-1 cm² mole⁻¹. The values clearly indicate that they are non-electrolytes (16).

3.2 Infrared Spectral Studies :

The infrared (IR) spectra of ligand show a broad peak band in the region 2600 - 2350 cm⁻¹, which has been

assigned to intermolecularly bonded (HO N) A bond occurring at 1570 - 1560 cm⁻¹ in the spectra of ligand and 1620 - 1603 cm⁻¹ in complexes has been assigned to (C = N) stretching. The shifting of the frequency suggest the co-ordination through nitrogen of azomethine group (17, 18). The spectra of most of the complexes exhibit a weak band in the range 2932 - 2916 cm⁻¹, which is assigned to the aromatic C - H stretching vibrations. The strong and sharp band appearing in the region 1540 - 1504 cm⁻¹ is attributed to C = C stretching vibrations. Very strong bands in the range 1461 - 1455 cm⁻¹ were assigned to aromatic C - N frequencies in the complexes. The strong and sharp band at 1376 cm⁻¹ in all the complexes is assigned to C - O stretching vibration. Thus a shift of 25 - 40 cm⁻¹ in C - O frequency is

observed from ligand to Binuclear Cobalt(II) complexes. The shifting of this frequency is characteristic feature (13) of the formation of binuclear complexes and therefore, can be used as a criteria for the formation of binuclear complexes. Further this shifting suggests (17 - 19). The formation of Cobalt - Oxygen (Co - O) bond and bridging through phenolic oxygen in the complexes.

3.3 Magnetic Measurements :

The magnetic moment of all these complexes are in the range of 1.88 to 2.28 B.M. these values are lower than those expected for square planar symmetry (20). The lowering in magnetic moment values show subnormal character of complexes. It clearly indicate (21) that there is antiferromagnetic exchange between

the two Cobalt Ions. The magnetic exchange has been observed by many workers (11,12, 21 - 23) which leads to lower values of magnetic moments.

3.4 The Proposed Structure :

With the help of elemental analysis data, conductivity measurements, infrared spectral data and magnetic susceptibility measurements, it may be suggested that the complexes have co-ordination number six with a planar to pseudotetrahedral structure. The molecular structure of the complexes is represented as structure - 2? **Structure - 2**

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