

Magnetic Behavior Studies on Co (II) Complexes with N- And O-Donor Sites Ligand

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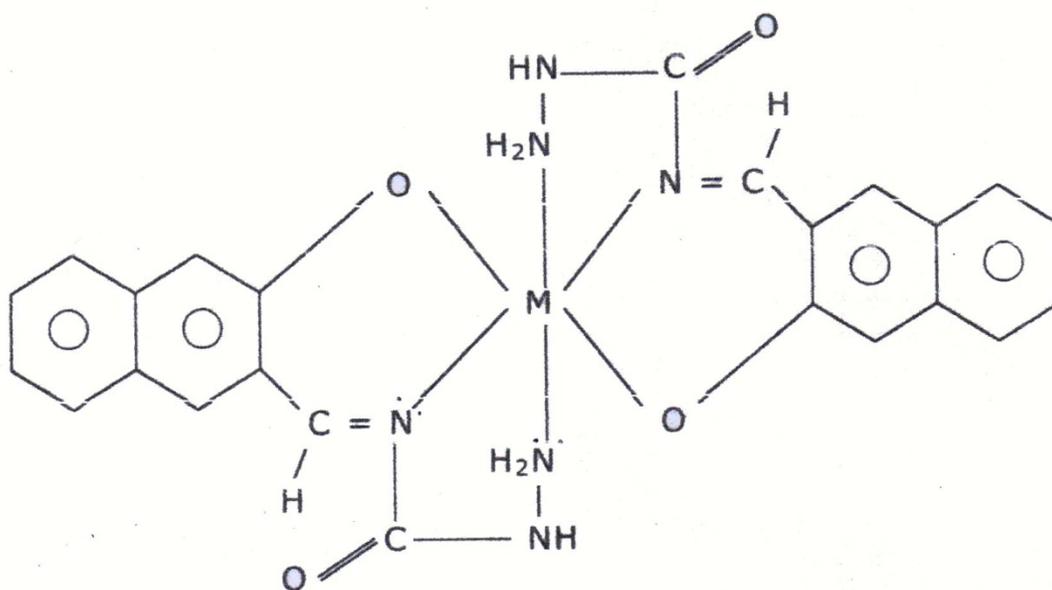
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I. INTRODUCTION

Co (II) Ni(II) and Cu(II) salts are found to form complexes of types



M = Co(II), Ni(II), Cu(II)

Fig. 1

1. The present investigation involves complexes of Co(II) With a semicarbazone ligand, 3-hydroxy-2-naphthalidene semicarbazone,
2. It was Gilbert Newton lewis who recognized magnetic moment data as a diagnostic tool for determining structure of complexes¹.

II. EXPERIMENTAL

The metal complexes have been prepared by allowing metal salts to catalyse the condensation of 3-hydroxy-2-naphthaldehyde with semicarbazide hydrochloride. The ligand 3-hydroxy-2-naphthalidene was prepared by refluxing the solution of equimolar amount of 3-hydroxy 2-naphthaldehyde and semicarbazide in methanol for 2 hours.

The hot solution was filtered when yellow crystals of the ligand were deposited on cooling, which were recrystallised from methanol (M.P. 230-232^oc)

III. RESULT AND DISCUSSION

Cobalt(II) forms generally four coordinated tetrahedral and six coordinated octahedral complexes, however, a few four coordinated planar and five coordinated trigonal bipyramidal complexes have also been reported. Cobalt(II) complexes with one unpaired electron can be either low spin octahedral or planar but complexes with three unpaired electron can be either octahedral or tetrahedral. The existence of high spin square planar complexes of cobalt (II) has been described but such reports have been found to be incorrect or unfounded.

Magnetic moment values of cobalt(II) complexes provides important information in distinguishing octahedral, planar and tetrahedral configurations. High-spin octahedral cobalt(II) complexes have magnetic moments ranging from 4.7 to 5.2 B.M.² i.e. they have very large orbital contribution since the spin only moment for three unpaired electrons is to the three-fold orbital degeneracy of ⁴T_{1g} ground state. The values of magnetic moment of octahedral complexes vary with temperature. In a high-spin tetrahedral complex the values of magnetic moments range between 4.3-4.7 B.M.³ which are temperature independent. In tetrahedral complexes, cobalt (II) has ground state ⁴A₂. The symmetrical and heavily populated ground state does not contribute large orbital moment to magnetic moment values. The low-spin octahedral cobalt(II) complexes exhibit magnetic moment value of 1.92-2.47 B.M. at room temperature and which varies with temperature. The planar complexes also exhibit magnetic moment value in the same range. A number of complexes with intermediate magnetic moment values between 2.5-4.3 B.M. have also been reported. Such complexes are viewed as anomalous.

Magnetic moments of several carbohydrates of cobalt(II) have been studied by Ranade and Subba Rao⁴. Magnetic moment values of cobalt(II) mandelate, malonate and tartarate lie between 5.00 to 5.22 B.M. and the values suggest that these complexes have a high-spin octahedral symmetry. The value of 4.79 B.M. observed in the case of cobalt (II) lactate can't rule out the possibility of the compound having a high-spin tetrahedral symmetry.

Gopal Narain⁵ isolated and measured magnetic moments of cobalt(II) phthalimide with 5-nitro-O-phenanthroline. Values of magnetic moment lie between 4.43-4.467 B.M. which suggest tetrahedral symmetry for those complexes.

Several complexes of cobalt(II) have been reported by Gill and Nyholm⁶ and the magnetic moment values are given in Table-1

Table-1
Observed magnetic moments of CoX₂.2Py at 20^oc.

Solid Complex	Color	B.M.	Color in Nitrobenzene	B.M.
CoCl ₂ .2Py	Blue	4.42	Blue	4.52
CoBr ₂ .2Py	Blue	4.50	Blue	4.52

CoI ₂ .2Py	Blue	4.47	Blue	4.59
Co(CNS) ₂ .2Py	Purple red	5.10	Blue	4.50
CoPy ₂ Br ₂ .2H ₂ O	Violet	5.00	Blue	4.56

Complexes of cobalt (II) with strong ligand field have been prepared by stoufer and Co-workers. They found that magnetic moment values of such complexes lie between 2.6 to 3.8 B.M. They have explained the intermediate magnetic moment values of these complexes due to occurrence of equilibrium mixture of complexes in two spin states (spin doublet and spin quartet) in which each of the electronic levels provide different amount of spin and orbital angular momentum to magnetic values. The complexes with such moment values are given in Table-2

Table-2

Compound	Temperature	μ_{eff} (B.M.)
[Co(ter Py) ₂] Br ₂ .H ₂ O	295 K	2.63
[Co(PBI) ₂] ₂	295 K	3.72
[Co(BMI) ₂](BF ₄) ₂	295 K	2.91
[Co(GdH) ₃]Br ₂	295 K	3.16
[Co(DTHB)](ClO ₄) ₂	295 K	2.36

These complexes exhibit a large deviation from normal Curie-Weiss behavior. They interpreted the results supporting a model in which there is a distribution of magnetic ions among two or more low lying electronic levels.

The Complex of cobalt(II) in the present investigation shows the magnetic moment value to be 2.25 B.M. at room temperature (34^oC). These values clearly indicate that the complexes have either four coordinated square planar stereochemistry or six coordinated low-spin octahedral structure. On the basis of magnetic moment it is difficult to distinguish between low-spin octahedral and square planar complexes of cobalt(II) as in principle for both cases the moment should be close to the spin-only value for one unpaired electron. Four coordinated planar complexes are aerielly easily oxidized to a diamagnetic octahedral cobalt(II) on exposure to air. But in the present case, on exposure to air for several days there is no change in colors and magnetic moment values of these complexes. Since the cobalt(II) are not oxidized readily to its Co(III) complexes. Therefore, it is suggested that the complexes do not have planar stereochemistry rather they possess low-spin octahedral structures.

Bis-2-quinideno cobalt(II) salts show magnetic moment in the range 4.15-4.60 B.M.⁷ where as the complex [(Me₂NC₆H₄)₃PO₄.Co](ClO₄)₂ shows magnetic moment value 4.76⁸.

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