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STUDY ON MAGNETIC SUSCEPTIBILITY OF CO(II) COMPLEXES AND ELECTRONIC SPECTRA OF CO(II) COMPLEXES

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ABSTRACT

The ground state of octahedral Co(II) complex is $^4T_{1g}$. The high spin octahedral Co(II) Complexes have magnetic moment in the range of 4.6-5.3 B.M. as reported by many workers. The high values of magnetic moment are in the favour of large orbital contribution.Several Workers[22-24] observed the magnetic moment values of many Co(II) complexes within the range of 5.00 – 5.22 B.M. These values indicate that the complexes of Co(II) are high spin complexes.The magnetic moment values of several Co(II) complexes were reported by Stoufer and co-workers[25] which fall within the range of 2.36 - 3.72 B.M. These low values of magnetic moment of octahedral Co(II) complexes may be due to the occurrence of equilibrium mixture in two spin states. The low magnetic moment values of Co(II) octahedral complexes were further explained by Stoufer on the basis of large tetragonal distribution along Z axis.

INTRODUCTION

It is well known that Schiff bases are important in multiple fields such as chemistry and biochemistry owing to their biocidal activities. The design and synthesis of metal organic coordination polymers have received considerable attention because of their fascinating self assembled structures and potential applications in magnetic[3] and enzyme catalytic process[4]. The recent development of self assembled supramolecular chemistry can rationally design and synthesize metal-organic coordination polymers depending on the ligand geometry and coordination propensity of the metal ion. Organic ligand formed by reaction between the amino acids and aldehydes are good candidates to construct metal clusters more and more geometrically intriguing.

MECHANISM AND RESULTS

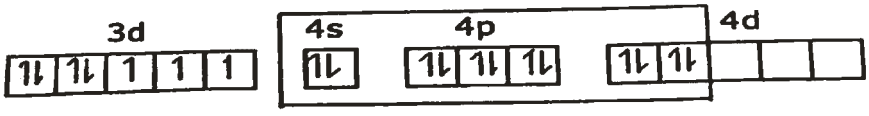
Cobalt has outermost electronic configuration $3d^74S^2$ and 0 in +2 oxidation state, it has $3d^7$ electronic configuration due to the , presence of three unpaired electrons. Co(II) usually forms the following type of complexes :-

(i) Tetrahedral having Sp^3 hybridisation with three unpaired electrons.

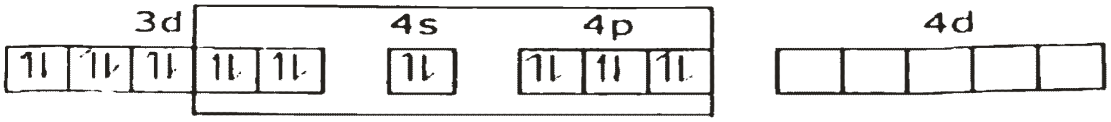
(ii) Square planar having dsp^2 hybridisation with one unpaired electron.

(iii) Octahedral having sp^3d^2 hybridisation with three unpaired electrons or d2sp3 hybridisation with one unpaired electron promoted in 5s orbital.

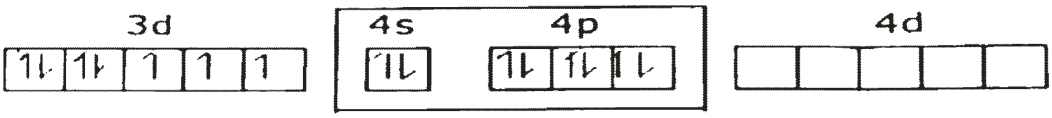
In outer orbital octahedral or tetrahedral Co(II) complexes, there would be three unpaired electrons and such complexes are paramagnetic. Co(II) complexes are also square planar or low spin octahedral having one unpaired electron due to promotion of one electron in the higher orbital.



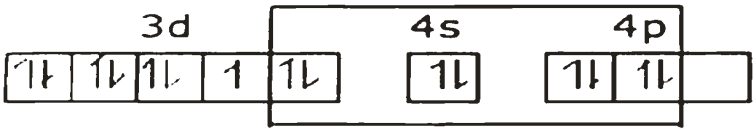
outer orbital sp^3d^2 hybridisation with three electrons in 3d orbitals.



Inner orbital d^2sp^3 hybridisation due to promotion of one electron in 5s orbital.



sp^3 hybridisation



The ground state of octahedral Co(II) complex is $^4T_{1g}$. The high spin octahedral Co(II) Complexes have magnetic moment in the range of 4.6-5.3 B.M. as reported by many workers. The high values of magnetic moment are in the favour of large orbital contribution.

Several Workers[22-24] observed the magnetic moment values of many Co(II) complexes within the range of 5.00 – 5.22 B.M. These values indicate that the complexes of Co(II) are high spin complexes.

The magnetic moment values of several Co(II) complexes were reported by Stoufer and co-workers[25] which fall within the range of 2.36 - 3.72 B.M. These low values of magnetic moment of octahedral Co(II) complexes may be due to the occurrence of equilibrium mixture in two spin states. The low magnetic moment values of Co(II) octahedral complexes were further explained by Stoufer on the basis of large tetragonal distribution along Z axis.

Many octahedral complexes of Co(II) have magnetic moments very near to 4.2 B.M. as reported by Ghosh and Banarjee[26] who studied Co(II) complexes within the range of 4.15 - 4.60 B.M. and tetrahedral geometry were proposed.

The high spin tetrahedral Co(II) complexes having the magnetic moment values in the range of 4.3 - 4.7 B.M. are temperature dependent.

The ground term of square planar Co(II) complexes is 2A19. The spin only value for one electron is equal to 1.9 B.M. However, experimental values of lief! for most of the square planar Co(II) complexes fall in the range of 2.1 - 2.9 B.M.[27]

In the present investigation magnetic moment values of Co(II) complexes were calculated at 25°C and tabulated in Table 1

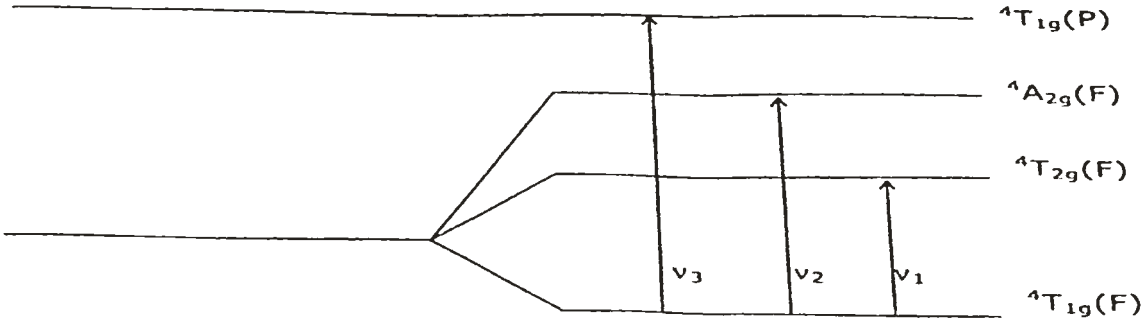
Table – 1 Magnetic moment of the Co(II) complexes of the type $[Co(MPQS)_2X_2]$ and $[Co(MPQT)_2X_2]$

Complexes	μeff in B.M.	Temperature
$[Co(MPQS)_2Cl_2]$	4.89	295^0K
$[Co(MPQS)_2Cl_2]$	4.89	295^0K
$[Co(MPQS)_2Br_2]$	4.90	295^0K
$[Co(MPQS)_2Br_2]$	4.94	295^0K
$[Co(MPQS)_2I_2]$	4.87	295^0K
$[Co(MPQS)_2I_2]$	4.88	295^0K
$[Co(MPQS)_2(NO_3)_2]$	4.93	295^0K
$[Co(MPQS)_2(NO_3)_2]$	4.96	295^0K

Magnetic moment values of all the complexes are in the range 4.84 - 4.96 B.M. indicating that all the complexes of Co(II) are high spin octahedra128-30. 7 I '7 1

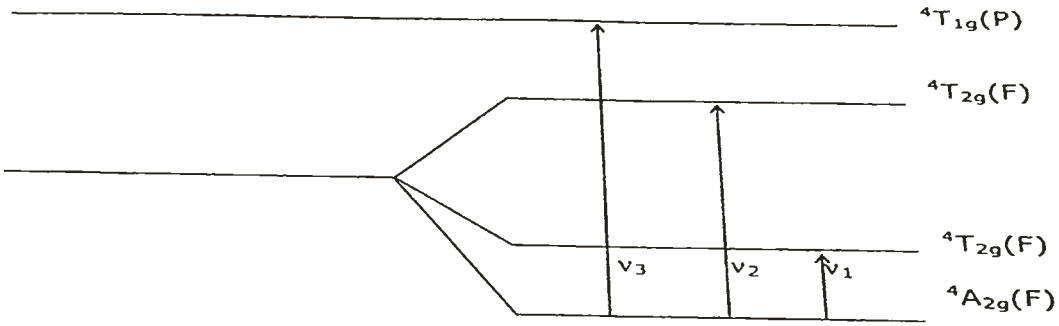
Electronic Spectra of Co(II) Complexes

The geometry of the complexes of Co(II) with the ligand MPQS and MPQT are decided on the basis of spectrophotometric data. The ground state for Co(II) is 4F and the next high state having the same spin multiplicity is 4P. In octahedral and tetrahedral fields, the splitting can be shown:



Simplified energy level diagram of octahedral d7 – system ion)

(Co(II)



Simplified

energy level diagram of tetrahedral d^7 - system

Thus in octahedral complexes of Co(II) ion expected bands corresponding to various transitions, are : -

(i) $^4T_{2g}(F) \leftarrow {}^4T_{2g}(F)$ at about — 8,000 cm^{-1}

(ii) $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ at about — 20,000 cm^{-1}

(iii) $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ at about — 22,000 cm^{-1}

For tetrahedral field Co(II) ion the expected bands corresponding to the following transitions in the region are noted below :-

(i) $^4T_{2g}(F) \leftarrow {}^4T_{2g}(F)$ at about — 8,000 cm^{-1}

(ii) $^4T_{2g}(F) \leftarrow {}^4T_{2g}(F)$ at about — 20,000 cm^{-1}

(iii) $^4T_{2g}(F) \leftarrow {}^4T_{2g}(F)$ at about — 22,000 cm^{-1}

In the present investigation spectra have been recorded in the region 10,000 – 25,000 cm^{-1} and all the complexes of Co(II) displayed three bands at 13000, 15000 and 18000 cm^{-1} corresponding to the transition $^4T_{1g} \longrightarrow {}^4T_{2g}(F)$, $^4T_{1g} \longrightarrow {}^4T_{2g}(F)$ and $^4T_{1g} \longrightarrow {}^4T_{1g}(P)$ respectively. The presence of three absorption bands at above mentioned regions suggest that Co(II) complex has an octahedral[31-33] geometry which is further supported[28-30] by the magnetic susceptibility value of Co(II) complexes 4.84-4.96 B.M. which is in close agreement with the octahedral geometry.

Table – 2

Electronic spectra of Co(II) complexes of the type $[Co(MPQS)_2X_2]$ and $[Co(MPQT)_2X_2]$

Complexes	Band position		
$[Co(MPQS)_2Cl_2]$	13200	15060	18200
$[Co(MPQT)_2Cl_2]$	13600	15210	18000
$[Co(MPQS)_2Br_2]$	13400	15140	18600
$[Co(MPQT)_2Br_2]$	13360	15280	18160
$[Co(MPQS)_2 I_2]$	13260	15300	18240
$[Co(MPQT)_2 l_2]$	13240	15140	18100
$[Co(MPQS)_2(NO_3)_2]$	13210	15010	18310
$[Co(MPQT)_2(NO_3)_2]$	13000	15005	18300
$[Co(MPQS)_2(ClO_4)_2]$	13160	15130	18060
$[Co(MPQT)_2(ClO_4)_2]$	13480	15150	18110

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