Studies on Bonding, Structure and Characterisation of Co(II) Complexes with Ligands Containing N and S Donars.

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Abstract— Transition metal complexes of Co(II) with nitrogen and Sulphur containing donars such as paramethoxy phenyldithiocarbamate and orthomethoxyphenyldithiocarbamate are characterized on the basis of structural, magnetic and spectral data. These complexes have been thoroughly investigated by means of physicochemical method. The present work deals mainly with the studies of bonding and structures in Co(II) complexes which is based on valence band theory. The magnetic susceptibility of these complexes are observed using Gau Balance method.

Keywords— Nitrogen, Sulphur, Complexes, Structural Properties, Magnetic Properties, Structural Properties.
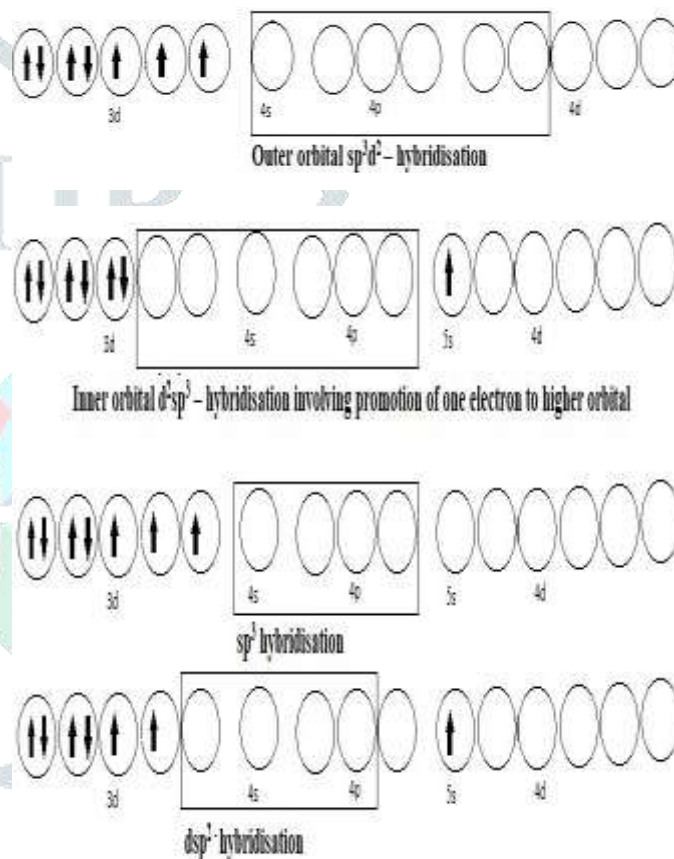
Introduction

Nowadays, coordination chemistry is a fundamental tool to elucidate nature of bonding, structures, magnetic and spectral properties. For this purpose, various theories are excepted such as valence bond theory, crystal field theory, ligand field theory, etc. At present work, the bonding and structures of Co(II) complexes of nitrogen and sulphur containing ligands are assigned. Such ligands are monosubstituted phoniledithiocarbamate, ortho-aminophenol, ortho-aminothiophenol, thiocarbohydrazide, etc. in which complexes of monosubstituted pheniledithiocarbamate ligand are of much discussion. The bonding and structure in Co(II) complexes with such ligands are also characterised by analytical, magnetic and spectral data.

Experimental Data on Bonding and Structure in Co(II) Complexes

1) With Paramethoxyphenyldithiocarbamate

Cobalt(II) is a d^7 system. It usually forms either octahedral, tetrahedral or square planar complexes in which cobalt atom uses sp^3d^2 (or d^2sp^3). sp^3 or dsp^2 hybridised orbitals respectively. The square planar complexes will have one unpaired electron and as such, they will have paramagnetism corresponding to one unpaired electron. In either tetrahedral or octahedral complexes there would be three unpaired electrons and such complexes will show paramagnetism corresponding to three unpaired electrons.

The ground state of the square planar Co(II) complex is ^2A_1g ($b_2{}^2g\ eg^4\ a_1{}^1g$). Mixing of the higher ligand field terms into the ground state is excepted to give some orbital contribution to the magnetic moment by raising the value of 'g'. Mixing of higher states does take place but the contribution is not excepted to be more than 10%, if the separation between the adjacent states is of the order of 10Dq (Oh). A 10% increase in the spin only moment value for one unpaired electron (s= 1/2) leads to Per = 1.9 B.M.

Outer orbital sp^3d^2 – hybridisation

Inner orbital d^2sp^3 – hybridisation involving promotion of one electron to higher orbital

sp^3 hybridisation

dsp^2 hybridisation

However, the experimental value of meff for most of the square planar cobalt complexes lie between 2.1- 2.9 B.M. A complex is $Co[(AsMe_2)_2C_6H_4]_2(CIO_4)_2$ with He value equal to 2.1 B.M. at 300°K, Q=10°. The presence of paramagnetism corresponding to three electrons (3.04 B.M.) in $Co(p-OCH_3C_6H_4NCSSNH_4)2\ (C_6H_6)_2\ 3H_2O$ thus rules ouf the possibility of a square planar arrangement of bonds around Co(II) ions. To form the inner orbital octahedral configuration electron will have to be promoted to 4d orbitals in order to hybridise two d- orbitals with 4s and 4p orbitals. In case it is accepted, the Co(II) complex should be highly oxidised because of the promoted electrons in the 4d orbital which is on a much higher energy level than 3d. This property is not shown by this complex and hence inner orbital octahedral structure is ruled out of question leaving two option only tetrahedral or outer orbital decahedral configuration. The distinction between these two configurations cannot be definitely made on the basis of

magnetic data alone. The only distinguishing feature between the two possibilities is as follows.

When Cobalt (II) ion having the ^4F ground state is surrounded by four monodentate ligand molecule at the corners of tetrahedron, the resulting cubic crystalline field gives rise to lowest lying single state, $^4A_1$ separated from two triply degenerate levels ($^4T_1$ and $^4T_2$) by energy intervals >> KT. As a result, the level almost exclusively occupied is the lowest lying singlet. This cause the metal ion to behave very much as though it was in a state for which orbital contribution is zero. In octahedral complexes, the lowest lying state is the triplet state. This triplet state is split by the small rhombic field component invariably present into three level separated by energy intervals << KT. Each of three sub-level is occupied to an extent dependent upon the relative sizes of KT and of the energy intervals. The orbital contribution is no longer small and the moment are expected somewhere between the "spin only" value 3.89 B.M. and the "spin only plus "orbital contribution value 5.2 B.M. On the other hand, moment close to 3.89 B.M. are expected for tetrahedral complexes. Experimentally it has been found that tetrahedral Co(II) complexes have moments in the range 4.2-4.7 B.M. while those of the octahedral complexes [1-3] in the range 4.4-5.6 B.M.

Recently "Stoufer has shown that there are several octahedral complexes where magnetic moments are as low as 4.20 B.M. The possible postulated reason for the low value of the magnetic moment of octahedral Co(II) complexes may be the large tetrahedral distribution along the Z-axis." The H value of 3.04 B.M. for bis-paramethoxy phenyldithiocarbamate bis aqua Co(II) dibenzenemonohydrate is very low and abnormal. Since μ_{eff} value as low as 2.1 B.M. has been observed [4] for distorted octahedral complexes Co(terpyr)$_2$Cl$_2$H$_2$O, no decision can be taken whether the complex is octahedral or tetrahedral simply on the basis of magnetic data alone.

Nyholm [5] also suggested that the orbital contribution depends on the electronegativity [6] of the attached ligand and is very sensitive to slight departure from the cubic symmetry of the octahedral complexes [7]. This is also obvious from the data given in Table-1.

S.No	Compound	Configuration	μ_{eff}(B.M.)
1.	[(C$_9$H$_8$N)$_2$(CoI$_4$)]	Td	4.88
2.	[Co{(C$_6$H$_5$)$_3$PO}$_2$I$_2$]	Td	4.82
3.	[(CH$_3$)$_4$N]$_2$Co(NCS)$_4$]	Td	4.40
4.	[HgCo(NCS)$_4$]	Td	4.32
5.	[Co(en)$_3$]Cl$_2$	Oh	4.82
6.	[Co(di pyr)$_6$]Cl$_2$	Oh	4.85
7.	[Co(BDH)$_3$]I$_2$	Oh	4.17
8.	[Co(BMI)$_3$I$_2$.H$_2$O]	Oh	2.91
9.	[Co(PMI)$_3$(BF$_4$)$_2$]	Oh	4.31
10.	[Co(terpyr)$_2$(ClO$_4$)$_2$]	Oh	4.30
11.	[Co(terpyr)$_2$Cl$_2$.H$_2$O]	Oh	2.10
12.	[Co{3-(4-pyr)triazoline-5-thione}$_2$(H$_2$O)$_2$]	Oh	4.30*
13.	[Co(Quinazoline 2,4-dithione)$_2$Py$_2$]	Oh	4.24**

*   B. Singh and R. Singh; J. inorg. nucl. chem.,34,3449,(1972)
**   B.Singh, U.Agarwala and Lakshmi; Inorg. Chem.8,2341(1969)

Table 1 Magnetic moments of tetrahedral and octahedral and Co(II) complexes.

In order to decide whether the present complex bis-paramethoxyphenyl dithiocarbamate bis aqua Co(II) dibenzene mono aqua is octahedral or tetrahedral on the basis of spectrophotometric data, it is assumed that the weak crystal field is a good approximation. The ground state for Co(II) is ^4F and the next higher state having the same spin multiplicity is 4p. In octahedral and tetrahedral fields, the splittings are shown in fig.1 and fig.2 respecively.
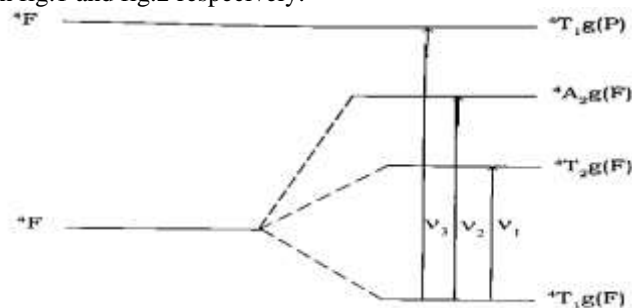

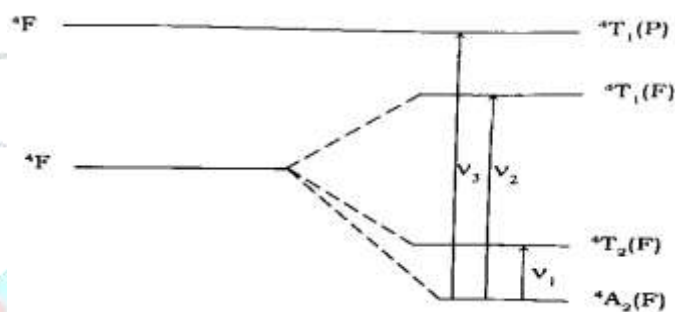**Fig. 1**. Simplified energy level diagram of octahedral d^7 system (Co II ion)

Fig. 2 Simplified energy level diagram of tetrahedral d^7 system (Co II ion)

Thus in octahedral complexes of Co(II) ion bands corresponding to various transitions, which are expected shown below :
(i) $^4T_1g \longrightarrow {}^4T_2g$ (F) at about 8000 cm^{-1}
(ii) $^4T_1g \longrightarrow {}^4A_2g$ (F) at about 20000 cm^{-1}
(iii) $^4T_1g \longrightarrow {}^4T_1g$ (P) at about 22000 cm^{-1}

There are Leporte's forbidden bands and their extinction coefficients are small lying between 2-20. For tetrahedral field around Co(II) ion three bands corresponding to the following transitions are expected in regions noted below :
(i) $^4A_2 \longrightarrow {}^4T_2$ (F) at about 4000 cm
(ii) $^4A_2 \longrightarrow {}^4T_1$ (F) at about 7000 cm
(iii) $^4A_2 \longrightarrow {}^4T_1$ (P) at about 15000 cm

The solution spectrum of this complex has been recorded between 300 mp to 1000. It has been found that the spectrum contains two bands in this range at 650 mu (15,300 cm ') and 520 mu (19,200 cm '). The presence of these two weak bands at the above mentioned positions suggests that the field may be octahedral around Co(II) ion. Since the lowest energy band corresponding to
(i) $^4T_1g(F) \longrightarrow {}^4T_2g(F)$ ....υ_1 beyond the above of the instrument.
(ii) $^4T_1g(F) \longrightarrow {}^4A_2g$ (F).... $\upsilon_2=$15300 cm^{-1}
(iii) $^4T_1g \longrightarrow {}^4T_1g$ (P) .....$\upsilon_3=$ 19200 cm^{-1}

It may be noted that β value for the complex is low. It is suggested by Cotton et al. [8] that low β value should be coupled with high intensity of the absorption band. This has been found to be true in the present case since the extinction co-efficient has been found to be 120 for 15,300 cm^{-1} band and 60 for 19,200 cm^{-1} band. Furthermore, the low value of β indicates that the metal ion is coordinated through the thiocarbonyl

Sulphur of the ligand, similar effects have been observed in the case of other Co(II) complexes [9-11]

Thus, the magnetic moment and electronic spectrum of this complex indicate distorted octahedral symmetry for this complex. It may be noted that v NH band is observed at 3400 cm^{-1} in the ligand, but this is completely absent in the Spectrum of the complex. This may be because of the fact that the ligand NH group is not present in the complex. This may be the case only when the NH group is deprotonated and metal ion attaches itself to nitrogen giving birth to metal nitrogen band in the complex. A medium band at 790 cm in spectrum of the ligand is most probably v C S band. This band shifts to lower frequency (780 cm) on complexation, A metal-Sulphur bonding seems probable because similar shift has been found for Sulphur bonded complexes.

Thus, infrared spectrum indicates coordination through nitrogen as well as Sulphur. In view of octahedral symmetry and metal-nitrogen as well as metal-Sulphur bonding following structure may be assigned to the complex. Its solubility in organic solvents shows its monomeric nature.
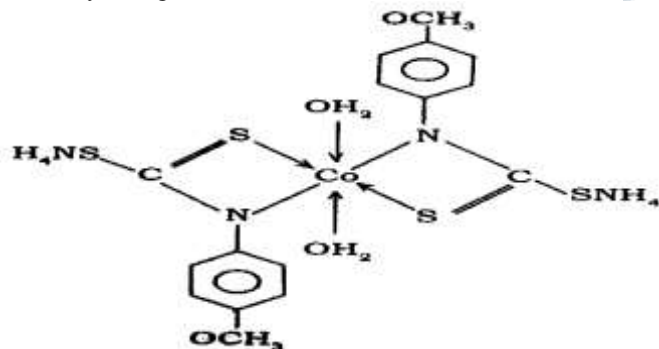

Fig. 3 Structure of Co(II) complex with p-methoxy phenyl dithiocarbamate.

2) With Orthomethoxyphenyldithiocarbamate

The analytical data of this complex indicates that the stoichiometry of this complex is $Co(OCH_3C_6H_4NCSSNH_4)_2$ $3C_6H_4$. The effective magnetic moment of this compound was found to be 1.98.M. On the basis of this low magnetic moment, the complex may be assigned either a square planar structure of inner orbital octahedral structure corresponding to $3d^24s4P^3$ hybridization. However, the latter choice may be eliminated due to the following reason.

As the level of next higher energy are 4s, 4p. 4d, inner $3d^24s4p^3$ hybridisation requires promotion of one electron to the 4d level.

Inner d^{3}sp^3 – hybridisation
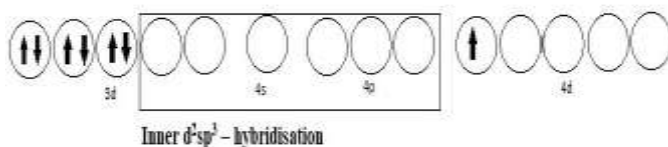
This requires that the removal of 4d electron would be relatively easy and the complex would be easily oxidized to Co(III) complex. However, this has not been found to be the case.

Thus, the magnetic moment value of 1.9 B.M. suggests square planar geometry of this complex is shown in fig. 4. It has two split bands at 600 mμ and 660 mμ. A comparison of this spectrum with the spectrum of octahedral complex bis(p-methoxyphenyldithiocarbamate) bis aqua Co (II) dibenzene monohydrate indicates probable splitting of the 650 cm band.

This may be taken as an evidence for square planar structure of this compound.

The infrared spectrum of the ligand as well as the complex have been recorded and similar charges in spectra on coordination have been found. This may be taken as an evidence for metal nitrogen as well as metal sulphur bonding. Because of the high solubility of this complex in organic solvents, the following monomeric structure may be assigned to it.
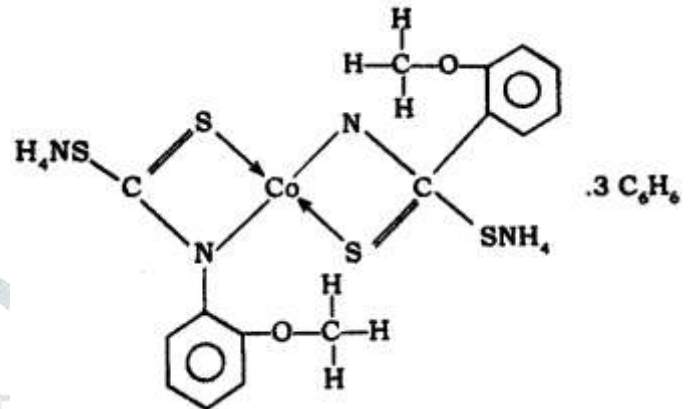

Fig. 4 Structure of Co(II) complex with orthomethoxy phenyldithiocarbamate.

Results and Discussion

From the above observations it is concluded that Co(II) complexes with nitrogen and sulphur containing ligands are of tetrahedral, octahedral and square planner geometry. Some of the configurations are given in Table 1. It is also found that most of them are paramagnetic in behaviour. The magnetic moment of some complexes are tabulated in Table 1. The Co(II) complexes show 3 bands in infrared spectrum as discussed earlier.

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