

PHYSICO-CHEMICAL BEHAVIOUR AND SPECTROSCOPIC STUDIES OF Mn(II) and Co(II) MIXED LIGAND COMPLEXES

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ABSTRACT

In the present study, we report here, the synthesis and spectroscopic characterization of Mn(II) and Co(II) mixed ligand transition metal picrate complexes with 1,2-Diaminobenzene and 1,10-Phenanthroline. The synthesized complexes were found to be coloured crystalline, solid, sparingly soluble in water and alcohol but soluble in DMF and DMSO. The complexes are quite stable at room temperature. Magnetic and spectral studies show that complexes are octahedral in nature.

Keywords- *Mixed ligand complexes, Physico-Chemical studies, Spectral Studies.*

I.INTRODUCTION

In recent years, there is a considerable interest on the use of transition metal ions as catalysts in many redox reactions. In various redox reactions Mn(II) has been extensively used as a homogeneous catalyst[1]. A number of complexes of Mn(II) with various organic and inorganic ligands have been reported[2,3]. In Metal coordination chemistry Schiff bases play a vital role due to ease of their preparation, various applications in the field of biochemical, industrial and medicinal chemistry. Recently, the studies based on transition metal complexes arose a deep interest. Several metal coordination compounds of Schiff bases have been recommended as antifungal, anti-inflammatory, antibacterial and cytotoxic agents[4-7]. As an extension of this research, we report here, the synthesis and spectroscopic characterization of Mn(II) and Co(II) mixed ligand transition metal picrate complexes with 1,2-Diaminobenzene and 1,10-Phenanthroline.

II.EXPERIMENTAL

All the chemicals used were of AR grade. Picric acid was dried over Conc. H₂SO₄. Methanol and Ethanol were further purified by double distillation. AgNO₃ was used as received. Transition metal picrates mixed ligand complexes of Mn(II) and Co(II) were synthesized as reported earlier [8,9]. Elemental analysis was conducted

carried out on Herbaceous Carlo Erba 1108 analyser. IR and electronic spectra were recorded on Perkin Elmer grating Spectrometer at CDRI, Lucknow. Magnetic measurements were carried out at room temperature by Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. The diamagnetic correction of metal ligand system was calculated using the Pascal's constant.

III.RESULTS AND DISCUSSION

The purity of metal picrate complexes was checked by TLC method. All the complexes were found to be in easily filterable, in solid state, insoluble in water but soluble in DMF and DMSO. The molar conductance values of the complexes in DMF (10^{-3} M) lies in the range 10.15-19.08, showing non-electrolytic behavior. The characterization data of the complexes are given in Table 1.

The IR spectra of the hydrated metal picrates give bands in the range $3210\text{-}3315\text{ cm}^{-1}$ and 1630 cm^{-1} which disappear in the anhydrous compounds. These bands may be attributed to νOH and δHOH respectively of water molecules present in the hydrated metal picrates. In Picric acid νNO_2 vibrations are present at 1560 cm^{-1} . In metal picrates these vibrations remain practically unchanged as compared to the location of these bands in Picric acid. The important IR bands of Mn(II) and Co(II) mixed ligand complexes and their tentative assignments are given in Table 2. The comparison of the spectral bands of Picric acid and metal picrate complexes gives some important clues about the chemistry of complexes. The two significant absorption bands at about 1560 and 3380 cm^{-1} may be attributed to $\nu_{\text{as}}\text{NO}_2$ and νOH (Hydrogen bonded) respectively. The absence of νOH mode at ~ 3380 and appearance of a medium band at $\sim 1565\text{ cm}^{-1}$ in both the complexes suggests the coordination of picrate ion in a monodentate fashion. The appearance of a new medium intensity band at $\sim 1250\text{-}1270\text{ cm}^{-1}$ in the complexes attributed to $\nu(\text{C-O})$ because of coordination of the phenolic oxygen [10] after deprotonation.

In case of metal (II) picrate complexes with Phenanthroline two significant bands are observed at about 1610 and 1040 cm^{-1} . These are assigned to ring $\nu(\text{C=N})$ and ring breathing modes respectively. This suggests the bidentate (N-N) coordination of Phenanthroline in the complex. The IR spectrum of 1,2-Diaminobenzene mixed ligand picrate complex

In case of 1,2-diaminobenzene complexes with metal picrate, the C-N stretching vibrations observed in the ligand shifted by $15\text{-}25\text{ cm}^{-1}$ due to the coordination of the nitrogen atom to the metal ions [11,12]. The complexes also show bands corresponding to phenyl ring vibrations [11]. The I.R. spectra of the complexes of 1,2-diaminobenzene gave bands in the region $1428\text{-}1528$, $1080\text{-}1120$ and $740\text{-}785\text{ cm}^{-1}$, which may be assigned to bands characteristic of phenyl group [13] and the bands observed in the region $2965\text{-}2990\text{ cm}^{-1}$ may be due to aromatic C-H group. In all the picrate complexes, new bands observed in the far infrared region of the complexes at $510\text{-}550$, $410\text{-}439$ and $340\text{-}375\text{ cm}^{-1}$, are probably due to the formation of M-O, M-N, and M-O-C bonds respectively [14] Table-2.

The diffused reflectance spectra of Mn(II) mixed ligand picrate complex exhibited three bands in the regions 15000-15150, 18200-19200 and 24500-25600 cm^{-1} , due to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G), (ν_1) ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (G) (ν_2) and ${}^6A_{1g} \rightarrow {}^4A_{1g}$ (G) (ν_3) respectively in an octahedral geometry[15,16]. In Co(II) mixed ligand picrate complex three bands in the regions 9010-9250 cm^{-1} , 18300-18500 cm^{-1} , 20350-20500 cm^{-1} , due to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (F) (ν_1), ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (F) (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}$ (P) (ν_3), respectively in an octahedral geometry.

TABLE-1 CHARACTERIZATION OF METAL(II) MIXED LIGAND COMPLEXES

S.N.	COMPLEX	M% calc (found)	N% calc (found)	C% calc (found)	H% calc (found)	μ_{eff} B.M.
1-	[Mn(Pic) ₂ (Phen) ₂]	6.30 (6.43)	16.07 (16.19)	49.61 (49.52)	2.31 (2.39)	5.86
2-	[Mn(Pic) ₂ (1,2-DB) ₂]	7.55 (7.81)	19.25 (19.32)	39.62 (39.68)	2.77 (2.71)	5.82
3-	[Co(Pic) ₂ (Phen) ₂]	6.73 (6.82)	15.99 (16.09)	49.38 (49.44)	2.30 (2.41)	4.98
4-	[Co(Pic) ₂ (1,2-DB) ₂]	8.05 (7.98)	19.15 (19.38)	39.41 (39.48)	2.75 (2.81)	4.80

TABLE-2 IR SPECTRAL BANDS(cm^{-1}) OF THE COMPLEXES

S.N.	COMPLEX	$\nu(\text{NH}_2)/\text{NH}$ stretching	$\nu(\text{C-N})+$ $\nu(\text{C-O})$	$\nu(\text{C-H})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{M-O-C})$	$\nu(\text{C=N})$ + $\nu(\text{C=C})$	$\nu(\text{NO}_2)$
1-	$[\text{Mn}(\text{Pic})_2(\text{Phen})_2]$	-	1296m	779m	431w	550w	374w	1625 s,br	1492m
2-	$[\text{Mn}(\text{Pic})_2(1,2\text{-DB})_2]$	3260s,br	1140s	1670s	430w	510m	340w	-	1495s
3-	$[\text{Co}(\text{Pic})_2(\text{Phen})_2]$	-	1268s,br	777m 724s	439w	529w	373w	1607s,b r	1498s
4-	$[\text{Co}(\text{Pic})_2(1,2\text{-DB})_2]$	3240m,br	1180s	-	410w	540m 520m	375w	-	1500w 1480s

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