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Synthesis and Characterization of complexes of Chromium (III), Manganese (II), Iron (III) & Cobalt (III) metals with Schiff's base β – Hydroxy naphthyl methanal thiosemicarbazone ligand

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Abstract

The synthesis, properties, elemental analysis magnetic susceptibility, electrical conductivity, electronic measurements and IR spectral studies of the ligand β – hydroxy naphthyl methanal thiosemicarbazone and its complexes with Chromium (III), Manganese (II), Iron (III) & Cobalt (III) have been discussed. On the basis of these observations, probable structures of all the metal complexes have been assigned.

Key words : Synthesis, Elemental analsysis, β – hydroxy naphthyl methanal thio- semicarbazone, Cr(III), Mn(II), Fe(III), Co(III), complex compound, IR spectra, Electronic spectra.

Introduction

Schiff's bases are organic compounds having an azomethine group (>C=N). Various studies[1-2] have shown that >C = N group has considerable biological importance[3-5]. Schiff base can be considered as useful chelating agents when a suitable functional group such as – OH, - SH, - NH_2 etc are present sufficiently close to azomethine group Metal complexes with Schiff bases have occupied an important place in the development of coordination chemistry[6 –10] due to its interesting structural features and important applications.

Experimental

Preparation of ligand : β – hydroxy naphthaldehyde (5.2 g) was dissolved in methanol and treated with an aqueous solution of thiosemicarbazide hydrochloride (3.85 gm) BDH, Anala R). The mixture was stirred well and refluxed for half an hour on a water bath. On cooling the mixture a white crystals separate out. The crude white product was recrystallised from alcohol as colourless needles (M.P. = 492 K). The pure and dried compound was chemically analyzed. The compound is slightly soluble in methanol and ethanol, highly soluble in DMF but insoluble in water and acetone.

Preparation of complexes :

Aqueous solution of chromium (III) chloride, Iron (III) chloride, cobalt (III) chloride and Manganese(II) chloride was mixed with the solution of ligand β – hydroxy naphthyl methanal thiosemicarbazide in DMF. Sodium acetate is mixed and the whole solution was refluxed for two hours and left to stand for one hour. The coloured crystal separated. These were filtered, washed with cold water, dried in air. The pure complexes were chemically analysed.

Chromium, Iron & Cobalt complexes are insoluble in water, methanol and ethanol but soluble in DMF whereas Manganese (II) complex is insoluble in water, slightly soluble in ethanol but fairly soluble in DMF.

PROPERTIES OF COMPLEXES

(i) Thermal stability :

Cr (III) and Iron (III) complex decompose below 480K , Co(III) complex at 508 K where as Mn(II) complex decomposes when heated above 573 K.

(ii) Electrical Conductivity :

The molar conductance values of the complexes in 10^{-3} M solution in DMF were found to be 89.3, 90.2, and 98.6 ohm^{-1} cm^{2} mol^{-1} for Cr(III), Fe(III) and Co(III) complexes respectively indicating 1:1 electrolytic nature. Whereas lower value (20.70 Ohm^{-1} cm^{2} mol^{-1}) for Mn(II) complex show its non electrolytic nature. Magnetic susceptibility value of Cr(III) (3.82 BM), Fe(III) (5.96 BM), Co(III) (0BM) & Mn(II) (1.10 BM) indicates presence of 3, 5, 0 and one unpaired electron respectively.

Result and Discussion

(a) Probable structure of ligand :

The interpretation of I.R. spectra is quite complicated due to the presence of various similar groups and hence many absorption bands. However, comparision of the spectral bands of the ligand (HN-TS), with those of its complexes gives some important informations regarding the nature of the ligand as well as the co – ordination sites through which metal ion is co - ordinated with the ligand.

The band at 3210 cm^{-1} in the ligand assignable to phenolic O - H (hydrogen bonded) stretching frequency disappears in the Co (III), Cr (III) and Fe (III) complexes, showing deprotonation of phenolic proton. The ligand also shows strong band at 1270 cm^{-1} which may be attributed to the phenolic C – O vibration. A shift of this band to higher frequency (~1310 cm^{-1}) in the complexes indicate chelation of the ligand to metal ion through phenolic oxygen. The presence of a band near 3250 cm^{-1} in Mn (II) complex may be due to O - H of co – ordinated water molecule[9]. This is further justified by the presence of a band around 1610 cm^{-1} as deformation band of water molecule.

The sharp band at 1590 cm^{-1} in the free ligand due to C=N of Schiff's base residue shifts to the lower frequency at (~ 1565 cm^{-1}) in the complexes showing co-ordination through the nitrogen atom[11-12]. The lowering may be very small in some cases. The ligand band at 1165 cm^{-1} may be assigned to n C = S group which shows downward shifting in metal complexes, indicating participation of this group in co – ordination.

The absorption band at 3390 cm^{-1} due to ν N – H group in the free ligand remains unaltered in the complexes, indicating non – participation of this group in coordination. Thus, we come to a conclusion that the ligand, β – Hydroxy – Naphthyl methanal thiosemicarbazone (HN – TS) behaves as a tridentate ligand for the metal ions, coordinating through phenolic oxygen (C – O),(i); nitrogen atom of C = N,(ii), of a azomethyne group and ketonic Sulphur of C = S, (III), of enolic group. Similar kind of situation has been reported by S.K. Thampy[13].

This ligand is monoprotonic in all the cases. It has been observed that in these cases a band present at 1165 cm^{-1} in the free ligand disappears perhaps due to deprotonation of the C = S (enolic) proton on the basis of these observations structure of ligand may be presented as

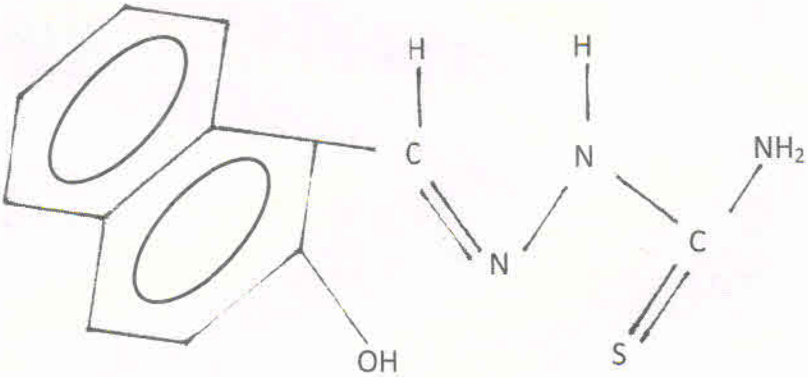

Fig. 1. Structure of β- hydroxy naphthyl methanal thio semicarbazone

(b) Probable structure of complexes :

(i) Generally Cr(III) complexes are hexa co-ordinate[14] the reflectance spectra of Cr(III) complex shows two bands at 17490 cm^{-1} and 22750 cm^{-1} which assigned to $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}$ (P) transition octahedral stereochemistry. The higher energy spin allowed transition band $^4A_{2g}(F) \rightarrow {}^4T_{1g}(p)$ and usually occurs above 3000 cm^{-1} which would have been obscured because of ligand absorption in this region[19].

(ii) The reflectance spectra of Fe(III) complex show three bands which may be assigned to $^6A_{1g} \rightarrow {}^6T_{1g}$ (14710 cm^{-1}), $^6A_{1g} \rightarrow {}^6T_{2g}$ (19040 cm^{-1}) and $^6A^{1g}$ (F) $\rightarrow$ ^{6}Eg 25000 cm^{-1} transition assuring ideal octahedral system[20].

The magnetic moment (5.9 BM) also supports outer orbital octahedral geometry[21] for this complex.

(iii) Generally Cobalt (III) complexes are octahedral the two absorption bands found in the complex are assigned to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ electronic absorption data suggests octahedral geometry for these complexes.

Magnetic moment measurements also suggests octahedral geometry for its complex.

(iv) The Mn(II) complex exhibit three bands at 11850, 16460 and 23810 cm^{-1} indicating hexa co-coordinated structure.[14-18]

The magnetic moment value of this complex (1.08 BM) looks subnormal. It may be due to metal – metal interaction[21]. This suggests that complex may be binuclear.

Table 1. Elemental analysis data of ligand and metal complex

Compounds	Colour	Elemental analysis% observed (calculated)					
		M	C	H	N	S	Cl
HNTS	Colourless		57.37 (58.75)	5.28 (4.49)	16.72 (17.13)	12.64 (13.10)	
[Cr(HNTS)$_2$]Cl	Yellowish	8.73 (8.72)	49.06 (49.07)	4.82 (3.47)	13.94 (14.59)	10.35 (11.15)	5.72 (6.17)
[Mn(HNTS)$_2$	Yellow	12.42 (10.12)	54.04 (53.03)	3.78 (3.68)	15.32 (15.46)	11.34 (11.78)	
[Fe(HNTS)$_2$Cl	Green	8.73 (9.63)	48.90 (49.70)	3.46 (3.45)	14.48 (14.49)	10.30 (11.09)	5.92 (6.12)
[Co(HNTS)$_2$Cl	Green	9.30 (10.11)	48.74 (49.43)	4.78 (3.43)	13.26 (14.42)	10.18 (11.02)	5.92 (6.09)

Table 2. Decomposition temperature, Electrical conductivity and magnetic moment value of complexes

Complex	Decomposition Temperature (K)	Electrical conductivity (S cm^2 mol^{-1})	Magnetic moment (μ_{ef}) (Bohr magneton)
[Cr(HNTS)$_2$]Cl	477	89.3	3.82
[Mn(HNTS)$_2$	570	20.70	1.10
[Fe(HNTS)$_2$Cl	478	90.2	5.96
[Co(HNTS)$_2$Cl	512	98.76	0.0

Table 3. IR spectral bands of ligand and metal complexes in cm^{-1} assignment of position of absorption bands

HNTS	Cr(III) [Cr(HNTS)$_2$]Cl	Mn(HNTS) [Mn(HNTS)$_2$	Fe(III) [Fe(HNTS)$_2$Cl	Co(III) [Co(HNTS)$_2$Cl	
3395	3395	3395	3395	3395	N-H Stretehing
3215					O – H (Hydrogen bonded)
3100	3100	3100	3100	3100	C – H Stretching
1595	1560	1570	1585	1580	C=N Stretching
1415	1415	1415	1415	1415	N – H bending
1275	1285	1295	1305	1290	C-O (phenolic)
1200	1130		1200		Skeletal in plane vibration
1175	1070		1170		
1160	1040	1145	1150	1145	C=S Stretching
1130	1130	1130			Characteristic vibrations of naphthalenening
1070	1070	1070			
1040	1040	1040			
935			935		C – N bending
835	835	835			
740	740	740			
780			780		Characteristic vibration of 1, 2- disubstituted naphthalene ring
	540	510	540	550	M – N bond
	510	470	470	500	M – O bond
	270	270	370	350	M – S bond
		3250			O – H stretching of water molecule
		1615			Deformation band of water molecule.

On the basis of facts discussed above structure of these complexes can be assigned as given below:

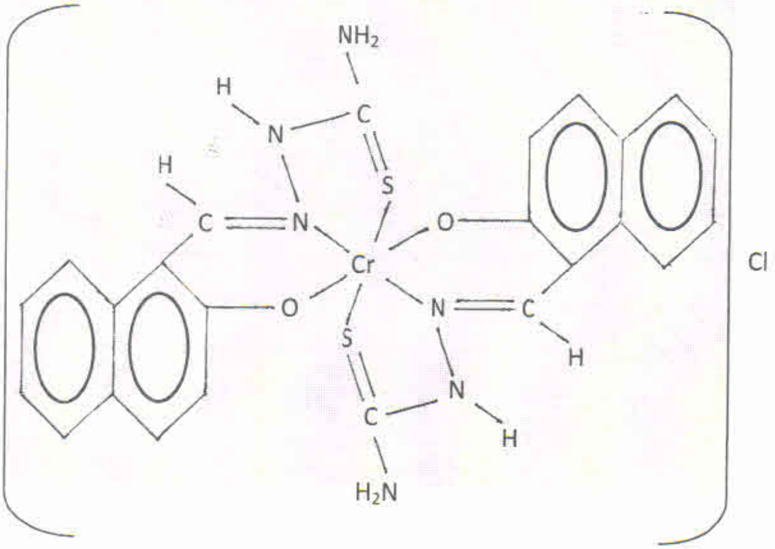

Fig. 2. Bis (β – Hydroxy naphthyl methanal thiosemicarbazone) Cr (III) chloride

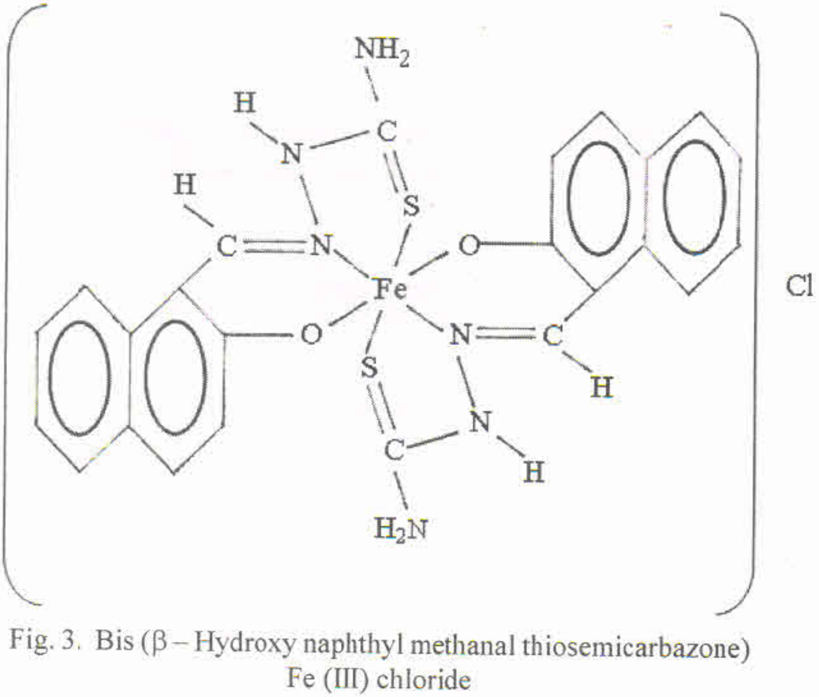

Fig. 3. Bis (β – Hydroxy naphthyl methanal thiosemicarbazone) Fe (III) chloride

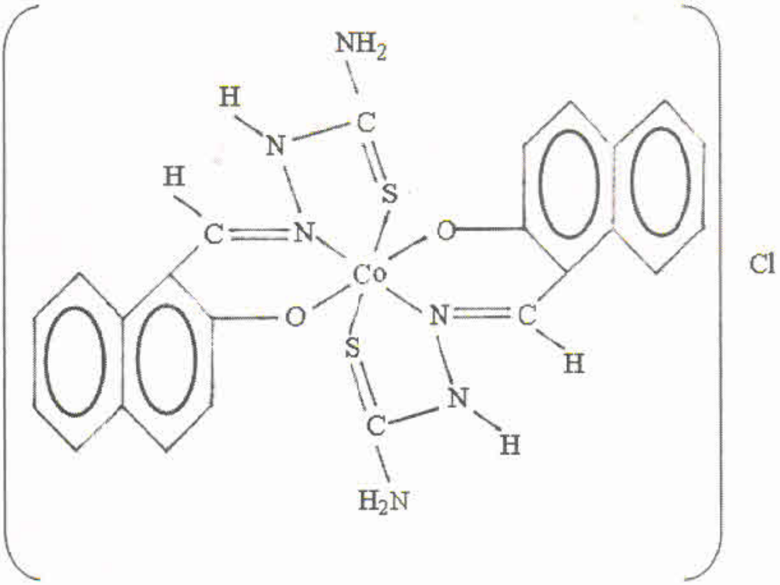

Fig. 4. Bis (β – Hydroxy naphthyl methanal thiosemicarbazone) Co (III) chloride

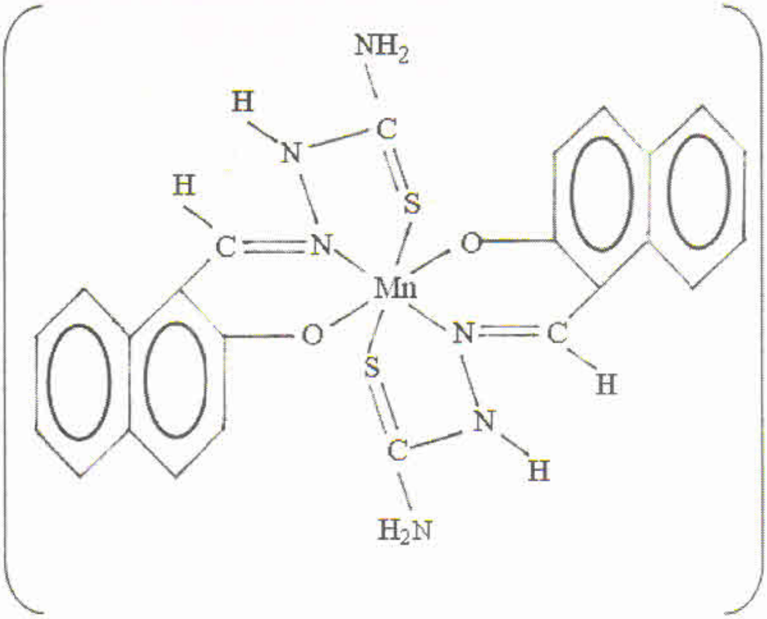

Fig. 5. Bis (β– Hydroxy naphthyl methanal thiosemicarbazone) Mn (II)

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