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Synthesis and Characterization of Complexes of 2-Hydroxy-3-nitro acetophenyl thiosemicarbazone with Some 3*d* Series Transition Metals

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The preparation, properties, elemental analysis, magnetic susceptibility, electrical conductivity, electronic and IR spectral properties of the ligand 2-hydroxy-3-nitro acetophenyl thiosemicarbazone and its complexes with chromium(III), iron(III), copper(II) and manganese(II) have been discussed. On the basis of these observations, probable structures of all the metal complexes have been assigned.

Key Words: Synthesis, Structure, Complex compound, 2-Hydroxy-3-nitro acetophenyl thiosemicarbazones, Cr(III), Fe(III), Cu(II), Mn(II), Elemental analysis, IR spectra, Electronic spectra.

INTRODUCTION

Due to interesting structural features and important applications metal complexes with Schiff bases have occupied an important place in the development of coordination chemistry[1-5]. Schiff bases are organic compounds having an azomethine group (>C=N-) and various studies[6,7] have shown that >C=N- group has considerable biological importance[8-10]. Schiff base can be considered as useful chelating agents when a suitable functional group such as -OH, -SH, *etc.* is present sufficiently close to azomethine group.

EXPERIMENTAL

Preparation of 2-hydroxy-3-nitro acetophenyl thiosemicarbazone: Ligand was prepared when 2-hydroxy-3-nitro acetophenone (5 g) was dissolved in methanol and was treated with a solution of thiosemicarbazide hydrochloride (3.9 g, BDH, AnalaR) in water. The mixture was stirred well and refluxed for 0.5 h on a water-bath and cooled when pale yellow crystals separated. The crude white product was crystallized from alcohol as colourless needles (m.p. 219 ºC).

This ligand was slightly soluble in methanol and ethanol. However, it was highly soluble in dimethyl formamide (DMF) but was insoluble in water and acetone.

Preparation of complexes: Aqueous solution of chromium(III) chloride and iron(III) chloride was mixed with the solution of the ligand in DMF separately and both the mixture were refluxed in the presence of sodium acetate for *ca.* 2 h, as well as 0.5 h, respectively and were cooled. The separated coloured solids were filtered and washed with ethanol and water. The ammonical solution (pH 9) of copper(II) chloride and manganese(II) chloride, both were treated with DMF solution of the ligand in 1:1 ratio separately and were refluxed for 2 h and left to stand for 1 h. The precipitated coloured solids were filtered and washed with cold water and were dried in air.

The Cr(III) and Fe(III) complexes were insoluble in water, methanol and ethanol but were soluble in DMF whereas the Cu(II) and Mn(II) were insoluble in water but dissolved in DMF. The Cr(III) and Fe(III) complexes decompose when heated to about and above 200 ºC where as the Cu(II) and Mn(II) complexes decompose to their metallic oxide when heated to above 220 ºC as well as 300 ºC, respectively.

The molar conductance value of Cr(III) and Fe(III) complexes in 10^{-3} M solution of DMF were found to be 89.2 and 90.3 ohm^{-1} cm^2 mol^{-1}, respectively indicating their 1:1 electrolytic nature where as molar conductance of Cu(II) complex in same solvent was 20.9 ohm^{-1} cm^2 mol^{-1} which indicated its non-electrolyte nature.

The μ_{eff} value of Cr(III), Fe(III), Cu(III) and Mn(II) complexes were determined by Gouy's balance and found to be 3.8, 5.9, 1.8 and 1.08 BM, respectively.

The reflectance spectra of Cr(III) complex show bands at 17490 and 22750 cm^{-1} which are assigned in $^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$ and $^4A_{2g}(F)\rightarrow{}^4T_{1g}(P)$ transition where as Fe(III) complex gives three bands at 14710, 19040 and 25000 cm^{-1} which corresponds to $^6A_{1g}\rightarrow{}^4T_{1g}$, $^6A_{1g}\rightarrow{}^4T_{2g}$ and $^6A_{1g}\rightarrow{}^4E_g$ transitions, respectively. A broad band was shown by Cu(II) complex at 19980 cm^{-1} which may be assigned to the envelop of $^2B_{1g}\rightarrow{}^2A_{1g}$, $^2B_{2g}$ and ^2E_g transitions whereas the Mn(II) complex exhibit bands at 11850, 16460 and 23810 cm^{-1}.

RESULTS AND DISCUSSION

The interpretation of IR spectra is quite complicated due to the presence of various similar groups and hence many absorption bands. However, comparing the spectral bands of the ligand (HNAPTS) with those of its complexes gives important informations regarding the nature of the ligand as well as the coordination sites through which metal ion is co-ordinated with the ligand.

The band at 3200 cm^{-1} in the ligand assignable to phenolic O-H (hydrogen bonded) stretching frequency[11] disappears in the Cr(III) and Fe(III) complexes, showing deprotonation of phenolic proton. The ligand also shows strong band at 1265 cm^{-1} which may be attributed to the phenolic C-O vibration. A shift of this band to higher frequency (*ca.* 1300 cm^{-1}) in the complexes indicates chelation of the ligand to metal ion through phenolic oxygen. The presence of a band near 3250 cm^{-1} in Cu(II) and Mn(II) complexes may be due to O-H of coordinated water molecule. This is further justified by the presence of a band around 1600 cm^{-1} as deformation band of water molecule (Table-2).

The sharp band at 1585 cm^{-1} in the free ligand due to ν(C=N) of Schiff base residue shifts to the frequency at (*ca.* 1560 cm^{-1}) in the complexes showing coordination through the nitrogen atom[12-18]. The lowering may be very small in some

TABLE-1
ELEMENTAL ANALYSIS OF LIGAND AND ITS COMPLEXES

Compounds		Elemental analysis (%): Found (Calcd.)					
		C	H	N	S	Cl	M
Ligand	($C_9H_{10}N_4O_3S$) (HNAPTS)	– (–)	36.98 (38.28)	4.06 (3.54)	30.04 (29.76)	10.73 (11.38)	– (–)
Complexes	[Cr(HNAPTS)$_2$]Cl	8.03 (8.76)	35.27 (36.38)	3.88 (3.03)	18.12 (18.86)	9.17 (10.81)	5.02 (5.99)
	[Fe(HNAPTS)$_2$]Cl	8.76 (9.34)	35.09 (36.14)	4.01 (3.01)	17.67 (18.74)	9.31 (10.77)	5.11 (5.94)
	Cu(HNAPTS)NH$_3$	17.96 (19.03)	31.33 (32.37)	4.42 (3.60)	19.93 (20.98)	8.91 (9.62)	– (–)
	Mn(HNAPTS)Cl·2H$_2$O	13.21 (14.47)	27.26 (28.46)	4.55 (3.46)	13.62 (14.76)	7.69 (8.47)	8.08 (9.35)

TABLE-2
IR SPECTRAL BANDS (cm^{-1}) OF LIGAND AND ITS COMPLEXES

Absorption band position (cm^{-1})					Assignments[16]
Ligand	Complexes				
HNAAPTS	**A**	**B**	**C**	**E**	
3385	3385	3385	3385	3385	N-H stretching
–	–	–	–	3250	O-H stretching of water molecule
3200	–	–	–	–	O-H (Hydrogen bonded)
3100	3100	3100	3100	3100	C-H stretching
–	–	–	–	1600	Deformation bond of water molecule
1585	1560	1575	1585	1570	C=N stretching
1400	1400	1400	–	–	N–H bending
1390	1390	1390	1390	1390	C–N stretching
1265	1275	1295	1280	1285	C–O (Phenolic)
1200	–	1200	1200	–	Skeletal in plane vibration
1170	–	1170	1170	–	
1160	1140	1150	–	1135	C=S stretching
1130	1130	–	–	1130	Characteristic vibrations of 1,2,3-tri substituted benzene ring
1070	1070	–	–	1070	
1040	1040	–	–	1040	
925-915	–	915-925	915-925	–	C–N bending
825	825	–	825	825	Skeletal vibrations
740	740	–	740	740	
780	–	780	780	–	Vibrations of 1,2,3- tri substituted benzene ring
630	–	630	630	–	
–	540	540	530	510	M–N bond
–	500	470	490	470	M–O bond
–	340	370	280	270	M–S bond

A = [Cr(HNAPTS)$_2$]Cl, **B** = [Fe(HNAPTS)$_2$]Cl,
C = Cu(HNAPTS)NH$_3$, **D** = Mn(HNAPTS)Cl·2H$_2$O

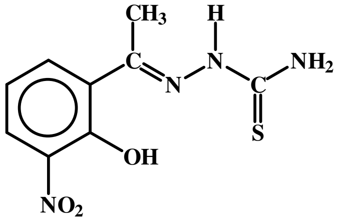
cases. The ligand band at 1160 cm^{-1} may be assigned to ν(C=S) group and shows downward shifting in metal complexes, indicating participation of this group in coordination. The absorption band at 3385 cm^{-1} due to ν(N-H) group in the free ligand remains unaltered in the complexes, indicating non-participation of this group in coordination. A band present at 1390 cm^{-1} in the IR spectra of the ligand is assigned[19] to ν(C-N) group due to nitro group. This band remains unchanged in all the complexes, suggesting non-participation of nitro group in coordination.

Thus, it may be concluded that the ligand 2-hydroxy-3-nitro acetophenyl thiosemicarbazone (HNAPTS) behaves as a tridentate ligand for the metal ions, coordinating through (i) phenolic oxygen (C-O), (ii); nitrogen atom of (C=N), (iii) of a azomethine group and ketonic sulphur of C=S, of enolic group. Similar kind of situation has been reported by Thampy[20].

This ligand is monoprotonic in all the case except Cu(II) at higher pH 9. It has been observed that in this case a band present at 1160 cm^{-1} in the free ligand disappears, perhaps due to deprotonation of the C=S (enolic) proton.

It is worth mentioning here that nitro group does not take part in co-ordination. Syamal and Gupta[21] have prepared a number of complexes with Schiff bases derived from substituted salicylaldehyde and reported non-participation of the substituents in co-ordination. However, stability of the complex is certainly influenced by the presence of the substituents.

Taking all the facts in account following structure has been suggested for the ligand:



Probable structures of complexes: Comparing the spectral bands of the ligand (HNAPTS) with those of its Cr(III), Fe(III), Cu(II) and Mn(II) complexes shows following characteristics:

Electronic spectra: Generally, Cr(III) complexes are hexa coordinate[22]. In the present investigation the reflectance spectra of Cr(III) complex shows bands at 17290 and 22730 cm^{-1} which are assigned to $^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$ and $^4A_{2g}(F)\rightarrow{}^4T_{1g}(P)$ transitions in octahedral stereochemistry[23]. The higher energy spin allowed transition band $^4A_{2g}(F)\rightarrow{}^4T_{1g}(P)$, usually occurs above 3000 cm^{-1} which would have been obscured because of ligand absorption in this region[24].

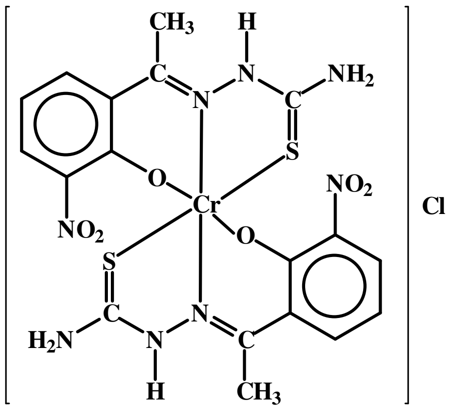
Where all the reflectance spectra of Fe(III) complex show three bands which may be assigned to $^6A_{1g}\rightarrow{}^4T_{1g}$, (14710 cm^{-1}), $^6A_{1g}\rightarrow{}^4T_{2g}$ (19040 cm^{-1}) and $^6A_{1g}\rightarrow{}^4E_g$ (25000 cm^{-1}) transitions assuming idealized octahedral symmetry[25].

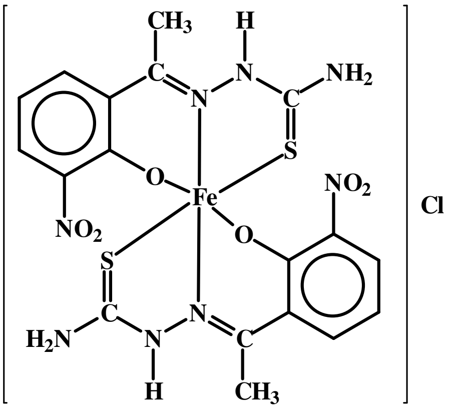
The Cu(II) complex show a band at 2000 cm^{-1} in it electronic spectra, which suggests its square planar geometry, assigned to envelop of $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{2g}$ and ^2E_g transitions[26], whereas the reflectance spectra of Mn(II) complex exhibit bands at 11910, 16660 and 23810 cm^{-1} indicating hexa coordinated structure.

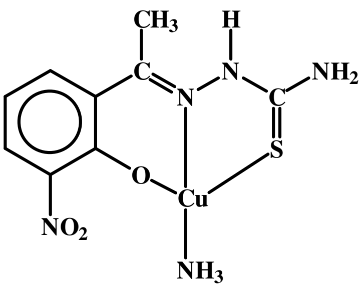
The μ_{eff} values of Cr(III) and Fe(III) complexes fall in the range of 3.8 and 5.9 BM, respectively which supports octahedral stereochemistry[27,28] for these complexes. The μ_{eff} values of Cu(II) complexes corresponds well with the presence of one unpaired electron and gives specific information about its stereochemistry, where as the magnetic moment value of Mn(II) complex (1.08 BM) looks subnormal. It may be due to metal-metal interaction[29]. This suggest that the complex may be binuclear. The presence of coordinated water molecule have been ascertained by IR spectral data.

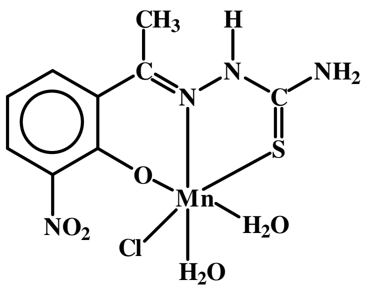
The molar conductance value 89.2 confirm the 1:1 electrolytic nature of Cr(III) and Fe(III) complexes where as the molar conductance value of Cu(II) and Mn(II) complexes suggests non-electrolytic nature of these complexes while IR band near 650 cm^{-1} in Cu(II) complex suggests M-NH_3 bonding[30,31] in it.

On the basis of all these facts the structures of these complexes can be assigned as:









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