



Structural and Biological Studies of Complexes Containing Metals With Micronutrient Properties

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ABSTRACT

The complexes of some micro-nutrient metals [Fe(III), Mn(III) and Mn(II)] were prepared with thiosemicarbazide, 4-aminoantipyrine, 2-hydroxy5-methylacetophenone and 2-hydroxy5-chloro acetophenone, having general formula $[\text{Fe}(\text{C}_9\text{H}_{10}\text{N}_3\text{SCl})_2 \cdot 2\text{H}_2\text{O}]3\text{Cl}$, $[\text{Mn}(\text{C}_9\text{H}_{10}\text{N}_3\text{SCl})_2 \cdot \text{H}_2\text{O}]3\text{Cl}$, $[\text{Fe}(\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_2)_2] \cdot \text{Cl}$, $[\text{Mn}(\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_2)_2] \cdot \text{Cl}$ and $[\text{Mn}(\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_2)_2] \cdot \text{Cl}$. These adducts have been characterized on the basis of elemental analyses, molar conductance, infrared, visible spectra, magnetic susceptibility measurements and TGA. The complexes prepared were screened for biological studies at IVRI Bareilly. The ligand behaves in bidentate manner. The complexes of Fe(III), Mn(III) and Mn(II) of 5-methyl-2-hydroxyacetophenoneantipyrine and Fe(III), Mn(II) of 2-hydroxy5-chloroacetophenonethiosemicarbazone are paramagnetic in character and have octahedral geometry. The complexes of Mn(III) of 5-methyl-2-hydroxy5-acetophenonethiosemicarbazone is also paramagnetic in nature and has square pyramidal geometry.

Key words: Square pyramidal geometry, Octahedral geometry, Molar conductance.

INTRODUCTION

Some of the transition metals act as micronutrient and perform various biological functions in plants and animal kingdom. Micronutrients are elements which are essential for plant growth, but are required in much smaller amounts than those of the primary nutrients; nitrogen, phosphorus and potassium. The micronutrients are Boron(B), Copper(Cu), Iron(Fe), Manganese(Mn), Molybdenum(Mo), Zinc(Zn) and Chloride(Cl)^{1,2}. The coordination chemistry has developed into a full fledged branch of chemistry during 19th century. The coordination compounds

result from the interaction of metal ion with the ligand. A Schiff base is synthesized by condensation of carbonyl compounds and amino compounds. Schiff bases are an important class of ligands in coordination chemistry and their complexing ability containing different donor atoms is widely reported³⁻⁵. The chemistry of Transition metal complexes containing heterocyclic donor continues to be on account of their biological importance⁶⁻⁸. Schiff base ligands have received more attention mainly because of their wide application of in the field of catalysis and due to their antimicrobial⁹, antituberculosis¹⁰ and antitumour activity¹¹.

The Schiff bases contain azomethine linkage which is obtained by the condensation of amino and carbonyl compounds. The amino compounds to be used were 4-amino antipyrine and thiosemicarbazide, which are biologically potent. Hence the complexes of biologically active ligands are formed with the Micro-nutrient metals(FeIII, MnIII and MnII) .

MATERIALS AND METHODS

The carbonyl compounds and the compounds of amino group used for the preparation of Schiff bases were of AR grade or equivalent purity. The carbonyl compound 5-chloro2-hydroxyacetophenone and 5-methyl2-hydroxyacetophenone are used while amino compounds Thiosemicarbazide and 4-Amino antipyrine were used for the preparation of Schiff base. The metal salts used were FeCl₃, MnCl₂ and MnCl₃ (Glaxo). Other chemicals like ethanol, methanol (Glaxo), DMF (Rankem), DMSO (Fluka) etc were of highest purity and used as such.

Infrared spectra and elemental analyses were carried out at CDRI (Lucknow). The magnetic susceptibility was measured by GOUY method. CuSO₄ .5H₂O was used as calibrant. U.V-visible

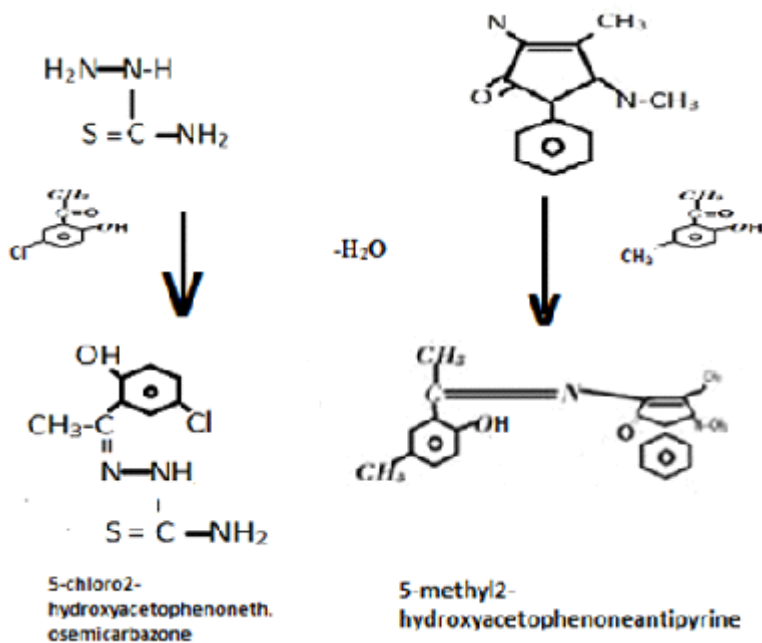
spectra were recorded with the help of Beckmans-DU at Chemistry Deptt. Bareilly College Bareilly. The conductivity measurement was carried out at room temperature and 10⁻³M dilution using conductivity bridge model 910. The thermo gravimetric analysis was carried out at G.N.D. University Amritsar. Anti bacterial and anti fungal activities were carried out at IVRI Izzat Nagar Bareilly.

EXPERIMENTAL

Preparation of ligands

The ligands (Schiff bases) were prepared by the condensation of Carbonyl compounds and compounds containing amino group. 0.91gm of Thiosemicarbazide was dissolved in Ethanol and refluxed on water bath for half an hour. Then 1.70 gm 5-methyl 2- hydroxy acetophenone was added to it and refluxed for about five hours.

Similarly 1.70 gm of 5-methyl 2-hydroxyacetophenone was added in 2.06 gm of 4-aminoantipyrine which is dissolved in ethanol and refluxed for about 5 to 6 hours. The crystals of ligands so obtained were purified by recrystallization. The purity of crystals were checked by TLC and melting point. The ligands were characterized by elemental analyses, electronic and i.r spectra.



Preparation of complexes

All the metal complexes were synthesized by adding respective metal salts solution as Ferric chloride(Rankem), $MnCl_3$ (Fluka) and $MnCl_2$ (BDH) dropwise to the solution of the ligands (5-Chloro 2-hydroxy acetophenone thiosemicarbazone and 5-methyl2-hydroxyacetophenoneantipyrine) prepared. The precipitate obtained was filtered and washed with suitable solvents (DMSO and DMF) and dried in vacuum desiccator over fused P_4O_{10} .

RESULTS AND DISCUSSION

The analytical data is indicative of 1:2 metal-ligand stoichiometry of the complexes. On the basis of the molecular formula of the chelate comes out to be $[Fe(C_9H_{10}N_3SCl)_2 \cdot 2H_2O]3Cl$, $[Mn(C_9H_{10}N_3SCl)_2 \cdot H_2O]3Cl$, and $[Fe(C_{20}H_{20}N_3O_2)_2]Cl$; $[Mn(C_{20}H_{20}N_3O_2)_2]Cl$ for 5-Chloro 2-hydroxy acetophenone thiosemi-

carbazone and 5-methyl 2-hydroxyacetophenone-antipyrine respectively. The vast difference in the melting points of the ligands and their corresponding complexes suggested the formation of the adduct.

The values of molar conductance in DMF and DMSO at 10^{-3} M dilution ($25^\circ C$) indicated 1:3 electrolytic nature of the complexes of Fe(III) and Mn(III) in 5-chloro2-hydroxyacetophenone-thiosemicarbazone chloride complexes. While 1:1 electrolytic nature is found in Mn(III) and Fe(III) complexes of 5-methyl2-hydroxyacetophenoneantipyrine chloride complexes. The Mn(II) complex of respective ligand shows non electrolytic nature.

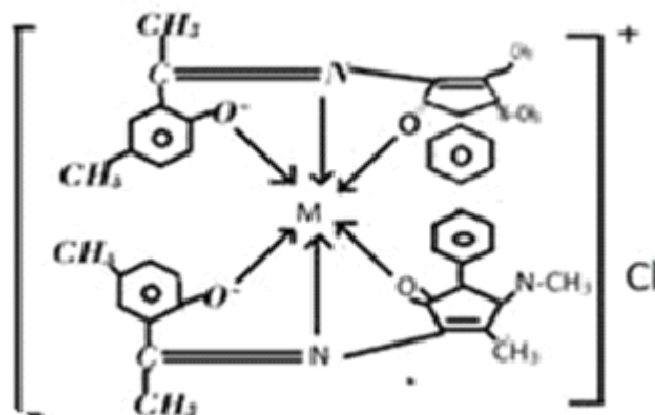
The magnetic susceptibility was measured by Gouy method and the spin only value of the magnetic moments were calculated from this

Table 1:

S N	Name of the complexes	Elemental analyses (%calc. and found)				
		C%	H%	N%	S%	M%
1.	5-methyl2-hydroxyacetophantipyrine.	63.4	5.27	11.06	—	7.37
	Fe(III)chloridecomplex	63.9	5.4	11.14	—	7.81
2.	5-methyl2-hydroxyacetophantipyrine.	63.3	5.27	11.08	—	7.25
	Mn(III)chloridecomplex	65.2	5.65	11.16	—	7.42
3.	5-meth2-hydracetoph.antipyrine	66.3	5.53	11.61	—	7.60
	Mn(II)complex	67.2	5.82	11.96	—	7.74
4.	5-chloro2-hydroxyacetophthiosemicarbazone	31.5	3.55	12.28	9.48	7.01
	Fe(III)chloridecomplex	32.1	4.01	12.78	9.62	7.10
5.	5-methyl2-hydr.acetph.thiosemicarbazone	32.5	3.31	12.65	9.63	8.28
	Mn(III)chloridecomplex	32.1	3.99	12.89	9.68	8.30

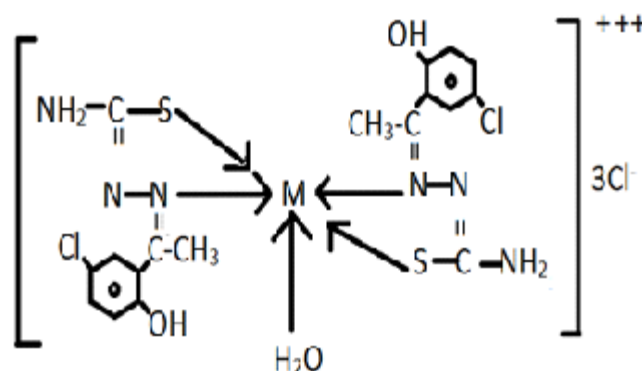
Table 2:

S. No	M.formula & Colour	Important I.R peaks				Melting Point
		C=O	N-NH	C=N	O-H	
1.	$[Fe(C_{20}H_{20}N_3O_2)_2]Cl$ Pale yellow	1625 cm^{-1}	-	1575 cm^{-1}	1270 cm^{-1}	326 $^\circ C$
2.	$[Mn(C_{20}H_{20}N_3O_2)_2]Cl$ Orange yellow	1620 cm^{-1}	-	1570 cm^{-1}	1275 cm^{-1}	332 $^\circ C$
3.	$[Mn(C_{20}H_{20}N_3O_2)_2]$.yellow	1620 cm^{-1}	-	1570 cm^{-1}	1265 cm^{-1}	340 $^\circ C$
4.	$[Fe(C_9H_{10}N_3SCl)_2 \cdot 2H_2O] \cdot 3Cl$ Yellow pink	-	3280 cm^{-1}	1590 cm^{-1}	-	351 $^\circ C$
5.	$[Mn(C_9H_{10}N_3SCl)_2 \cdot H_2O] \cdot 3Cl$ Brownish yellow	-	3275 cm^{-1}	1595 cm^{-1}	-	356 $^\circ C$



Where M= Fe(III),Mn(III) and Mn(II)

- (a) 5-methyl 2-hydroxyacetophenoneantipyrineMn(III)chloride complex
- (b) 5-methyl 2-hydroxyacetophenoneantipyrineMn(II) complex
- (c) 5-methyl 2-hydroxyacetophenoneantipyrineFe(III)chloride complex



Where M= Fe(III),Mn(III)

- (d) 5-chloro2-hydroxyacetophenonethiosemicarbazoneFe(III)chloridcomplex
- (e) 5chloro2-hydroxyacetophenonethiosemicarbazoneMn(III)chloride complex

Scheme 1:

value of magnetic susceptibility which came out to be 5.95 BM in Fe(III)¹², 4.93 BM in Mn(III)¹² and 5.70BM for Mn(II) chloride complexes¹³. Which suggested the paramagnetic nature and octahedral environment around the metal ion Fe(III) and Mn(II) but in Mn(III) the value is in agreement with the reputed value of square pyramidal for Mn⁺³ complexes .

The electronic spectrum of the 2-hydroxy5-chloroacetophenone thiosemicarbazone and 5-methyl2-hydroxyacetophenone Mn(III) complexes

showed bands at 13600, 16500 and 18000cm⁻¹ which may be due to ⁵B₁ → ⁵B₂, ⁵B₁ → ³A₁ and ⁵B₁ → ¹E transitions respectively suggesting square pyramidal geometry of the complex¹⁴.

The electronic spectra of the Fe(III) complexes exhibited three bands at 11225, 21730 and 27770 cm⁻¹ corresponding to ⁶A_{1g} → ⁴T_{1g}, ⁶A_{1g} → ⁴T_{2g} and ⁶A_{1g} → ⁴E_g transitions respectively . The transitions are characteristic of octahedral geometry¹⁵.

The electronic spectra of the Mn(II) complexes exhibit three bands at 17000, 24000 and 28000 cm^{-1} corresponding to the transitions to ${}^6A_{1g} \rightarrow {}^4T_{1g}(v_1)$, ${}^6A_{1g} \rightarrow {}^4T_{1g}(v_2)$ and ${}^6A_{1g} \rightarrow {}^4E_g(v_3)$ ¹⁶.

The comparison of the IR spectra of the ligands and complex 2-hydroxy5-chloroacetophenone thiosemicarbazone revealed bidentate nature of the ligand. IR spectra of the free ligand exhibited characteristic bands at 3280, 1610, 830, 1045 and 1690 cm^{-1} due to $\nu\text{N-NH}$, $\text{VC}=\text{N}$, $\nu\text{C}=\text{S}$, coupled vibrations of $\nu\text{C}=\text{S}$ with $\nu\text{N-N}$ and $-\text{N-C-N-}$ deformation respectively¹⁷. A comparative study of IR spectra of the ligand and its complexes showed that the bands due to $\nu\text{N-H}$ disappeared in the IR spectrum of the complex indicating elimination of the proton from this group. The band due to $\nu\text{C}=\text{S}$ was absent from its position in the IR spectrum of the complex indicating change in character of this moiety on co-ordination of sulphur atom with the metal ion^{18,19}. The bands in the free ligand at 3440 and 3320 cm^{-1} assignable to asymmetric and symmetric mode of $-\text{NH}_2$ group respectively remain at the same position in the IR spectrum of the complex suggesting non involvement of this group in co-ordination²⁰.

The fore said co-ordination pattern is further supported by the appearance of non ligand band in the IR spectrum of the chelate at the range of 435-450 and 250-300 cm^{-1} which may be assigned to $\nu\text{M-O}$ and $\nu\text{M-N}$ vibrations.

The IR spectrum of the complexes exhibited two new bands at the range of 3370-3410 and 870-890 cm^{-1} , which suggested the presence of co-ordinated water molecule. This is also indicated by thermogram which shows the percent weight loss at 150-170 $^\circ\text{C}$ corresponding to the loss of two water molecules and presence of one water molecule in their respective complexes²¹.

The analytical data indicated 1:2 metal-ligand ratio for the 5-methyl2-hydroxyacetophenoneantipyrine Fe(III), Mn(III) and Mn(II) chloride complexes. Hence the M.F formula of the adduct may be written as $[\text{Fe}(\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_2)_2]\text{Cl}$ and $[\text{Mn}(\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_2)_2]\text{Cl}$ and $[\text{Mn}(\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_2)_2]$ respectively. The m.p of the metal complexes was found to be much higher than that of the ligand

which indicated the formation of the adduct. The I.R. spectra of the complexes of 5-methyl2-hydroxyacetophenoneantipyrine on comparison with that of ligands indicated co-ordination through cyclic $\text{C}=\text{O}$, phenolic oxygen and azomethine nitrogen. This indicated monobasic tridentate nature of the ligand. The band due to iOH present at 3500 cm^{-1} which disappeared on complexation and appearance of new band at 1250 to 1270 cm^{-1} which indicated the bonding of ionized phenolic oxygen to the metal ion²². The strong band at 1590 cm^{-1} characteristics of the azomethine group in the free Schiff base has shifted to lower frequency of 1560-1570 cm^{-1} in the complexes indicating that azomethine N is one of the co-coordinating atoms in schiff base. The band observed at 1656 cm^{-1} characteristics of the cyclic carbonyl group of the pyrazolone ring of free Schiff base has shifted to lower frequency in the i.r range of 1610-1620 cm^{-1} in the complexes, indicated the co-ordination of the above group with metal ion²³. This is further supported by the formation of new bands in i.r spectrum of the complex at 460-475 cm^{-1} and 410-415 cm^{-1} . Which are due to $\nu\text{M-O}$ and $\nu\text{M-N}$ bands respectively.

Biological studies

The ligands and the complexes were screened for antibacterial and antifungal activities. The antifungal activity was done against *Macrophomia Phaseolina* and *Fusarium oxysporum* using a procedure using for testing new chemicals²³.

The linear growth of the fungus was recorded by measuring their diameter of the fungus colony after 96 hours and the percentage inhibition was calculated by the formula $100 \times (d_c - d_t) / d_c$ where d_c and d_t are the diameters of fungus colony in the control and the test plates respectively.

Antibacterial activity was tested against *Bacillus substilis* and *Salmonella* species using the paper disc plate method²⁴.

CONCLUSION

On the basis of above discussion octahedral geometry may be proposed for the complexes of Fe(III), Mn(II) and Mn(III) (5-methyl2-

hydroxyacetophenoneantipyrine) and square pyramidal geometry for Mn(III) complex (2-hydroxy-5-chloroacetophenone thiosemicarbazone). All these complexes were found to possess some antibacterial and antifungal activities. Hence the

structures of these complexes are as follows

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