



Synthesis, Characterisation and Structural Studies of Complexes Containing Different Schiff Bases with Mn (III) and Mn (II) Transition Metals

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ABSTRACT

The Schiff bases 5-methyl2-hydroxyacetophenonemorpholine-N-thiohydrazide, 5-methyl2-hydroxyacetophenoneantipyrine 5-chloro2-hydroxyacetophenonemorpholine-N-thiohydrazone has reacted with MnII and MnIII to form co-ordination compounds having general formula $[M(C_{14}H_{19}O_2N_3S)3H_2O]Cl$; $[M(C_{14}H_{19}O_2N_3S).3H_2O]$; $[M(C_{20}H_{20}N_3O_2)_2]Cl$; $[M(C_{20}H_{20}N_3O_2)_2]$; $[M(C_{13}H_{14}O_2N_3SCl).3H_2O]Cl$ and $[M(C_{13}H_{14}O_2N_3SCl).3H_2O]$ respectively. Where M=Mn III and Mn II. The adducts have been characterized on the basis of elemental analyses molar conductance, I.R, visible spectra, magnetic susceptibility measurement and TGA. The ligands behave in dibasic tridentate manner in 5-methyl2-hydroxyacetophenon emorpholine-N-thiohydrazone and 5-chloro2-hydroxyacetophenonemorpholine-N-thiohydrazone. While 5-methyl2hydroxyacetoph enoneantipyrine behaves in monobasic tridentate manner. All these compounds are paramagnetic in nature and have octahedral geometry.

Key words: Coordination compounds, Molar conductance and magnetic susceptibility.

INTRODUCTION

Schiff bases have been used as chelating ligands in the field of co-ordination chemistry and their metal complexes are of great interest for many years. It is well known that N and S atoms play a key role in the co-ordination of metals at the active sites of numerous metallo-biomolecules¹. Schiff base metal complexes have been widely studied because they have industrial, antiungal, antibacterial,

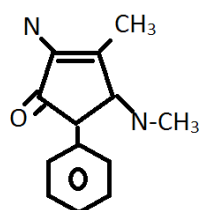
anticancer and herbicidal applications^{2,3}. They serve as models for biologically important species and find applications in biomimetic catalytic reaction. Chelating ligands containing N, O and S donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. It is known that the existence of metal of metal ions bonded to biologically active compounds may enhance their activities^{4,6}. The variety of possible Schiff base

metal complexes with wide choice of ligands and coordination environments, has prompted us to undertake research in this area⁷. The survey of chemical literature has revealed that Schiff bases possess strong ability to form complexes⁸. The Schiff bases have been investigated because of easy synthesis & remarkable versatility towards coordinating ability with transition metals⁹⁻¹³. The Schiff base compounds have received much attention owing to their significant biological activities and medicinal properties such as anti oxidative¹⁴, anti tumor¹⁵, antiviral¹⁶, antineoplastic¹⁷ and antimicrobial activities¹⁸.

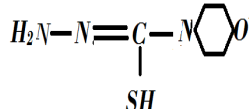
The complexes of different Schiff bases (5- methyl 2- hydroxy acetophenone morpholine-N-thiohydrazone, 5-chloro2hydroxy acetophenone-morpholine-N-thiohydrazone and 5-methyl 2-hydroxy acetophenone antipyrine) with Mn (III) and Mn (II) have been synthesized in the lab. The structures of these complexes have been proposed on the basis of elemental analyses, electronic and IR spectral data and magnetic properties.

EXPERIMENTAL

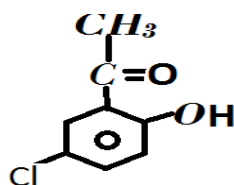
The carbonyl compounds and the compounds of amino group used for the preparation



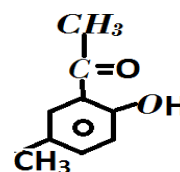
4-Aminoantipyrine



MorpholineNthiohydrazone



5-chloro2-hydroxyacetophenon

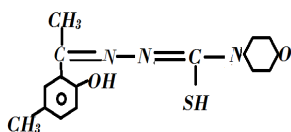


5-methyl2-hydroxyacetophenon

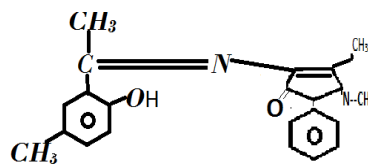
of Schiff bases were of AR grade or equivalent purity. The carbonyl compounds (5-methyl2-hydroxy acetophenone and 5-chloro2-hydroxy acetophenone) and amino compounds (morpholine-N-thiohydrazone and 4-amino antipyrine) were used for the preparation of Schiff base. The metal salts used were $MnCl_2$ and $MnCl_3$ (Glaxo). Other chemicals like ethanol, methanol (Glaxo) DMF (Rankem), DMSO (Glaxo) etc were of highest purity and used as such.

were carried out at CDRI (Lucknow). The magnetic susceptibility was measured by GOUY method. $CuSO_4 \cdot 5H_2O$ 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 Bareilly.

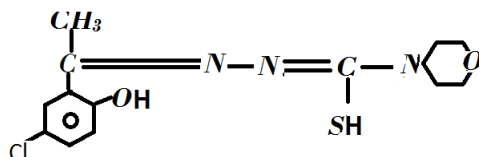
Infrared spectra and elemental analyses



5-methyl2-hydroxyacetophenone-morpholine-N-thiohydrazone



5-methyl2-hydroxyacetophenone-antipyrine



5-Chloro2-hydroxyacetophenone-morpholine-N-thiohydrazone

Preparation of ligands

The Schiff bases were prepared by the condensation of Carbonyl compounds and compounds containing amino group. 1.41 gm of Morpholine N-Thiohydrazide was dissolved in Ethanol and refluxed on water bath for half an hour. Then 1.50 gm 5- methyl 2- hydroxy acetophenone was added to it and refluxed for about five hours. . 1.41 gm of Morpholine N-Thiohydrazide was dissolved in Ethanol and refluxed on water bath for half an hour. Then one mole 5- chloro 2- hydroxy acetophenone was added to it and refluxed for about five hours. Similarly 2.06 gm of 4-Amino antipyrine was dissolved in methanol. Then 1.50 gm 5- methyl 2- hydroxy acetophenone was added to it and refluxed for about five hours. The crystal of ligand so obtained was purified by recrystallization. The purity of crystal was checked by TLC and melting point. The ligands were characterized by elemental analysis, electronic and I-R spectra.

Preparation of complexes

All the metal complexes were synthesized by adding respective metal salts solution drop wise to the solution of the ligand (5- methyl 2- hydroxy acetophenone morpholine –N- thiohydrozone, 5chloro 2 hydroxy acetophenone morpholine N thiohydrozone, 5 methyl 2 hydroxy acetophenone anti pyrine) 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

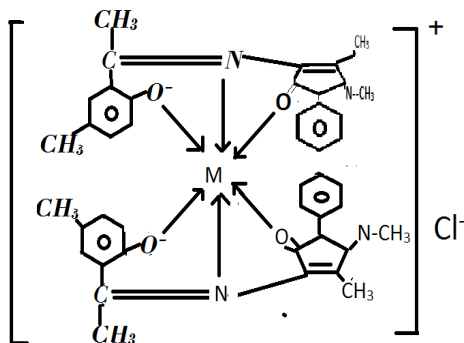
The analytical data of 5-methyl 2-hydroxy acetophenone morpholine N thiohydrozone Mn III chloride complex and 5- methyl 2- hydroxy acetophenone morpholine N thiohydrozone Mn II complexes indicated 1/1 metal-ligands stoichiometry for the complex and hence the molecular formulae comes out to be $[Mn(C_{14}H_{19}O_2N_3S)3H_2O]^+Cl^-$ & $[Mn(C_{14}H_{19}O_2N_3S) 3H_2O]$ respectively. Similarly 5-chloro 2- hydroxy acetophenone morpholine N thiohydrozone Mn III chloride, 5chloro 2 hydroxy acetophenone morpholine N thiohydrozone Mn II complexes also indicated M/L ratio 1/1. Hence molecular formulae of complex comes out to be $[Mn(C_{13}H_{14}N_3O_2SCl) 3H_2O] Cl$ and $[Mn(C_{13}H_{14}N_3O_2SCl)3H_2O]$ respectively.

Table 1:

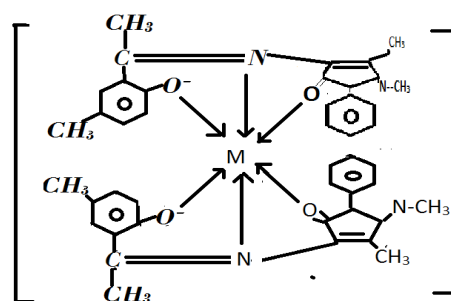
S. No	Name of complexes Molecular .Formula	Magnetic moment B.M	Important I.R Peaks (cm^{-1})				Molar conductance $Ohm^{-1}cm^2mol^{-1}$	
			C=O	C=N	OH	DMF	DMSO	
1.	5.Me2hyd.acet.mor.N.thMn(III)chloride $[Mn(C_{14}H_{19}O_2N_3S) 3H_2O]Cl$	4.93	-	1610	765	72	67	
2.	5.Me2hyd.acet.mor.N.thMn(II)complex $[Mn(C_{14}H_{19}O_2N_3S) 3H_2O]$	5.70	-	1613	745	-	-	
3.	5.Me2hyd.acet.antipy.Mn(III)chloride $[Mn(C_{20}H_{20}N_3O_2)_2] Cl;$	4.86	1625	1570	1270	80	79	
4.	5.Me2hyd.acet.antipy.Mn(II)complex $[Mn(C_{20}H_{20}N_3O_2)_2]$	5.70	1620	1575	1260	-	-	
5.	5.Chl.2hyd.acet.mor.N.thMn(III)chloride [Mn $(C_{13}H_{14}N_3O_2SCl).3H_2O] Cl$	4.90	-	1615	760	73	63	
6.	5.Chl.2hyd.acet.mor.N.thMn(II)chloride $[Mn(C_{13}H_{14}N_3O_2SCl).2H_2O]$	5.65	-	1620	765	-	-	

The analytical data indicated 1:2 metal-ligand ratio for the 5-methyl-2-hydroxyacetophenonean tipyrineMn(III)chloride complex and 5-methyl-2-hydroxyacetophenonean-tipyrineMn(II) complex. Hence the M.F formula of the adduct may be written

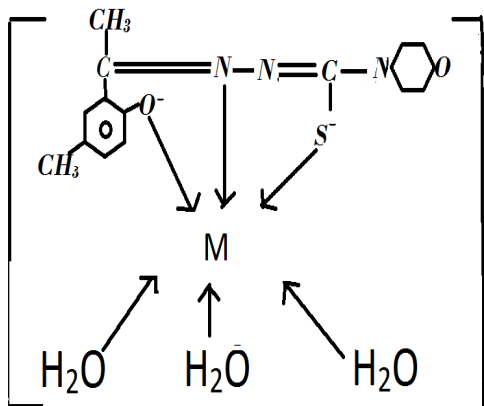
as $[\text{Mn}(\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_2\text{S})_2]\text{Cl}$ & $[\text{Mn}(\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_2\text{S})_2]$ respectively. The m.p of the metal complexes was found to be much higher than that of the ligand which indicated the formation of the adduct.



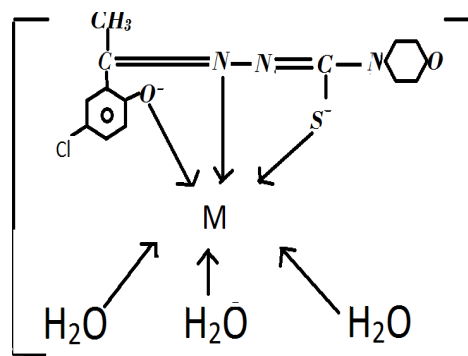
5-methyl-2-hydroxyacetophenoneanti pyrineMn(III) chloride complex



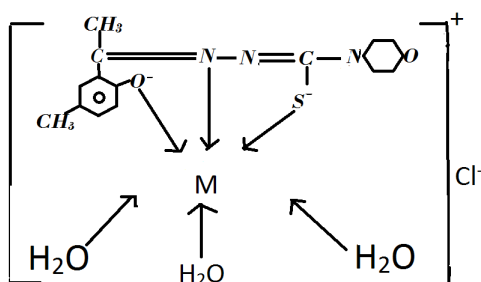
5-methyl-2-hydroxyacetophenoneantipyrine Mn(II) complex



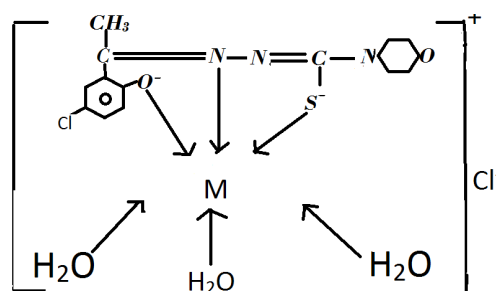
5me2-hydacetophenonemorpholine-N-thiohydrazideMn(II)Complex



5chl2-hydacetophmorpholine thiohydrazideMn(II) Complex



5me2-hydacetophenonemorpholine-N-thiohydrazid eMn(III)chlorideComplex



5chl2-hydacetophenonemorpholine-N-thiohydrazid Mn(III)chlorideComplex

The values of molar conductance in DMF and DMSO AT 10^{-3} dilution and 25°C indicated 1:1 electrolytic nature of 5-methyl 2- hydroxy acetophenone morpholine-N-thiohydrazone Mn (III) chloride and 5-chloro2-hydroxy acetophenone morpholine N-thiohydrozone Mn (III) chloride complex. While Mn (II) complexes of respective ligands were found to be non electrolytic in nature. 5-methyl 2-hydroxy acetophenone antipyrine Mn (III), chloride complex indicated 1:1 electrolytic nature and Mn (II) complex of respective ligand indicated non electrolytic nature of the complex. The values of magnetic moment Came out to be about 5.93 B.M for Mn+3 and About 4.70 for Mn+2 complexes¹⁸⁻²⁰.

The electronic spectra of Mn (III) complexes recorded in DMF, exhibited four bands in the range of 13590 to 14084 cm^{-1} , 16450 to 1695 cm^{-1} , 18220 to 20202 cm^{-1} and 25600 to 25641 cm^{-1} (16) may be assigned respectively to the transitions ${}^5B_1 \rightarrow {}^5A_1$, ${}^5B_1 \rightarrow {}^5B_1$, ${}^5B_1 \rightarrow {}^5E$ & LMCT.

The electronic spectra of Mn (II) complexes were also recorded in DMF, exhibited three bands at 17000, 24000 and 28000 cm^{-1} corresponding to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g} (1/21)$, ${}^6A_{1g} \rightarrow {}^4T_{1g} (v2)$ and ${}^6A_{1g} \rightarrow {}^4E_g (v3)$ respectively¹⁷. These are characteristics of octahedral geometry²¹.

The IR spectra of complexes of 5-methyl 2-hydroxy acetophenone morpholine N thiohydrozone and 2-hydroxy 5-chloro acetophenone morpholine N thiohydrozone indicated di-basic tri-dentate nature of the ligand as revealed by the comparison of this spectrum with that of the ligand shows band due to phenolic OH and $\nu_{C=S}$, which disappeared in the IR spectra of the complexes and a new band has appeared at the range of 745 to 760 cm^{-1} . This suggested the coordination of metal ion with the ligand through thiol-sulphur and phenolic oxygen via deprotonation. In addition to that the lowering of $\nu_{C=N}$ in the IR spectrum complexes by 15 to 20 cm^{-1} indicated the coordination of azomethine N, which is further substantiated by the appearance of azine chromophore at 1610 to 1615 cm^{-1} ²². This indicated that ligand is behaving in dibasic tridentate manner coordinating through oxygen, nitrogen and sulphur atoms.

The IR spectrum of the complexes exhibited some new bands. The band at 3100 to 3480 cm^{-1} may be attributed to ν_{OH} of coordinated water. This is further supported by the band at 810 to 880 cm^{-1} may be due to rocking & wagging modes of coordinated water molecules²³⁻²⁴.

This inference of IR spectrum regarding the presence of coordinating water molecule is further supported by TGA. The thermogram shows the loss of three water molecules above 150 to 1700°C. In the far IR region two bands were observed at the range of 400 to 480 & 500 to 590 cm^{-1} which may be assigned to ν_{M-N} & ν_{M-O} vibrations respectively²².

The i.r. spectra of the complexes of 5- methyl 2-hydroxyacetophenoneantipyrine on comparison with that of ligands indicated coordination through cyclic C=O, phenolic oxygen and azomethine nitrogen. This indicated monobasic tridentate nature of the ligand. The band due to ν_{OH} 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 ion²⁶⁻²⁸. 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 coordination of the above group with metal ion²⁹. 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 ν_{M-O} and ν_{M-N} bands respectively³⁰.

CONCLUSION

On the basis of above mentioned facts the complexes may be tentatively assigned the following octahedral geometry.

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