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Synthesis and Characterization of Transition Metals Complexes with 2-Hydroxy-5-chloro Acetophenone Antipyrine

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The Schiff base 2-hydroxy-5-chloro acetophenone antipyrine on reaction with Ti(III),V(III), VO(IV), Mn(II), Mn(III) and Fe(III) to form coordination compounds having general formula $[M(C_{19}H_{18}N_3O_2)_2\cdot 2H_2O]\cdot 3Cl$ where M = Ti(III), V(III), Fe(III) $[VO(C_{19}H_{18}N_3O_2)_2\cdot 2H_2O]SO_4$, $[Mn(C_{19}H_{18}N_3O_2)_2]\cdot 3Cl$ and $Mn(C_{19}H_{18}N_3O_2)_2]\cdot 2H_2O]\cdot 2Cl$. These adducts have been characterized on the basis of elemental analyses, molar conductance, infrared and visible spectra, magnetic susceptibility measuements and TGA. The ligand behaves in bidentate manner. All these compounds are paramagnetic in character. Ti(III), V(III), VO(IV), Mn(II) and Fe(III) complexes have octahedral geometry, while Mn(III) complex show square pyramidal geometry.

Key Words: Synthesis, Transition Metals Complexes, 2-Hydroxy-5-chloro acetophenone antipyrine.

INTRODUCTION

Metal complexes of schiff bases have played a central role in the development of coordination chemistry. Schiff bases offer a versatile and flexible sites of ligands capable to bind with various metal ions to give complexes with suitable properties for theoretical and practical applications. The synthesis and coordination ability of compartmental ligands have been the goal of much research in recent years owing to the specific properties of schiff bases and their transition metal complexes which have significant biological and medicinal properties as antioxidative,antitumour, antiviral, antineoplastic and antimicrobial activities[1-5]. The survey of chemical literature has revealed that Schiff bases possess strong ability to form complexes[6] and they deserve a proper attention because of their biological properties[7]. The Schiff bases have been investigated because of the easy synthesis and remarkable versatility towards coordinating ability with transition metals[8,9].

The complex compounds of Ti, V, Mn and Fe with schiff bases have been found to be biologically active. We have synthesized different transition metals [Ti(III), V(III), VO(IV), Mn(II), Mn(III) and Fe(III)] complexes with schiff base (2-hydroxy-5-chloro acetophenone antipyrine). The structures of these complexes have been proposed on the basis of elemental analyses, electronic and IR spectral data and magnetic properties.

EXPERIMENTAL

All the chemicals used were of AR grade or equvalent purity. The carbonyl compound 5-methyl-2-hydroxy acetophenone and used for the preparation of Schiff base were procured. The metal salts used were $MnCl_2$ (Glaxo), $FeCl_3$ (Rankem), V(III) chloride (BDH), oxovanadium(IV) sulphate (Fluka), *etc*. Other chemicals, ethanol, methanol (Glaxo), DMF (Rankem), DMSO (Glaxo), *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. $CuSO_4\cdot 5H_2O$ was used as calibrant. UV/visible spectra were recorded with the help of Backmann-DU. The conductivity measurement was carried out at room temperature and 10^{-3} M dilution using conductivity bridge model 910.

Preparations of ligand: 1.70 g of 2-hydroxy-5-chloro acetophenone was dissolved in ethanol and refluxed on water bath for 0.5 h. Then 2.06 g of 4-amino antipyrine was added to it and refluxed for *ca*. 5 h. The crystals of ligand so obtained were purified by recrystallization. The purity of the crystals was checked by the TLC and melting point. The ligands were characterized by elemental analyses, electronic and IR spectra.

Preparation of metal complexes: All the metal complexes were synthesized by adding respective metal salt solution ($TiCl_3$, $MnCl_2$, $FeCl_3$, $VOSO_4$ or VCl_3) dropwise to the solution of the ligand (2-hydroxy-5-chloro acetophenone antipyrine) prepared. The precipitate so obtained was filtered and washed with suitable solvent (DMSO, DMF, *etc*.) and dried in vaccum desiccator over fused P_4O_{10}.

RESULTS AND DISCUSSION

The analytical data suggested 1:2 metal ligand ratio for all the complexes, so that molecular formula of the complexes may be written as $[Ti(C_{19}H_{18}N_3O_2)_2\cdot 2H_2O]\cdot 3Cl$, $[V(C_{19}H_{18}N_3O_2)_2.2H_2O]\cdot 3Cl$, $[VO(C_{19}H_{18}N_3O_2)_2.H_2O]SO_4$, $[Mn(C_{19}H_{18}N_3O_2)_2]\cdot 3Cl$, $[Mn(C_{19}H_{18}N_3O_2)_2.2H_2O]\cdot 2Cl$, $[Fe(C_{19}H_{18}N_3O_2)_2.2H_2O]\cdot 3Cl$.

The molar conductivity of these complexes were measured at room temperature and 10^{-3} M dilution in DMF and DMSO. In case of Ti(III), V(III), Mn(III) and Fe(III) complexes the values of molar conductance in both the solvents indicated 1:3 electrolytic nature. While in case of oxovanadium(IV) and Mn(II) complexes indicated 1:1 and 1:2 electrolytic nature, respectively. These complexes are paramagnetic in nature. The values of magnetic moment were in the range of 1.70 to 5.95 BM (Table-1).

The electronic spectrum of the Ti(III) complex was recorded in DMF which exhibited a single band at 20500 cm^{-1} with the shoulder at 19000 cm^{-1}. This indicates the *d-d* transition $^2T_{2g}\rightarrow{}^2E_g$ for O_h symmetry[10].

The electronic spectrum of vanadium(III) complex was recorded in pyridine complex, which showed two bands at 16700 cm^{-1}, 21600 cm^{-1} which have been assigned to $^3T_{1g}\rightarrow{}^3T_{2g}$ and $^3T_{1g}\rightarrow{}^3T_{2g}$ transitions, respectively[11].

TABLE-1
CHARACTERIZATION OF COMPLEXES PREPARED

Name of complex	m.f. (colour)	m.p. (ºC)	Magnetic moment (BM)
2-Hydroxy-5-chloro acetophenone antipyrine Ti(III) chloride complex	$[Ti(C_{19}H_{18}N_3O_2)_2.2H_2O]3Cl$ (Brown)	320	1.70
2-Hydroxy-5-chloro acetophenone antipyrine V(III) chloride complex	$[Vi(C_{19}H_{18}N_3O_2)_2.2H_2O]3Cl$ (Light brown)	340	2.86
2-Hydroxy-5-chloro acetophenone antipyrine oxovanadium(IV) complex	$[VO(C_{19}H_{18}N_3O_2)_2.H_2O]SO_4$ (Orange red)	348	1.74
2-Hydroxy-5-chloro acetophenone antipyrine Mn(III) chloride complex	$[Mn(C_{19}H_{18}N_3O_2)_2]3Cl$ (Orange pink)	352	4.86
2-Hydroxy-5-chloro acetophenone antipyrine Mn(II) chloride complex	$[Mn(C_{19}H_{18}N_3O_2)_2.2H_2O]2Cl$ (Light pink)	359	5.60
2-Hydroxy-5-chloro acetophenone antipyrine Fe(III) complex	$[Fe(C_{19}H_{18}N_3O_2)_2.2H_2O]3Cl$ (Brownish pink)	362	5.95

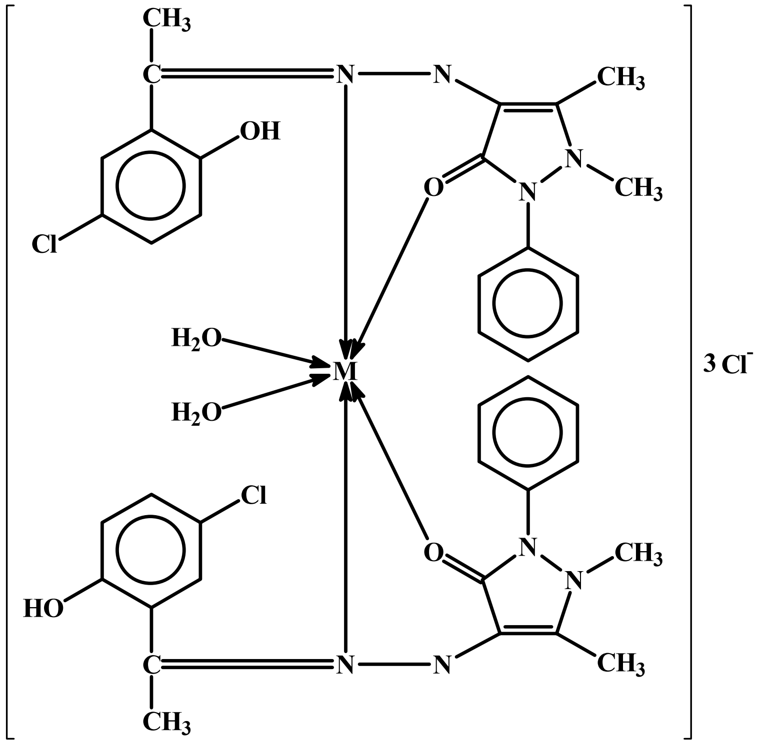
The electronic spectrum of oxovanadium(IV) complex displayed three bands at 33800, 30700 and 25840 cm^{-1} which are attributed to charge transfer transitions and $^2T_{2g}\rightarrow{}^2E_g$ transition[12]. The electronic spectrum of Mn(II) chloride complex exhibits three bands at 17000, 25000 and 29000 cm^{-1} which correspond to $^6A_{1g}\rightarrow{}^4A_{1g}(1)$, $^6A_{1g}\rightarrow{}^4T_{1g}(2)$ and $^6A_{1g}\rightarrow{}^4E_g(3)$, respectively[13].

The electronic spectrum of Fe(III) complex showed three bands at 11200, 21700 and 27700 cm^{-1} corresponded to $^6A_{1g}\rightarrow{}^4T_{1g}$, $^6A_{1g}\rightarrow{}^4T_{2g}$ and $^6A_{1g}\rightarrow{}^4E_g$ transitions, respectively[14]. In all these complexes, these transitions are characteristic of octahedral geometry. The electronic spectrum of Mn(III) complex exhibited three bands at 13600, 16500 and 18000 cm^{-1} assigned to $^5B_1\rightarrow{}^5B_2$, $^5B_1\rightarrow{}^5A_1$ and $^5B_1\rightarrow{}^5E$ transitions, respectively, suggesting square pyramidal geometry[15].

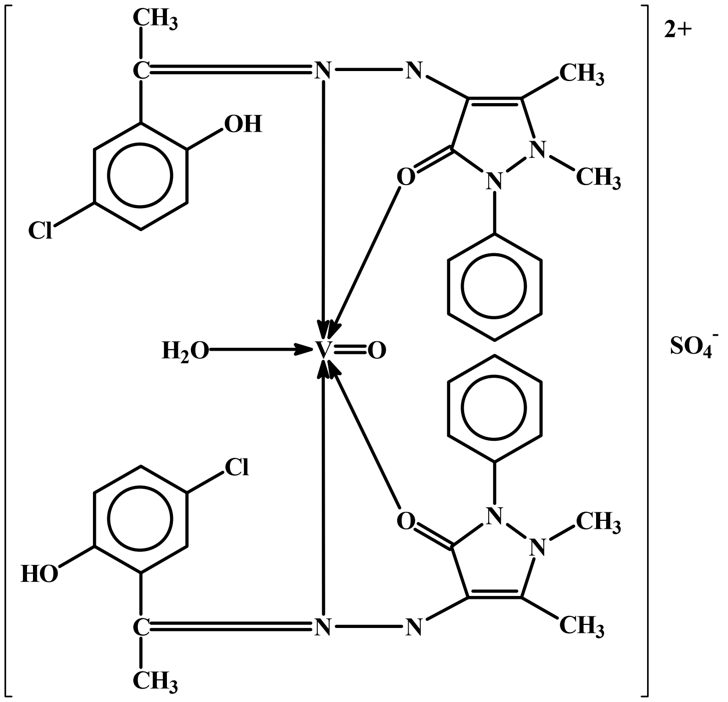
In all the metal complexes of 2-hydroxy-5-chloro acetophenone antipyrine, the IR spectra of the ligand and the complexes on comparison revealed bidentate nature of the ligand. As the broad band for the OH group of the ligand at 3400 cm^{-1} remain unaltered, this excluded the possibility of involvement of the third donor site in coordination. The ligand and the complexes on comparison revealed the lowering of two bands which were in the range of 20 to 40 cm^{-1} in the IR spectra of the complexes. These bands have been assigned to C=N of azomethine group and C=O of pyrazolone ring. This indicated the involvement of these two groups in coordination with metal ion. Which is further supported by the appearance of new bands in the far IR region due to M-O and M-N bands. The M-O bands were observed in the range of 500 to 480 cm^{-1}, while M-N bands came in the range of 430 to 415 cm^{-1}. The IR spectrum of oxovanadium complex showed an additional band[16,17] at 960 cm^{-1} which has been assigned to (V=O). In oxovanadium complex another important band was found at 970 cm^{-1} which is due to the presence of sulphate ion[18].

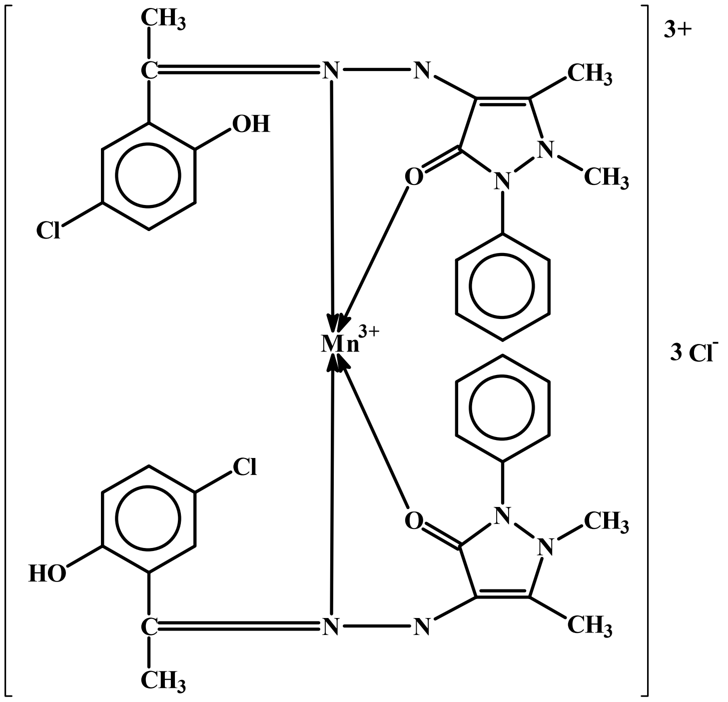
In Ti(III), V(III), Mn(II) and Fe(III) complexes the IR spectra indicated the presence of coordinated water molecules. The band for -OH of coordinated water has been observed with in the range of 3140-3310 cm^{-1}. This is further supported by the appearance of band in the range of 780-890 cm^{-1}. which may be due to rocking and wagging modes of coordinated water molecules[19,20]. The inference of IR spectrum regarding the presence of coordinated water molecules is further supported by TGA. The thermograms of all these complexes except oxovanadium (IV) complex and Mn(III) complex show the loss of two water molecules at the temperature ranging from 150 to 170 ºC. The IR spectrum of oxovanadium(IV) complex exhibited a medium intensity band at 3300 cm^{-1} which have been assigned to new mode of coordinate water which is further supported by the presence of another band at 875 cm^{-1} due to rocking and wagging modes of coordinated water. In oxovanadium the thermogram shows the percent weight loss corresponding to the loss of one water molecule at 150 ºC.

On the basis of the above discussed spectral studies, the tentative structures of metal complexes are assigned as below:



where M = Ti(III), V(III), Mn(II) and Fe(III)


CH3
C
N
N
CH3
OH
N
O
N
CH3
Cl
H2O
V
O
2+
SO4-
Cl
O
N
CH3
N
HO
C
N
N
CH3
CH3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C
N
N
CH3
OH
N
O
N
CH3
Cl
Mn3+
3+
3 Cl-
Cl
O
N
CH3
N
HO
C
N
N
CH3
CH3

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