

Synthesis and characterization of transition metal derivatives with 5-methyl 2-hydroxy acetophenone morpholine N-thiohydrazone

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ABSTRACT

The Schiff base 5-methyl 2-hydroxy acetophenone morpholine N-thiohydrazone has reacted with Ti (III), V(III), oxovanadium (IV), Mn (II), Mn (III), and Fe (III) to form co-ordination compounds having general formula $[M(C_{14}H_{19}O_2N_3S).3H_2O]+Cl^-$ where M=Ti, V, Fe Mn etc. These adducts have been characterized on the basis of elemental analyses, molar conductance, infrared and visible spectra, magnetic susceptibility measurements and TGA. The ligand behaves in dibasic tridentate manner. All these compounds are paramagnetic in character and have octahedral geometry.

Key words: Co-ordination compounds, octahedral geometry and Paramagnetism.

INTRODUCTION

Chemistry of co-ordination compounds containing ligands as Schiff base has received much attention owing to their significant biological activities and medicinal properties such as antioxidative¹, antimour², antiviral³ antineoplastic⁴ and antimicrobial activities⁵.

We have synthesized different transition metals [Ti (III), V(III), VO (IV), Mn (II), Mn (III), and Fe (III)] complexes with schiff base (5 methyl 2-hydroxy acetophenone morpholine N-thiohydrazone). The structures of these complexes have been proposed on the basis of elemental analyses, electronic and I.R. spectral data and magnetic properties.

MATERIAL AND METHODS

All the chemicals used were of AR grade or equivalent purity. The carbonyl compound 5 methyl 2-hydroxy acetophenone and compound containing amino group morpholin-N-thiohydrazone

used for the preparation of Schiff base were collected from different pharmaceuticals such as koach light & otto. The metal salts used were $MnCl_2$ (Glaxo), $FeCl_3$ (Rankem), V(III) chloride (BDH), oxovanadium IV sulphate (Fluka) etc. Other chemicals used were ethanol, which was purified by distillation in the lab, 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 at chemistry department Bareilly College Bareilly. $CuSO_4.5H_2O$ was used as calibrant. UV/visible spectra were recorded with the help of Backmann-DU at chemistry lab Bareilly, College Bareilly. The conductivity measurement was carried out at room temperature and 10^{-3} M dilution using conductivity bridge model 910 at chemistry department Bareilly College Bareilly. The thermogravimetric analysis was carried out at GND university (Amritsar). Antibacterial and antifungal activities were carried out at I.V.R.I. Izzatnagar Bareilly.

Preparation of ligands

The schiff base was prepared by the condensation of carbonyl compound and compounds containing amino group. 1.41 gram of morpholine N-thiohydrazone was dissolved in ethanol and refluxed on water bath for half an hour. Then 1.50 gram of 5-methyl 2-hydroxy acetophenone was added to it and refluxed for about 5 hours. The crystals of ligand so obtained were purified by recrystallisation. The purity of the crystals was checked by the TLC and melting point. The ligands were characterized by elemental analyses, electronic and I.R. spectra.

RESULTS AND DISCUSSION

The analytical data suggested the composition of the complexes as $[\text{Ti}(\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_2\text{S}) \cdot 3\text{H}_2\text{O}] + \text{Cl}^-$, $[\text{V}(\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_2\text{S}) \cdot 3\text{H}_2\text{O}] + \text{Cl}^-$, $[\text{VO}(\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_2\text{S}) \cdot 2\text{H}_2\text{O}]$, $[\text{Fe}(\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_2\text{S}) \cdot 3\text{H}_2\text{O}] + \text{Cl}^-$, $[\text{Mn}(\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_2\text{S}) \cdot 3\text{H}_2\text{O}] + \text{Cl}^-$ and $[\text{Mn}(\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_2\text{S}) \cdot 3\text{H}_2\text{O}]$.

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 1:1 electrolytic nature. While in case of oxovanadium (IV) and Mn(II) complexes indicated non electrolytic nature of complexes. These complexes are

paramagnetic in nature. The value of magnetic moment were in the range of 1.69 to 5.98 B.M.(6)

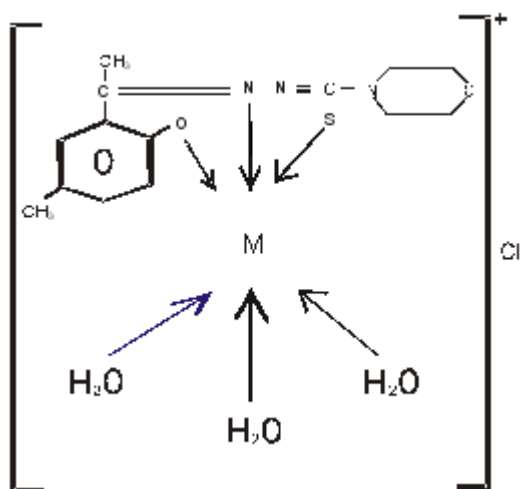
The electronic spectrum of the Ti (III) complex exhibited a single band at 21000 cm^{-1} with the shoulder at 23000 cm^{-1} . This indicates the d-d electronic transition and octahedral geometry⁷.

The electronic spectrum of the complex of vanadium (III) shows bands at 16600 cm^{-1} with the shoulder at 21500 cm^{-1} . The bands have been assigned to ${}^3\text{T}_{1g}$ ${}^3\text{T}_{2g}$ transitions⁸.

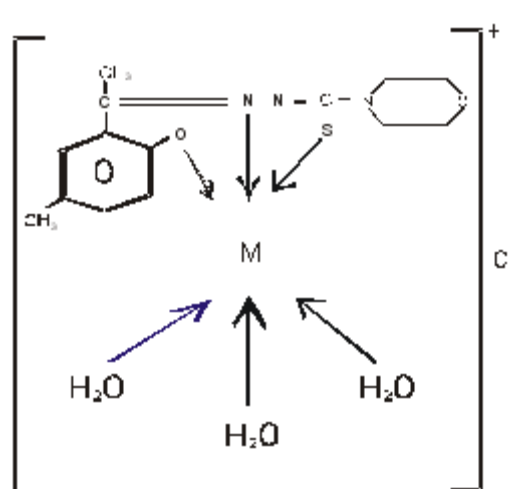
The electronic spectrum of oxovanadium (IV) complex shows four bands at 17600 cm^{-1} , 22900 cm^{-1} , 31600 cm^{-1} and 38600 cm^{-1} respectively⁹. The first two bands correspond to electronic transitions ${}^2\text{B}_2$ ${}^2\text{B}_1$ and ${}^2\text{B}_2$ ${}^2\text{A}_1$ respectively and the later two bands are charge transfer in nature.

The electronic spectrum of Fe(III) chloride complex exhibits three bands at 14200 , 18280 and 23200 cm^{-1} assigned to the transitions ${}^6\text{A}_1\text{g}(\text{S})$ ${}^4\text{T}_{1g}(\text{G})$, ${}^6\text{A}_1\text{g}(\text{S})$ ${}^4\text{T}_{2g}(\text{G})$ & ${}^6\text{A}_1\text{g}(\text{S})$ ${}^4\text{Eg}$ ${}^4\text{A}^1\text{g}(\text{G})$ ¹⁰.

The electronic spectrum of Mn(III) complex exhibited bands at 14084 , 16950 , 20202 and 25641 cm^{-1} may be assigned to ${}^5\text{B}_1$ ${}^5\text{A}_1$, ${}^5\text{B}_1$ ${}^5\text{B}_2$ ${}^5\text{B}_1$ ${}^5\text{E}$ & LMCT¹¹.



Scheme 1



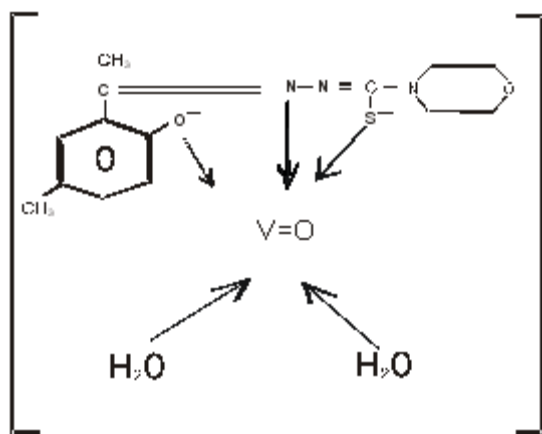
Scheme 2

Mn(II) complex exhibits three bands at 17000, 24000 and 28000 cm^{-1} corresponding to the transitions ${}^6A_1g^4T_1g(G)_1$, ${}^6A_1g^4T_1g(G)_2$ and ${}^6A_1g^4Eg(G)_3$. In all these complexes, these transitions are characteristic of octahedral geometry.

In Ti(III), V(III), VO(IV) & Mn(II) complexes the IR spectra of the ligand and the complex on comparison indicated that both the phenolic OH and C=S disappeared and a new band appeared in the range of 745-765 cm^{-1} . This suggested the co-ordination of respective metal ions with the ligand through thiol sulphur and phenolic oxygen via deprotonation. In addition to that the lowering of C=N in the I.R. spectra of the complexes by about 20 cm^{-1} indicated the co-ordination of azomethine nitrogen which is further substantiated by the appearance of azine chromophore in the range of

1610-1630 cm^{-1} ¹². This indicated that the ligand is behaving in dibasic tridentate manner co-ordinating through O, N and S atoms. The dibasic nature of the ligand is also in agreement with the results of molar conductance measurements. The I.R. spectrum of oxovanadium complex showed an additional band at 940 cm^{-1} which has been assigned to V=O. (13-14)

The I.R. spectra of all the complexes indicated the presence of co-ordinated water molecules. The band for OH of co-ordinated water has been observed with in the range of 3100-3480 cm^{-1} ¹⁵. This is further supported by the appearance of band in the range of 780-880 cm^{-1} . Which may be due to rocking & wagging modes of co-ordinated water molecules¹⁶. The inference of I.R. spectrum regarding the presence of co-ordinated water molecules is further supported by TGA. The thermograms of all the complexes except oxovanadium(IV) complex show the loss of three water molecules at the temperature ranging from 150 to 170°C. In the far I.R. region two bands were observed at M-N and M-O. The M-O bands were observed in the range of 400 to 440 cm^{-1} and M-N bands came in the range of 480-510 cm^{-1} .



Scheme 3

CONCLUSION

On the basis of above mentioned facts the complexes have been tentatively assigned the following structures.

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