

SPECTROSCOPIC CHARACTERIZATION OF SOME METAL COMPLEXES OF Fe(III) AND Co(III).

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ABSTRACT

A Schiff base Vanillin semicarbazone has been prepared by the condensation of 3-hydroxy-4-methoxybenzaldehyde (m-vanillin) and semicarbazide. This Schiff base has been made to undergo complexation with Fe(III) and Co(III) metal ions. On the basis of percentage composition and molar conductivity values, the complexes have been formulated as ML_3X_3 . Where, M-stands for Fe(II) & Co(III) while L is m-vanilline semicarbazone (VSC) and X is chlorine and bromine. The mode of coordination of the ligand has been determined by the comparison of the FTIR spectra of the complexes and that of the free ligand. The appearance of some new bands in the FTIR spectra of complexes confirms of the complexes and that of the free ligand. The appearance of some new bands in the FTIR spectra of complexes confirms the presence of chlorine and bromine in the coordination sphere of respective complexes. The magnetic moment of two Fe(III) complexes have been found at room temperature in the range of 5.80-5.83 BM which are very close to μ_s values corresponding to five unpaired electrons ($\mu_s = 5.91$ BM) and are indicative of spin free octahedral nature of the complexes. The complexes of Fe(III) display three weak band in their electronic spectra due to ${}^6A_{1g} \rightarrow {}^4T_{1g} ({}^4G)$, ${}^6A_{1g} \rightarrow {}^4T_{1g} ({}^4P)$ and ${}^6A_{1g} \rightarrow {}^4T_{2g} ({}^4D)$. Spin forbidden transitions. The magnetic moment of Co(III) complexes are found diamagnetic which indicate that all the d^6 electrons are paired up in t_{2g} favoring the formation of spin paired octahedral complexes. The electronic spectra of Co(III) complexes display several spin forbidden and also several spin allowed transitions like ${}^1A_{1g} \rightarrow {}^3T_{1g}$, ${}^1A_{1g} \rightarrow {}^3T_{2g} ({}^4P)$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$. The value of ν_2/ν_1 also support octahedral geometry around metal ions.

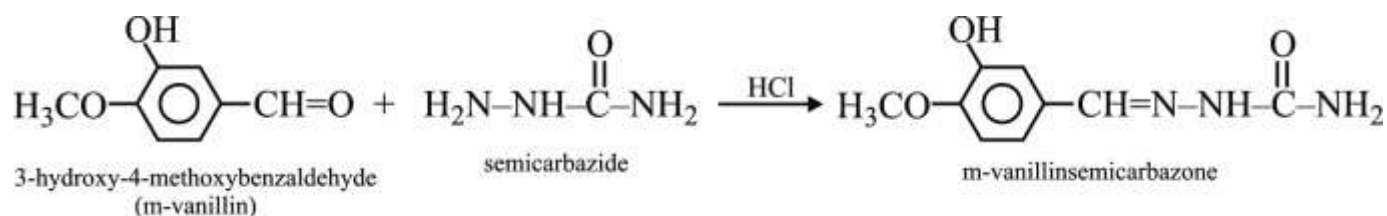
Keywords : Vanilline, Macrocyclic Ligand, Distorted Octahedral, Diamagnetic.

1. INTRODUCTION

The Schiff base and its transition metal complexes have very fascinating and interesting^[1] chemistry as they play a central role in inorganic chemistry of chelate system. Particularly, the Schiff base containing semicarbazone moiety are vastly studied and their metal complexes show a wide spectrum of biological activities. Vanillin are of considerable pharmacological interest since a number of derivatives have been reported to possess various biological activities. It is of great interest because of their chemistry and biological activities such as antiviral, antimalarial, antibacterial and antifungal activities.^[2-4] The perusal of literature reveals that the work reported on the complexes of semicarbazone of vanillin is very scarce. This fact motivated us to pursue research on spectral characterization of complexes of vanillin semicarbazone with Fe(III) & Co(III) metal ions.

2. METHODS AND MATERIALS

All the chemical used were Anal.R.grade, 3-hydroxy-4-methoxybenzaldehyde (m-vanillin) was procured from Merck & semicarbazone was procured from Nice. The ligand vanillin semicarbazone has been prepared by refluxing of vanillin and semicarbazone in the presence of HCl for one hour and was cooled at room temperature, whereby a colourless precipitate appeared which was filtered on suction pump and it was recrystallised in ethanol.



Scheme – I

The complexes were prepared by refluxing the ethanolic solution of the Schiff base ligand i.e., m-vanillin semicarbazone and ethanolic solution of metal chloride of Fe(III) and Co(III) taken in 1 : 1 molar ratio for about one and half an hour. The solution was kept overnight

whereby precipitation completed. The precipitate was filtered and washed with alcohol and then it was dried in vacuum desiccator. The IR Spectra of ligand and complexes were recorded on Fourier Transform Infrared Spectrometer model RZX (Perkin Elmer) by KBr disc method. The electronic spectra of complexes in DMSO were recorded on Hitachi-330, UV-Vis Spectrometer. The magnetic susceptibility of complexes was determined on Gouy balance at room temperature.

3. RESULTS AND DISCUSSION

The microanalytical data and molar conductivity of ligand and complexes have been presented in table – 1.

Table – 1

Sl. No.	Compounds	M. P. (°C)	% Analysis Found/(Calculated)				λ_m (ohm ⁻¹ cm ² mol ⁻¹)	μ (BM)
			M	C	H	N		
1.	Ligand (VSC)	228°C	—	51.5 (51.67)	05.15 (05.26)	20.10 (20.09)	—	—
2.	[Fe(VSC) ₃ Cl ₃]	315°C	6.94 (7.09)	41.42 (41.03)	4.00 (4.18)	15.77 (15.96)	190	5.83
3.	[Fe(VSC) ₃ Br ₃]	318°C	5.92 (6.06)	35.45 (35.10)	3.38 (3.57)	13.49 (13.65)	185	5.80
4.	[Co(VSC) ₃ Cl ₃]	321°C	7.26 (7.44)	40.99 (40.88)	4.00 (4.16)	15.74 (15.90)	181	Diamagnetic
5.	[Co(VSC) ₃ Br ₃]	328°C	6.21 (6.37)	35.24 (34.99)	3.45 (3.56)	3.49 (13.60)	180	Diamagnetic

Conductivity :

The conductivity of complexes lies in the range of 180-190 ohm⁻¹cm²mol⁻¹ which is indicated electrolytic nature of complexes.^[5-9] On the basis of elemental analysis and conductance values, complexes were formulated as (M(VSC)₃X₃) where, M stands for Fe(III) and Co(III), VSC stands for Schiff base ligand and X stands for Cl and Br.

4. FTIR SPECTRA

The important and significant IR bands before and after complexation have been detected and assigned. The free ligand display two broad band at 3520 cm^{-1} and 3470 cm^{-1} which may be assigned to free ν_{OH} absorption and terminal OH, while the OH group situated in the middle of the chain absorbs at 3290 cm^{-1} for vanillin semicarbazone is assigned as free phenolic OH. The ligand which remain predominantly in enroll from as conducted from the presence of bands at 1505 cm^{-1} have enough opportunity for carbonyl group to occur as H-bonded and hence the frequencies $1680\text{-}1690\text{ cm}^{-1}$ appearing in the spectra of ligand have been assigned to stretching of carbonyl group.^[10] The band at 3345 cm^{-1} does not show any appreciable change in its position in complexes indicating the non-participation of N–H group in bonding. The weak band appears at 2890 cm^{-1} due to $\nu_{\text{C-H}}$ of OCH_3 group of the ligand. The strong band at 1680 cm^{-1} is assigned to $\nu_{\text{C=O}}$ of α unsaturated keto group. The free ligand does not display band at 1650 cm^{-1} due to amide group i.e., $\nu_{\text{NH-C=O}}$ rather a broad band appear at 3200 cm^{-1} due to $\nu_{\text{O-H}}$ (Aliphatic) H-bonded with other $\nu_{\text{C=O}}$ group.^[11] The above supposition is further supported by the appearance of bands at 3040 cm^{-1} , 1590 cm^{-1} , 1440 cm^{-1} and 1240 cm^{-1} due to $\nu_{\text{C-H}}$, $\nu_{\text{CH=N-N-C}}$, $\nu_{\text{C=C}}$ and $\nu_{\text{C-O}}$ (Enolic) respectively. In all the complexes the band at 3200 cm^{-1} due to H-bonded $\nu_{\text{O-H}}$ of enolic form is found absent confirming the deprotonation and coordination through deprotonated oxygen to metal ion.^[12] A band of medium intensity is observed at 1610 cm^{-1} due to $\nu_{\text{CH=N}}$ azomethine stretching vibration.^[13] In the ligand the band appears at $1570\text{-}1580\text{ cm}^{-1}$ in complexes which is indicative of coordination through azomethine nitrogen.^[14] The band near 560 cm^{-1} is assigned to $\nu_{\text{M-O}}$ while the other at 420 cm^{-1} is assigned to $\nu_{\text{M-N}}$.^[15] Thus, the ligand act as neutral bidentate ligand forming five members chelate ring with Fe(III) & Co(III) metal ions.

5. MAGNETIC SUSCEPTIBILITY AND ELECTRONIC SPECTRA

The Fe(III) complexes exhibit magnetic moment of 5.80-5.83 BM. These values very close to μ_s value corresponding to five unpaired electrons ($\mu_s = 5.91$ BM) and are indicative of spin free octahedral nature of the complexes. The complexes display three very weak band in their electronic spectra which may be assigned as below :

$$\nu_1 = 14600 - 14680 \text{ cm}^{-1} = {}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g} ({}^4\text{G})$$

$$\nu_2 = 16850 - 16890 \text{ cm}^{-1} = {}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g} ({}^4\text{P})$$

$$\nu_3 = 27700 - 27710 \text{ cm}^{-1} = {}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g} ({}^4\text{D})$$

The magnetic moment values and electronic spectral bands suggest octahedral geometry around Fe(III) in these complexes.

The complexes of Co(III) are found diamagnetic which indicate that all the d^6 -electrons are paired up in t_{2g} favoring the formation of spin paired octahedral complex. The electronic spectral bands of Co(III) complexes show the possibilities of several spin forbidden and also several spin allowed transitions. The complexes display three bands which are given as below:

$$\nu_1 = 9250 - 9100 \text{ cm}^{-1} = {}^1\text{A}_{1g} \rightarrow {}^3\text{T}_{1g}$$

$$\nu_2 = 16100 - 16000 \text{ cm}^{-1} = {}^1\text{A}_{1g} \rightarrow {}^3\text{T}_{2g}$$

$$\text{and } \nu_3 = 19050 - 19000 \text{ cm}^{-1} = {}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$$

The two very-very weak bands are assigned to the two spin forbidden transitions while the comparatively stronger band has been assigned to spin allowed transition. The values of ν_1 , ν_2 and ν_3 their assignments are in good agreement with the values reported for octahedral complexes of Co(III).

6. CONCLUSION

The present study reveals that the Schiff base vanillinsemicarbazone contains two potential sites for coordination to metal ions. Thus, the ligand has been found to coordinate through carboxyl oxygen and azomethine nitrogen to all the metal ions. It behaves as a neutral bidentate ligand forming five members chelate ring with Fe(III) and Co(III) metal ions. vanillinsemicarbazone led to new compounds with a very interesting pharmacological profile. From these finding, it can be suggested that the designing of new chemical analogues with vanillin semicarbazones lead the necessity of further research.

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