

THE EFFECT OF STERIC BULK OF LIGANDS ON THE STRUCTURE AND MAGNETIC PROPERTIES OF Mn(II) COMPLEXES.

Santosh Kumar¹, Sahdeo Kumar¹, Lalit Kishore¹ and S. S. Rai²

¹University Department of Chemistry
Magadh University, Bodh-Gaya (Bihar) - 824234

²S. D. S. College, Kaler, Arwal (Bihar)
E-mail :- skprovider45@gmail.com

ABSTRACT

Schiff base of 3-hydroxylamino-2-butenone have been prepared by the condensation of o-toluidine, m-toluidine and p-toluidine. This Schiff's base ligands have been made to undergo complexation with Mn(II) metal ion. On the basis of their elemental analysis and molar conductivity values, the complexes have been formulated as $[MnL_2X_2]$ where, L is N-phenyl-3-hydroxyimine-2-butyldeneamine (HPHB), N-o-toluene-3-hydroxyimine-2-butyldeneamine (HOTHB), N-m-toluene-3-hydroxyimine-2-butyldeneamine (HMTHB) and N-p-toluene-3-hydroxyimine-2-butyldeneamine (HPTHB) while X stands for chlorine. The comparison of infrared spectra of metal complexes with that of HPHB, HOTHB, HMTHB and HPTHB indicates its coordination through azomethine Nitrogen and Oxime oxygen. Thus, they behaves as neutral bidentate ligand forming six member chelate ring with metal ion. The magnetic moment of Mn(II) complexes have been found to be in the range of 5.80-5.82 BM which are very close to μ_s value ($\mu_s = 5.92$ BM) corresponding to five unpaired electrons and indicative of octahedral geometry of complexes. The electronic spectra of Mn(II) complexes display four bands due to ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$, ${}^6A_{1g} \rightarrow {}^4A_{1g}$, ${}^4E_g({}^4G)$, ${}^6A_{1g} \rightarrow {}^4E_g({}^4D)$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4P)$ spin allowed transitions. Steric bulk was increased by introducing methyl group on benzene ring, the coordinating ability of N is found to decrease.

Keywords : Octahedral Geometry, Steric bulk, Bidenticity, Macrocyclic ligand.

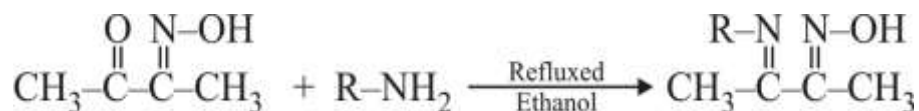
1. INTRODUCTION

Transition metal complexes of Schiff's base have been considerable interest in terms of structural complexity and biological functions^[1, 2]. Bidentate Schiff's base ligands are able to coordinate with many different metal ions forming stable compounds. The importance of coordination compounds of bidentate Schiff's base is widely used in the field of pharmaceutical as antibacterial, antifungal, anticancer and herbicidal. These Schiff's base complexes have also been used a catalectic reaction and as biological model for understanding the structure of biomeolcules^[3-5]. Keeping this fact in mind a number of Mn(II) complexes of ligands having different steric bulk of ligands on the spectra of complexes have been studied the present paper deals with the synthesis of complexes of Schiff's base N-phenyl-3-hydroxyimino-2-butylideneamine (HPHB), N-o-toluene-3-hydroxyimine-2-butylideneamine (HOTHB), N-m-toluene-3-hydroxyimine-2-butylideneamine (HMTHB) and N-p-toluene-3-hydroxyimine-2-butylideneamine (HPTHB) with Mn(II). These nobel complexes have been characterised by their Infrared spectra, Electronic spectra, Molar conductivity and Magnetic moment at room temperature.

2. METHODS AND MATERIALS

All the chemicals used were Anal.R.Grade, 3-hydroxylamino-2-butenone was procured from laba and ortho toluidine, meta toluidine and para toluidine were produred from B. D. H. (British Drug House). The required ligands have been prepared by refluxing the appropriate toluene with 3-hydroxylamine-2-butenone taken in 1 : 1 molar ratio in ethanolic medium for 5 to 6 hours. The yellowish solid appeared in the bottom of conical flask.

The solid was dried in electronic oven at 100°C and it was recrystallised in ethanol. It has been given in scheme – I below.



Scheme – I

where, R = C₆H₅, o-toluene (C₆H₄CH₃), m-toluene (C₆H₄CH₃) and p-toluene (C₆H₄CH₃)

The complexes were prepared by refluxing the ethanolic solution of the Schiff's base ligand and ethanolic solution of metal chloride of Mn(II) taken in 1 : 1 molar ratio and the resulting solution was refluxed on water bath for 2-3 hours. The solution was left overnight to settle. The next day precipitate appeared which was filtered on suction pump and it was dried in desiccator on anhydrous calcium chloride. The melting points of the compounds were determined on digital melting point apparatus Sturt SMP-40. The molar conductance of complexes were determined on a digital conductivity meter MCD, HPG-3001 in DMSO solution of 10⁻³ M concentration. The IR-Spectra of ligand and complexes were recorded on KBR Disc on Nicolet-5 FTIR Spectrometer. The electronic spectra of complexes in DMSO were recorded on C.G-857 Scott Grate GnbH. The magnetic moment of complexes were determined by 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 given below, the complexes were formulated [MnL₂X₂] where, L = HPHM, HOTHB, HMTHB and HPTHB and X stands for Cl. The molar conductivity values of the complexes in DMSO solution of 10⁻³ M concentration were found in the range of 15 to 19 ohm⁻¹cm²mol⁻¹ which indicated that all the complexes were non-electrolytic in nature.

Table – 1 : Analytical, Melting Point, Magnetic Moment, Conductivity Measurement of Ligands and its metal complexes

Sl. No.	Compounds	M. P. (°C)	% Analysis Found/(Calculated)				λ_m ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	μ (BM)
			M	C	H	N		
1.	HPHB	180°C	—	38.18 (68.64)	6.81 (6.48)	15.90 (15.79)	—	—
2.	HOTHB	184°C	—	69.47 (69.72)	7.03 (7.00)	14.73 (14.60)	—	—
3.	HMTHB	184.1°C	—	69.47 (69.78)	7.03 (7.02)	14.73 (14.58)	—	—
4.	HPTHB	184°C	—	69.47 (69.80)	7.03 (7.01)	14.73 (14.62)	—	—
5.	[Mn(HPHB) ₂ Cl ₂]	297°C	11.50 (11.23)	50.20 (50.63)	5.02 (4.92)	11.71 (11.60)	19	5.80
6.	[Mn(HOTHB) ₂ Cl ₂]	304°C	10.86 (10.48)	52.17 (52.43)	5.50 (5.32)	11.06 (10.92)	17	5.81
7.	[Mn(HMTHB) ₂ Cl ₂]	304.2°C	10.86 (10.52)	52.17 (52.45)	5.50 (5.35)	11.06 (10.95)	18	5.80
8.	[Mn(HPTHB) ₂ Cl ₂]	304°C	10.86 (10.55)	52.17 (52.40)	5.50 (5.40)	11.06 (10.96)	15	5.82

4. FTIR SPECTRA

The important and significant IR bands before and after complexation have been detected and assigned. The free ligand displays two medium broad bands at 3400 cm^{-1} and 3410 cm^{-1} which may be assigned to ν_{OH} vibration of free ligand^[6-10]. The strong band appear at 2950 cm^{-1} and a medium band appear at 2860 cm^{-1} are assigned to $\nu_{\text{CH}_3(\text{assy})}$ and $\nu_{\text{CH}_3(\text{sym})}$ ^[11-12]. The IR Spectra of ligands and all the complexes are quite complex but the structurally important vibrational band such as O–H stretching, C–H stretching and $\nu_{\text{N-O}}$ stretching vibration are quite discernible. IR Spectra of ligands don't show a broad band near 3350 cm^{-1} . This indicate the fact that there is no H-bond between OH of oxime group and nitrogen of azomethine of the free ligands^[13-14]. The band appears at 1780 cm^{-1} due to bending mode of vibration of $\nu_{\text{N-OH}}$ group of oxime. In the present study the band absorb nearly 1770 cm^{-1} is well assigned to $\delta_{\text{N-OH}}$. Hence our supposition of the band at 1740 cm^{-1} in the IR Spectra of free ligands to bonding vibration of

$\nu_{\text{N-OH}}$ group a quite reasonable. The $\nu_{\text{C=N}}$ stretching band due to $\nu_{\text{C=N-OH}}$ in diethyl glyoxime appears at 1450 cm^{-1} which shift to a higher frequency reason in its complexes and appear in the range of $1550\text{-}1590 \text{ cm}^{-1}$. The medium intensity bands appearing at 1290 cm^{-1} and 1150 cm^{-1} may be attributed to $\nu_{\text{C-CH}_3}$ and $\nu_{\text{C-CH}_3}$ rocking vibration^[15]. The spectra of free ligand one band appears at 710 cm^{-1} due to out of plane bending vibration of $\nu_{\text{C-H}}$ of mono substituted benzene. In the second ligand a band at 760 cm^{-1} due to out of plane bending vibration of ortho substituted benzene ring. The band appears at 730 cm^{-1} and 810 cm^{-1} which shows the presence of metal substituted benzene and para substituted benzene ring respectively. The weak bands appear at $325\text{-}335 \text{ cm}^{-1}$ due to $\nu_{\text{M-Cl}}$ in the IR Spectra of complexes indicates the presence of Cl in the coordination sphere in all the complexes. Thus the ligands act as neutral bidentate coordinating through azomethine nitrogen and oxime oxygen forming six membered chelate ring with metal ions.

5. MAGNETIC SUSCEPTIBILITY AND ELECTRONIC SPECTRA

The magnetic moment of complexes have been given in table – 1. The Mn(II) complexes exhibit magnetic moment of $5.80\text{-}5.82 \text{ BM}$ which are very close to the value of $\mu_s = 5.92 \text{ BM}$ corresponding to five unpaired electrons and indicative of octahedral geometry of the complexes. These complexes displays four bands in their electronic spectra which may be assigned as below :-

$$\nu_1 = 18,000 - 18,480 \text{ cm}^{-1} = {}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g} ({}^4\text{G})$$

$$\nu_2 = 20,780 - 21,240 \text{ cm}^{-1} = {}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g, {}^4\text{A}_{1g} ({}^4\text{G})$$

$$\nu_3 = 25,240 - 26,625 \text{ cm}^{-1} = {}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g ({}^4\text{D})$$

$$\nu_4 = 26,500 - 27,810 \text{ cm}^{-1} = {}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g} ({}^4\text{P})$$

The various crystal field parameters derived from electronic spectral bands of Mn(II) complexes using Tanabe Sugano Diagram have been given in Table – 2.

Table – 2

Sl. No.	Complexes	10Dq (cm^{-1})	B (cm^{-1})	$\beta(\%)$	ν_2/ν_1
1.	[Mn(HPHB) ₂ Cl ₂]	8670	788.08	17.91	1.150
2.	[Mn(HOTHB) ₂ Cl ₂]	8932	769.80	19.17	1.154
3.	[Mn(HMTHB) ₂ Cl ₂]	8892	780.07	18.75	1.149
4.	[Mn(HPTHB) ₂ Cl ₂]	8840	768.61	19.93	1.150

The values of various crystal field parameters are in good agreements with values reported for octahedral complexes of Mn(II)^[16-20].

6. CONCLUSION

The present study reveals that the Schiff base 3-hydroxylamine-2-butenone contains two potential sites for coordination to metal ions. Thus, it behaves as neutral bidentate coordinating through azomethine nitrogen and oxime oxygen. On the basis of magnetic moment values and electronic spectra of Mn(II), they are found to be octahedral symmetry. This may be attributed to the fact that due to increase in bulkiness around the donor atoms decreases the donor capacity of the ligands leading to 10Dq values. As the bulk was increased by introducing methyl group on benzene ring the coordinating ability of N is found to decrease.

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