



SYNTHESIS, SPECTRAL AND PHYSICOCHEMICAL STUDIES OF Mn (II) AND Fe (III) COMPLEXES DERIVED FROM SCHIFF BASES

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ABSTRACT

Ligation properties of Schiff bases derived from 2- aminophenol and substituted aldehydes have been investigated for this purpose. Mn (II) and Fe (III) complexes of these are synthesized and characterized on the basis of elemental analysis, magnetic, thermal and spectral studies. The complexes conform to 1 : 1 stoichiometry and are non-electrolytic in nature. The coordination of the ligand to the metal ions is found to be through azomethine nitrogen and phenolic oxygen of the Schiff bases in the octahedral environment. Most of the metal complexes show antimicrobial activity.

Key words : Schiff base, Transition metal complex, Mn (II), Fe (III)

INTRODUCTION

Metal complexes of Schiff bases have been extensively studied due to their synthetic flexibility, selectivity and sensitivity towards the central metal atom. The chemistry of Schiff base complexes continues to attract many chemists because of their applications in various fields like food and dyes industry^{1,2}, analytical chemistry^{3,4}, catalysis^{5,6} and biological studies⁷. The literature survey reveals a wealth of data on the transition metal complexes, but complexes of Schiff bases derived from aromatic amines with different substituted aldehydes have been comparatively less investigated as ligands. It was, therefore, proposed to investigate the ligation properties of Schiff bases derived from 2 - aminophenol with substituted aldehydes and their complexes with transition metal ions.

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EXPERIMENTAL

All the chemicals and solvents used were of A.R. grade. Elemental analysis was done on Perkin Elmer elemental auto analyzer and CHNS thermoquest auto analyzer. IR spectra were recorded on Bomem MB 104 FTIR spectrophotometer. ^1H NMR spectra were recorded on Bruker FT 300 at 300 MHz NMR spectrometer in $\text{CDCl}_3 + \text{DMSO}_d_6$ solvent, using TMS as an internal standard. Magnetic measurements were carried out by the Gouy method at room temperature. The magnetometer was calibrated using $\text{Hg}[\text{Co}(\text{NCS})_4]$. Diamagnetic corrections were made by using Pascal's constants. The TGA and DTA were recorded on 'Mettler Toledo star system' at RSIC Nagar University, Nagpur. The analytical data are presented in Table 1.

Synthesis of Schiff bases

The ligands, Schiff bases, were synthesized by following the procedure described earlier⁹. The purity was checked by M. P. and TLC technique. Further the structures of the Schiff bases were conformed by subjecting them to IR, NMR and mass spectral studies.

Synthesis of metal complexes

The metal chlorides and Schiff bases in the molar ratio of 1 : 2 were dissolved in ethanol. The pH of the resulting solution was adjusted just below the value of hydrolysis of the respective metal ion, using alcoholic ammonia. The reaction mixture was refluxed for 3 - 4 hours while stirring continuously. The precipitate formed was separated by filtration and washed with hot ethanol followed by pet ether (40-60°C) and dried *in vacuo*.

RESULTS AND DISCUSSION

The complexes have different colors and seem to be semicrystalline. All the complexes are stable in air for extended periods of time. The solids do not melt sharply and undergo decomposition. These are insoluble in water and soluble in organic solvents such as DMF, DMSO giving respective colors to the solutions. All compounds gave satisfactory elemental analysis. Values are in close agreement with the values calculated for expected molecular formulae assigned to these complexes, suggesting 1 : 1 (M : L) stoichiometry. The molar conductance values of all the complexes in DMSO reveal their non-electrolytic nature.

The IR spectra of the free ligands show an – OH absorption band in the region 3325- 3382 cm^{-1} . This sharp band disappeared in the complexes, indicating its involvement

Table 1: Analytical data of the ligands and complexes

S. No.	Compound	Molecular formula (Molecular weight)	Color	% Metal found (Calculated)	Elemental analysis			Molar conductance λ_m	Magnetic susceptibility χ_g B.M.
					%C	%H	%N		
1	Ligand A	$C_{13}H_{11}NO$ (197.236)	Pale yellow	79.10 (79.16)	5.58 (5.62)	7.02 (7.10)	---	---	
	Mn (II) - A	$Mn(II)$ $C_3H_{11}NOCl_2 \cdot 2H_2O$ (359.108)	Dark brown	15.102 (15.298)	2.888 (3.09)	3.782 (3.90)	14.924 (19.74)	5.713	
	Fe (III) - A	$Fe(III)$ $C_{13}H_{11}NOCl_2 \cdot 2H_2O$	Blackish red (faint)	15.392 (15.51)	2.891 (3.08)	3.683 (3.89)	24.302 (19.70)	5.762	
2	Ligand - B	$C_{13}H_{10}ClNO$ (231.68)	Greenish yellow	---	67.34 (67.40)	4.32 (4.35)	14.93 (15.30)	---	
	Mn (II) - B	$Mn(II)$ $C_{13}H_{10}ClNOCl_2 \cdot 2H_2O$ (393.55)	Dark brown	13.835 (13.96)	2.485 (2.56)	3.496 (3.56)	16.324 (18.02)	5.556	
	Fe (III) - B	$Fe(III)C_{13}H_{10}ClNOCl_2 \cdot 2H_2O$ (394.46)	Shining brown black	14.023 (14.16)	2.388 (2.56)	3.402 (3.55)	23.538 (17.98)	5.628	

Cont...

S. No.	Compound	Molecular formula (Molecular weight)	Color	% Metal found (Calculated)	Elemental analysis			Molar conductance λ_m	Magnetic susceptibility χ_g B.M.
					%C	%H	%N		
3	Ligand - C	$C_{13}H_{10}ClNO$ (231.680)	Greenish yellow (Faint)	--	67.32 (67.40)	4.31 (4.35)	5.98 (6.05)	14.93 (15.30)	--
	Mn (II) - C	$Mn(II)C_{13}H_{10}ClNOCl_2 \cdot 2H_2O$ (393.552)	Faint brown	13.883 (13.959)	39.503 (39.68)	2.501 (2.56)	3.492 (3.56)	17935 (18.02)	5.645
	Fe (III) - C	$Fe(III)C_{13}H_{10}ClNOCl_2 \cdot 2H_2O$ (397.307)	Light green	14.695 (14.773)	39.188 (39.30)	2.465 (2.54)	3.413 (3.56)	17.698 (17.85)	5.633
4	Ligand - D	$C_{14}H_{13}NO_2$ (227.264)	Yellow green	--	73.95 (73.99)	5.72 (5.77)	6.11 (6.16)	---	--
	Mn (II) - D	$Mn(II)C_{14}H_{13}NO_2Cl_2 \cdot 2H_2O$ (389.314)	Dark brown	14.012 (14.118)	43.107 (43.21)	3.288 (3.34)	3.492 (3.60)	18.135 (18.22)	5.783
	Fe (III) - D	$Fe(III)C_{14}H_{13}NO_2Cl_2 \cdot 2H_2O$ (392.889)	Brick red	14.235 (14.32)	43.018 (43.11)	3.248 (3.36)	3.468 (3.59)	18.015 (18.20)	5.787
		Ligand A: N - (Benzilidene) - 2-hydroxyaniline	Ligand C: N - (4' -chlorobenzilidene) - 2 -hydroxyaniline						
		Ligand B: N - (2' -chlorobenzilidene) - 2 -hydroxyaniline	Ligand D: N - (4' -methoxybenzilidene) - 2 -hydroxyaniline						

involvement in the bond formation process^{1°}. The strong band at 1623 – 1625 cm¹ due to C=N stretching frequency is lowered by 9-25 cm¹ in the spectra of the complexes, indicating coordination through azomethine nitrogen of the Schiff bases^{11,12}. The new bands appearing in the region 400- 450 and 500- 624 cm¹ may be probably due to coordinated water molecule and the formation of ν (M-N) and ν (M-O) bands, respectively^{13,14}. The broad absorption band observed in all the complexes in the region 3200- 3600 cm¹ could be attributed to the lattice water present in the metal complexes.

The ¹H NMR spectra of ligands A, B, C and D have been recorded in CDCl₃. In all the ligands – OH group appeared in the range 6.9 to 8.15 δ ppm and C=N group at 8.65 to 9.10 δ ppm. In ligand D, the -OCH₃ proton appears at 3.8 δ ppm. The rest of the proton appeared in the aromatic region at 6.5 to 8.0 δ ppm. An examination of NMR spectra of the ligand reveals that these are on expected lines according to their structures. A comparison of these spectra with those of the complexes gives a clear picture of the changes taking place in the ligands. The ¹H NMR spectra of the complexes were also recorded. Unfortunately, however, due to the presence of a metal ion, proton resonance was not affected and one could observe only broad peaks indicating the formation of the complexes.

In the mass spectra of the ligands, probable fragmentation into certain structural units was observed for the ligands under investigations and it was as follows –

Ligands	Fragments
A	M ⁺ 197, 180, 120 (100%) 104.
B	M ⁺ 231 (having isotopic peaks), 196, 167, 120 (100%), 93.
C	M ⁺ 231 (100% with isotopic peaks), 196, 167, 120, 93.
D	M ⁺ 227 (100%), 205, 183, 120, 77.

The theoretical molecular weight was calculated for the ligands, which matches the experimental molecular weight of the ligands.

In the present investigation, the presence of water molecules in the metal complexes as indicated in the IR spectra was ascertained and verified by the thermal analysis. The thermal studies indicate that complexes decompose after dehydration.

The thermogram of the Mn (II) and Fe (III) complexes showed weight loss in the range 45-140°C. This could be due to loss of absorbed water or water of crystallization and lattice water molecules. The further weight loss between 260-450°C could be due to escape of chloride ions. The losses thereafter could be attributed to the loss of ligand; finally the complexes were converted into their metal oxides^{15,16}.

The magnetic moment values at room temperature for the complexes under study are given in Table 1.

The magnetic moment values of the Mn (II) and Fe III complexes under present investigation are in the range 5.56-6.11 and 5.63-5.91 B. M. These values are close to that expected (5.70-6.00) for octahedral geometry¹⁷.

The molar conductance of 10^{-3} M solutions in DMSO at room temperature of the complexes has been measured and the values are reported in Table 1.

These values were found to be ranging between 16, 324-25, 423 $\text{ohm}^{-1} \cdot \text{cm}^2 \text{mol}^{-1}$ and these values indicate that all the complexes are nonelectrolytes^{18,19}.

The ligands and their metal complexes were screened for their antibacterial and antifungal activity in vitro against *S. aureus* 209p, *E. coli* ESS 2231, *Aspergillus fumigatus*, *Candida albicans*, *Candida albicans* ATCC 10231, *Candida krusei* GO 3 and *Candida glabrata* HO5, using standard agar well diffusion assay method²⁰. The Mn (II) complexes showed good antifungal and moderate antibacterial activity, while Fe (III) complexes were inactive towards all organisms. From the results, one is tempted to conclude that though the ligands are not effective against these microbes, but their metal complexes seem to have developed a fair antimicrobial activity. Such enhanced antimicrobial activity in the metal complexes was also reported earlier²¹.

ACKNOWLEDGEMENT

The authors thank the NCL, Pune, RSIC, Chandigrah and Nagpur for spectral and TGA/DTA analysis. One of the authors, GRP is thankful to UGC (WRO), Pune for award of research fellowship.

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