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Synthesis, Characterization and Antimicrobial Studies of Some Metal Complexes with Schiff Bases

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Ligation properties of Schiff bases derived from 2-aminophenol and substituted aldehydes have been investigated. Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of the Schiff bases were synthesized and characterized on the basis of elemental analysis, magnetic, thermal and spectral studies. The complexes confirmed the 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 phonolic oxygen of the Schiff bases in the octahedral environment. Most of the metal complexes show antimicrobial activity.

Key Words: Synthesis, Schiff base, Biological activities, Transition metal complexes.

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 because of their applications in various fields like food and dyes industry[1], analytical chemistry[2], catalysis[3] and biological studies[4]. The literature survey reveals a wealth of data on the transition metal complexes of Schiff bases derived from aromatic amines with different substituted aldehydes. In the present paper, the ligation properties of Schiff bases derived from 2-aminophenol with substituted aldehydes and their complexes with transition metal ions were studied.

EXPERIMENTAL

All the experimental work was carried out in corning glass apparatus. The burettes, pipettes and volumetric flasks were calibrated by standard methods[5]. All the chemicals and solvents used were of AR 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. ^{1}H NMR spectra were recorded on Brucker FT

300 at 300 MHz NMR spectrometer in $CDCl_3$ + 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 $Hg(Co(NCS)_4)$. Diamagnetic corrections were made by using Pascal's constants. The TGA, DTA were recorded on 'Mettler Toledo Star System' at RSIC, Nagpur University, Nagpur.

Synthesis of Schiff bases: The ligands, Schiff bases, were synthesized according to the procedure described earlier[6]. The purity was checked by m.p. and TLC technique. The structures of the Schiff bases were confirmed by 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 h, while stirring continuously. The precipitate formed was separated by filtration and washed with hot ethanol followed by petroleum ether (40-60 ºC) and dried *in vacuo*.

RESULTS AND DISCUSSION

The complexes have different colours and seem to be semi-crystalline. All the complexes are stable in air for certain 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 colours to the solutions. All compounds gave satisfactory elemental analysis. The values are in close agreement with the values calculated for expected molecular formulae assigned to these complexes, suggesting 1:1 stoichiometry. The molar conductance values of all the complexes in DMSO reveal their non-electrolytic nature. The analytical data are presented in Table-1.

The IR spectra of the free ligands show an -OH absorption band at 3419 and 3340 cm^{-1}. This sharp band has disappeared in the complexes, indicating its involvement in the bond formation process[7]. The strong band at 1625-1618 cm^{-1} due to C=N stretching frequency is lowered by 25-29 cm^{-1} in the spectra of the complexes, indicating coordination through azomethine nitrogen of the Schiff bases[8]. The new bands appearing in the region 450-420 and 659-599 cm^{-1} may probably due to coordinated water molecule and the formation of ν(M-N) and ν(M-O) bands, respectively[9]. The broad absorption band observed in all the complexes in the region 3600-3200 cm^{-1} could be attributed to the lattice water present in the metal complexes.

^{1}H NMR spectra of ligands A and B have been recorded in $CDCl_3$. In both ligands -OH group appeared in the range 6.9 to 8.15 δ ppm. While C=N group at 8.85 to 9.10 δ ppm. In ligand B, the $-CH_3$ proton appear at

TABLE-1
ANALYTICAL DATA OF THE LIGANDS AND COMPLEXES

Compd.	m.f. (m.w.)	Colour	Elemental analysis (%): Found (Calcd.)					Molar cond. λ_m	Magnetic susceptibility χ_g (BM)
			M	C	H	N	Cl		
Ligand A	$C_{13}H_{10}N_2O_3$	Light yellow	–	67.38	4.11	11.50	–	–	–
	(242.232)			(67.46)	(4.16)	(11.56)			
Mn(II)-A	$Mn(II)C_{13}H_{10}N_2O_3Cl_2\cdot 2H_2O$	Dark brown	13.488	38.599	2.315	6.807	17.464	17.538	6.105
	(404.104)		(13.595)	(38.639)	(2.494)	(6.932)	(17.546)		
Fe(III)-A	$Fe(III)C_{13}H_{10}N_2O_3Cl_2\cdot 2H_2O$	Shine dark red	13.789	38.435	2.368	6.812	17.402	23.103	5.919
	(405.017)		(14.698)	(38.553)	(2.489)	(6.917)	(17.507)		
Co(II)-A	$Co(II)C_{13}H_{10}N_2O_3Cl_2\cdot 2H_2O$	Dark reddish brown	14.303	38.123	2.312	6.698	17.212	29.438	4.815
	(408.099)		(14.441)	(38.261)	(2.470)	(6.864)	(17.374)		
Ni(II)-A	$Ni(II)C_{13}H_{10}N_2O_3Cl_2\cdot 2H_2O$	Shine dark red	14.282	38.103	2.401	6.722	17.225	20.596	3.241
	(407.859)		(14.391)	(38.284)	(2.471)	(6.868)	(17.384)		
Cu(II)-A	$Cu(II)C_{13}H_{10}N_2O_3Cl_2\cdot 2H_2O$	Shine dark red	15.198	37.718	2.382	6.616	17.025	11.765	2.189
	(412.712)		(15.397)	(37.833)	(2.442)	(6.788)	(17.180)		
Ligand B	$C_{14}H_{13}NO$	Yellowish brown	–	79.54	6.15	6.59	–	–	–
	(211.263)			(79.59)	(6.20)	(6.63)			
Mn(II)-B	$Mn(II)C_{14}H_{13}NOCl_2\cdot 2H_2O$	Reddish brown	14.628	45.003	3.395	3.635	18.894	15.048	5.698
	(373.135)		(14.723)	(45.065)	(3.512)	(3.754)	(19.002)		
Fe(III)-B	$Fe(III)C_{14}H_{13}NOCl_2\cdot 2H_2O$	Shining brown	14.815	44.812	3.401	3.690	18.783	22.689	5.782
	(374.041)		(14.930)	(44.956)	(3.503)	(3.745)	(18.956)		
Co(II)-B	$Co(II)C_{14}H_{13}NOCl_2\cdot 2H_2O$	Reddish brown (dark)	15.512	44.435	3.312	3.612	18.710	27.530	4.642
	(377.130)		(15.627)	(44.588)	(3.474)	(3.714)	(18.801)		
Ni(II)-B	$Ni(II)C_{14}H_{13}NOCl_2\cdot 2H_2O$	Dirty green	15.423	44.502	3.321	3.603	18.693	21.095	3.308
	(376.890)		(15.573)	(44.611)	(3.477)	(3.716)	(18.813)		
Cu(II)-B	$Cu(II)C_{14}H_{13}NOCl_2\cdot 2H_2O$	Chocolate brown	16.531	44.002	3.312	3.523	18.432	15.905	1.964
	(381.743)		(16.646)	(44.049)	(3.432)	(3.669)	(18.574)		

Ligand A = N-(4′-Nitrobenzilidine)-2-hydroxyaniline; Ligand B = N-(4′-Methylbenzilidine)-2-hydroxyaniline.

2.4 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 would have given a clear picture of the changes taking place in the ligands. However, due to the presence of a metal ion, proton resonance was not effected 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 it was as follows:

Ligands	Fragments
Ligand A	M^+ 242, 195, 167, 120 (100 %), 93.
Ligand B	M^+ 210, 120 (100 %), 91, 77.

The theoretical molecular weight calculated for the ligands, which matches with 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 as certained and verified by the thermal analysis. The thermal studies indicate that complexes decompose after dehydration.

The thermogram of the Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes showed weight loss in the range 133-190 ºC. This could be due to loss of lattice water molecules. The further weight loss between 230-270 ºC could be attributed to the loss of one chloride while the loss between 360-620 ºC could be due to simultaneous loss of another chloride and ligand moiety. Finally the complexes were converted into its metal oxide[10,11].

The magnetic moment values of the Mn(II) and Fe(III) complexes are in the range 5.70-6.11 BM. While for Ni(II) 3.24-3.31 BM and Co(II) 4.64-4.82 BM for high spin Co(II) complexes are on expected lines and agree with the previously ones for octahedral configuration[12]. The slightly higher value could be due to some orbital contribution. The magnetic moment values of Cu(II) complexes are marginally higher (1.96-2.19) than the spin only value of 1.73 BM expected for d^9 system and could be attributed to spin orbit coupling. The complex might be undergoing Jahn-Teller distortion[13].

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 11.77-29.44 ohm^{-1} cm^2 mol^{-1} and values indicate that all the complexes are non-electrolytes[14].

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* GO3 and *Candida glabrata* HO5, using standard agar well diffusion assay method[15]. The Mn(II) and Cu(II) complexes showed good antifungal and moderate antibacterial activity while Co(II) complexes showed moderate antimicrobial activity. It is interesting to note that Ni(II) complexes are moderately active against *Candida* spp. 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 their metal complexes seem to have developed a fair antimicrobial activity. Such enhanced antimicrobial activity in the metal complexes was reported earlier[16].

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