Studies on Synthesis and Characterisation of Complexes with Schiff Base as Ligand Derived from 4-Hydroxybenzaldehyde and 2-Aminothiazole

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***Abstract*— The present work embodies metal complexes of Cr(III), Co(II), Ni(II) and Cu(II) with Schiff base p-HBAT as ligand having oxygen, nitrogen and Sulphur donars these complexes are characterized on the basis of analytical, magnetic moment, IR spectra and electronic spectral data. Various ligand filled parameters are used to evaluated the structure of complexes containing Schiff base as ligand and their structures have been found to be octahedral. The ligand and complexes have also been tested against bacteria E.Coli.**

Keywords— p-HBAT, Complexes, Structural Properties, Biocidal.

Introduction

Schiff base p-HBAT is a weak ligand and form high spin complexes with Cr(III), Co(II), Ni(II) and Cu(II) ions. These complexes have a vital role in practical utility and biological activity. The synthesis of complexes with p-HBAT as ligand has been of growing importance in the development of coordination chemistry[1-6]. Thiazole derivatives are receiving attention due to their biological and pharmaceutical activities[7]. On coordination the biological activity of thiazoles changes markedly. The sulphur containing organic compounds have been found variegated use in medicine e.g. antituberculous[8], hypnotics[9], Local anaesthetics[10],etc.

Experimental Synthesis of p-HBAT (Schiff Base)

For the preparation of p-HBAT, the equimolar amount of 4-Hydroxybenzaldehyde and 2-aminothiazole are dissolved in 15ml of ethanol. The mixture is refluxed on a water bath for about 14 hours using water condenser. The solution thus obtained is cooled at room temperature and the excess of ethanol is allowed to evaporate slowly. The concentrated solution is cooled. The product obtained is filtered, washed with ether and dried under reduced pressure.

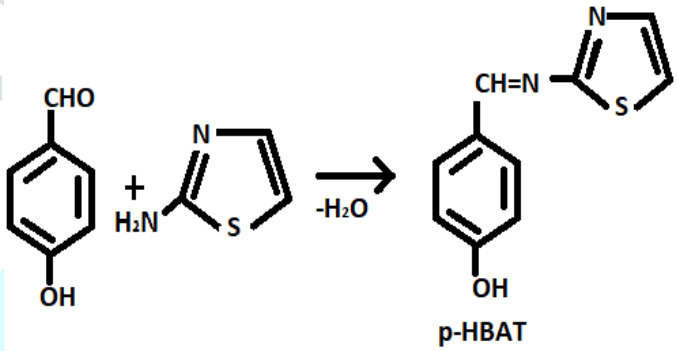
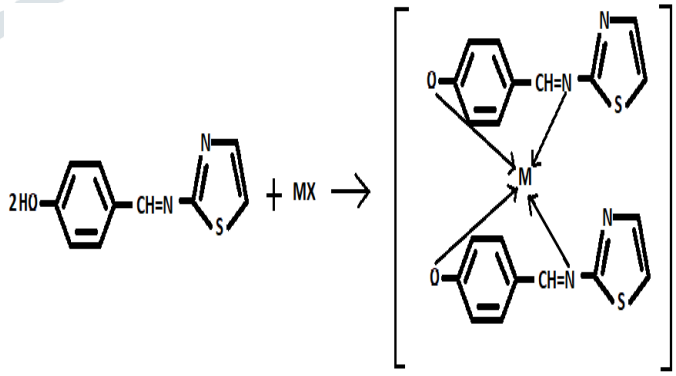


Fig 1.

Synthesis of Metal Complexes

At present work complexes of Cr(III), Co(II), Ni(II) and Cu(II) are prepared using Schiff base as –

5m mole of metal ion and 10m mole Schiff base (p-HBAT) are dissolved in 25ml of ethanol separately. These alcoholic solutions are refluxed on a water bath for 2 to 3 hours.the content is cooled and the solvent is evaporated slowly. The residue is washed with ethanol and either and dried in air.



Where M= Co(II), Ni(II), Cu(II) and Cr(III),X= Cl^-, CH_3COO^-

Fig 2.

Magnetic Measurements

The magnetic moment values of above complexes suggest that these complexes have octahedral geometry [11]. These complexes are spin free complexes and paramagnetic in

nature. The magnetic moment of these complexes are given in Table 1.

Complex	μ_s (BM)	μ_{obs}(BM)
$Co[(C_{10}H_8N_2OS)_2]Cl_2$	3.87	4.20 to 4.35
$Ni[(C_{10}H_8N_2OS)_2]Cl_2$	2.82	2.80 to 2.95
$Cu[(C_{10}H_8N_2OS)_2]Cl_2$	1.73	1.75 to 1.80
$Cr[(C_{10}H_8N_2OS)_2](CH_3COO)_3$	3.87	3.66 to 3.75

Table 1

Electronic Spectra

The electronic spectra of isolated Co(II) complex shows 3 clear bands assigned by transition $^4T_{1g} \longrightarrow {}^4T_{2g}$ (F) (υ_1), $^4T_{1g} \longrightarrow {}^4A_{1g}$ (F) (υ_2) and $^4T_{1g} \longrightarrow {}^4T_{2g}$ (P) (υ_3) in order of increasing energy. There assignments are in good agreement for octahedral geometry [12,13]. The Ni(II) chelate exibits 3 absorption bands assigned by transition $^3B_{1g} \longrightarrow {}^3B_{2g}(\upsilon_1)$, $^3A_{2g}$ (F) $\longrightarrow {}^3T_{1g}$ (F) (υ_2) and $^3A_{2g}$ (F) $\longrightarrow {}^3T_{2g}$ (P) (υ_3) transitions, respectively indicating an tetragonal geometry [14]. The electronic spectrum of Cu(II) complex shows three clear bands which may be assigned due to transition $^2B_{1g} \longrightarrow$

Complex	υ_1(cm^{-1})	υ_2(cm^{-1})	υ_3(cm^{-1})
$Co[(C_{10}H_8N_2OS)_2]Cl_2$	8428	18018	20300
$Ni[(C_{10}H_8N_2OS)_2]Cl_2$	10790	16790	25900
$Cu[(C_{10}H_8N_2OS)_2]Cl_2$	12000 to 17000	15500 to 18000	17000 to 20000
$Cr[(C_{10}H_8N_2OS)_2](CH_3COO)_3$	17810	24570	38050

$^2A_{1g}(\upsilon_1)$,$^2B_{1g} \longrightarrow {}^2B_{2g}(\upsilon_2)$, $^2B_{2g} \longrightarrow {}^2E_g(\upsilon_3)$.

Table 2

The electronic spectrum of Cr(III) complex exhibit three absorption bands due to the transitions $^4A_{2g} \longrightarrow {}^4T_{1g}$(P) ($\upsilon_1$), $^4A_{2g} \longrightarrow {}^4T_{1g}$(F) ($\upsilon_2$) and $^4T_{1g} \longrightarrow {}^4T_{2g}$(F) ($\upsilon_3$) respectively.

The different bands shown by these complexes are given in Table 2.

NMR spectral studies

The NMR spectra of the Schiff base was recorded in DMSO, assigned as a solvent peak in the spectrum at 3.41 ppm. A doublet may be due to heterocyclic proton (2H) present in thiazole ring were observed in the spectrum at 7.0 ppm. A quartet at 7.1 ppm equivalent to 411 was present in the aromatic benzene ring. The quartet is in the form of 2 equal height and doublet, which indicate para substitute benzene ring. A singlet was observed at 5.2 ppm equivalent to 1 H, may be assigned as O-H proton on para position. A singlet at6.3 ppm equivalent to 1H was present in the (CH=N) azomethine linkage. All the NMR spectral data are given in Table-3.

Peak Position	No.of Protons	Chemical Schift (δ ppm)	Group Assigned
Doublet	2H	7.0	Thiazole
Singlet	1H	5.2	O-H
Singlet	1H	6.3	Azomethine
Quartet	4H	7.1	Benzene ring

Table 3

IR spectral studies

IR spectra of Schiff base shows a band at 1598 cm^{-1}may be due to azomethine linkage. A shift of 20 cm^{-1} in this frequency is observed suggestive of the coordination of metal ion with azomethine linkage[15] in the spectrum of ligand a broad band of -OH stretching vibration appear at 3630cm, which disappeared in complexes thus indicating deprotonation of phenolic oxygen. Other bands that a appeared in the spectra of complexes in the region 580-500, 490-380 and 293-297 cm-may be assigned toM-0, M-N and M-Cl modes[16].

The characteristics infrared band in the spectra of the ligand are observed at 1517 (C N cyclic), 1378 (C-N) and 849 cm^{-1} (C-S-C) of the thiazole moiety[17]. The position of these bands remains unaltered in the complexes ruling out the possibility of coordination of ring nitrogen of the thiazole moiety. In halogen complexes [18] bridging halogen bands were identified in the region 300-200 cm. So on the basis of above discussion we may assigned that Synthesized Schiff base ($C_{10}H_8N_2OS$) is most probably bidentate in nature having ON donor system. All the IR spectral data are given in Table-4.

Ligands/Complexes	Ligand Modes				Coordination Modes		
	v(CH=N)	v(OH)	v(C-S-C) Thiazole	v(C=N) cyclic	vM-O	vM-N	vM-C
$C_{10}H_8N_2OS$	1598	3630	849	1517	-	-	-
$Co[(C_{10}H_8N_2OS)_2]Cl_2$	1605	-	843	1512	516	420	293
$Ni[(C_{10}H_8N_2OS)_2]Cl_2$	1608	-	845	1513	518	425	295
$Cu[(C_{10}H_8N_2OS)_2]Cl_2$	1611	-	846	1515	526	430	297
$Cr[(C_{10}H_8N_2OS)_2](CH_3COO)_3$	1617	-	848	1516	525	435	-

Table 4

Physical measurements

The metal and sulphur contents were estimated hy the standard methods [19]. The carbon, hydrogen and nitrogen contents were analysed on C-H micro analyzer at C.S.I.F., C.D.R.L. Lucknow. Infrared spectra were recorded on 'Perkin Elmer 577' spectrophotometer at C.S.I.F.. CDRI Lucknow. The magnetic susceptibility measurements were carried out at room temperature on EG & G model-155' by VSM (Vibrating Sample Magnetorneter) method at C.S.I.F., IIT,Chennai. The

electronic spectra were recorded on Elico SL - 17!'spectrophotometer at room temperature at Desartn:ent of Chemistry, L.B.S., Agra. The NMR-and Mass spectral studies were carried out from C.S.1.F., CDRI,Lucknow.

underground water for drinking of Langat Singh College Campus is not fit for direct human consumption with respect to total dissolved solids, total hardness, fluoride and chloride concentration. The ground water of most of the campus is polluted and not safe for public health as well as plants. Its pH total dissolved solids and total hardness are much more than thein maximum permissible limit. Excess fluoride was also encountered in almost all samples to the prescribed limit set by WHO. Therefore, the use of ordinary hand pumps should be discoursed people dependent on this water are often prone to health hazards due to polluted drinking water. Therefore, indigenous technologies should be adopted to make the water fit for drinking after desalination treatment. The safe drinking water in the affected areas could also be provided by sanctioning schemes based on surface water source. One should must remember the fact that water and especially drinking water is an important essential component to stay alive for the human beings and animals and especially for any living organism8-12.

Anti-microbial studies

Synthesized Schiff base and their corresponding metal complexes were tested for the growth inhibitory activity against pathogenic bacteria Escherichia coli. The comparative studies indicate that the complexes are more active than the parent ligand against E.coli and the solvent did not exhibit any activity at the concentrations used. Filter paper disc method [20] at various concentrations using nutrients agar as medium. The Schiff base C10H8N2OS is almost inactive against E coli at the conc. Of 250 ppm and 500 ppm, while it showed optimum activity at 750 ppm. The activity of Co (II) complex increases with conc. i.e. at 250 ppm they are less active but at 750 ppm they showed good activity. The Ni complex is also found biologically active at 500 ppm conc. The activity of Ni (I1) and Co (II) complexes are almost different, while at 750 ppm conc. Ni (II) complex shows better activity against E.coli in comparison to Co (II) complex. The activity of Cu (1I) complex increases with conc. i.e., at 250 ppm they are less active but at 750 ppm they showed good activity against E. coli in comparison to Co (II), Ni Q) complexes. The acetate salt of Cr.(III),complex is almost inactive at nearly all concentrations. The data is presented in Table-5.

Results and Discussion

All these complexes are spin free complexes. These are partially soluble in inorganic solvents while moderately soluble in organic solvents DMF, DMSO and Dioxan.

Compounds	Concentration (ppm)		
	250	500	750
$C_{10}H_8N_2OS$	-	-	4.5
$Co[(C_{10}H_8N_2OS)_2]Cl_2$	4.4	5.5	6.5
$Ni[(C_{10}H_8N_2OS)_2]Cl_2$	4.4	6.5	7.5
$Cu[(C_{10}H_8N_2OS)_2]Cl_2$	4.4	7.0	8.5
$Cr[(C_{10}H_8N_2OS)_2](CH_3COO)_3$	-	4.2	4.5

Schiff base/ Metal Complexes	MP(°C)	Formula Weight	Color	Percentage of elements (found/calculated)						μ(B.M)
				C%	H%	N%	S%	Cl%	M%	
$C_{10}H_8N_2OS$	135	204.15	Brown	56.95/ 58.82	3.96/ 3.92	13.81/ 13.72	15.77/ 15.70	-	-	-
$Co[(C_{10}H_8N_2OS)_2]Cl_2$	150	538.13	Dark Green	47.75/ 44.63	2.98/ 2.97	10.46/ 10.39	11.76/ 11.89	13.10/ 13.18	10.96/ 10.95	4.25
$Ni[(C_{10}H_8N_2OS)_2]Cl_2$	250	537.89	Dark Brown	47.55/ 44.66	2.85/ 2.98	10.55/ 10.41	11.86/ 11.92	13.29/ 13.18	10.94/ 10.91	2.86
$Cu[(C_{10}H_8N_2OS)_2]Cl_2$	155	542.74	Dirty Black	47.57 /44.26	2.89/ 2.95	10.26/ 10.32	11.74/ 11.81	13.26/ 13.06	11.77/ 11.71	1.78
$Cr[(C_{10}H_8N_2OS)_2](CH_3COO)_3$	230	637.29	Dark Brown	39.56/ 37.69	2.57/ 2.51	8.66/ 8.79	10.16/ 10.06		8.44/ 8.16	3.70

Table 6

The analytical and physical data of these complexes are given in table 6.

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