

## **Synthesis and Characterization of the Complexes of Some Transition Metals with 4-[2'-hydroxy salicylidene -5' (2''-thiazolyazo) Chlorobenzene**

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### **ABSTRACT**

Complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 4-[2'-hydroxy salicylidene 5' (2''-thiozylazo) chlorobenzene have been synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility, spectral studies, IR. electronic, ESR and X-ray diffraction studies. All complexes exhibit the composition  $M_2 L_2 X_2$ , where M = Co (II), Ni (II), Cu (II), Zn (II) and Cd (II), L = 4-[2'-hydroxy salicylidene 5' (2''4thiazolyazo) chlorobenzene and X=C1. The metal coordinate with Schiff base nitrogen atom azo nitrogen, atom and phenolic hydroxyl oxygen atom of the ligand. The ONN donor ligand acts as a tridentate ligand in all complexes. The spectral analysis indicate tetrahedral geometry for Co(II), Ni(II), Zn(II) and Cd(II) complexes while distorted tetrahedral geometry for the Cu (II) complex. The X-ray powder diffraction of some complexes were studied and suggest tetragonal crystal system.

The ligand and complexes have been screened for their antimicrobial activity against some bacterial and fungal activity.

**Key words :** *Azo Schiff Base, metal complexes.*

### **1. Introduction**

Transition metal complexes with Schiff bases as ligands have been amongst the widely studied coordination compounds in the past few year, since they are found to be important as biochemical, analytical and antimicrobial reagent [1,3]. The complexes of azo compounds also exhibits bacteriostatic and other biochemical activities, Heterocyclic azo Schiff base and their complexes with transition metal ions are also of importance due to their complexing, catalytical biological properties [4,5].

Heterocyclic ring containing sulphur, nitrogen and oxygen impart special

biological activity to these Schiff bases and their metal complexes [6]. In view of the interesting ligating behavior of such system, we considered it worthwhile to prepare Co (II), Ni (II), Cu (II), Zn (II) and Cd (II) complexes of tridentate ligand derived from 5-(2'-thiazolylazo) salicylaldehyde and p-chloroaniline. The complexes have been characterized by various physicochemical methods.

## **2. Experimental**

All the chemicals, materials and solvents used were AR grade. The compound 5-(2'-thiazolylazo) salicylaldehyde was prepared according to the literature method [7]. The purity of these compounds was checked by TLC and melting point determination.

## **3. Preparation of Ligand**

The ligand Schiff base was prepared by refluxing equimolar concentration of 5-(2'-thiazolylazo) salicylaldehyde (0.2334 g, 1 mole) in 50 ml ethanol with p-chloroaniline (0.1412 g, 1mole) in 15 ml ethanol for 4 hour. It was then cooled and poured into crushed ice, when a brick-red compound separated out, which was filtered washed and recrystallised from ethanol.

## **4. Synthesis of Complexes**

To a ethanolic solution of ligand 4-[(2'- hydroxy salicylidene 5'- (2''-thiazolylazo)] chlorobenzene (1 mole), a solution of appropriate metal (II) chloride (1 mole) in 25ml hot ethanol was added drop-wise with constant stirring. The reaction mixture was refluxed on water bath for about 2-3 hours and then cooled to room temperature. The  $pH$  was adjusted to 7.5 using alcoholic ammonia solution. The respective metal complexes separated were filtered, washed with ethanol, and then dried.

## **5. Physical Measurements**

The analyses of C, H and N of ligand and metal complexes was carried out on a Carlo-Erba-1108 elemental analyzer. Chloride and sulphur were estimated by standard method [8]. Metal content were determined gravimetrically and atomic absorption technique.

IR spectra were recorded on a Perkin-Elmer spectrophotometer using KBr pellets. The conductance was measured in DMF ( $10^{-3}$  M) on ELICO digital conductivity meter at room temperature. Magnetic susceptibility measurements of the complexes were done on Gouy balance at room temperature using Hg [Co (CNS)<sub>4</sub>] as a calibrating agent. The electronic spectra were recorded in DMF ( $10^{-3}$  M and  $10^{-5}$  M) solution on a Shimadzu UV-160 spectrometer. The TGA and DTA curves of the complexes were recorded

simultaneously on a TGA/DTA detector (SDT) TA - 2960, the rate of heating was maintained at 10°C/min. ESR spectra of the complexes in solid state and in DMF solution at liquid nitrogen temperature were recorded on Varian E-1700 spectrometer in the X-band region with 9.1 GHz modulation frequency using TCNE as a 'g' marker. X-ray diffraction data were recorded on Philips PW 3710 diffractometer attached to digitized computer along with graphical assembly in which radiation source was connected with the tube Cu-K $\alpha$ , 25 Kv/20 mA. The antibacterial and anti fungal activities were evaluated by agar diffusion method.

## 6. Result and Discussion

The elemental analyses, molecular weight, colour and melting point of the ligand and their complexes given in Table 1. The complexes are brightly coloured and thermally stable at least up to 200°C. They are insoluble in water and common organic solvents but shows maximum solubility in DMF and DM SO at room temperature. They show very low molar conductance  $\sim 20 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  indicates their non-electrolytic nature [9]. The analytical delta of complexes indicates 1:1 metal ligand stoichiometry.

The IR spectra of the ligand shows a medium broad band centered at 3000  $\text{cm}^{-1}$  due to intra-molecularly hydrogen bonded  $\nu(\text{O-H})$  [10]. In the spectra of metal complexes, the broad band disappears indicating deprotonation and the involvement of the phenolic oxygen in bonding with metal ions. The strong band at 1625  $\text{cm}^{-1}$  is assigned to the  $\nu(\text{C=N})$  stretching vibration observed in the ligand and this band undergoes a negative shift ( $\sim 10 \text{cm}^{-1}$ ) in the complexes indicating the participation of the azomethine nitrogen in co-ordination [11].

The spectral region at 1600-1400  $\text{cm}^{-1}$  is complicated because of the stretching modes of  $\nu(\text{C=C})$  and  $\nu(\text{N=N})$  which are superimposed in the same region. However a band appearing at 1550-1525  $\text{cm}^{-1}$  can be assigned to  $\nu(\text{N=N})$  of the azo group of the ligand which is also observed to be lowered in complexes due to involvement of one of the azo nitrogen in bonding with metal ion. The characteristic band due to cyclic  $\nu(\text{C=N})$  and  $\nu(\text{C-S})$  in the thiazole ring system at 1377 and 1460  $\text{cm}^{-1}$  are almost unaffected in the metal complexes. The bands observed in region - 470  $\text{cm}^{-1}$  and 320  $\text{cm}^{-1}$  etc can be attributed to M-O and M-N atom [12].

The electronic spectra of the ligand and its complexes were studied in DMF ( $10^{-5}$  M) as a solvent. The ligand shows four bands in UV and visible region. The bands at 45150  $\text{cm}^{-1}$  and 38200  $\text{cm}^{-1}$  ( $\epsilon = 0.218 \times 10^5$  and  $0.483 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) undoubtedly originate from the perturbed local excitation of the phenyl group. The band located at 25225  $\text{cm}^{-1}$ . ( $\epsilon = 0.582 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) corresponds to the  $\pi - \pi^*$  transition, which is the perturbed orbital originating from the anti-bonding  $\pi$ -orbital of the diazo group. One additional band in the visible region at 20416  $\text{cm}^{-1}$  ( $\epsilon = 0.233 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) is due

to the  $n-\pi^*$  transition. The band due to the  $n-\pi^*$  transition obtained in the miscible region mainly associated with colour of the respective compounds [13].

The Co(II) complex shows d-d transition at  $10471\text{ cm}^{-1}$  and  $16000\text{ cm}^{-1}$  ( $\epsilon = 0.93 \times 10^{-3}\text{ L mol}^{-1}\text{ cm}^{-1}$  and  $1.51 \times 10^{-3}\text{ L mol}^{-1}\text{ cm}^{-1}$ , which are assigned to  ${}^4A_{1g}(F) \rightarrow {}^4T_{1g}(F)$  and  ${}^4A_{2g} \rightarrow {}^4T_g(P)$  transition respectively. B value (823.68) calculated indicates about 71% reduction in free ion value, which is attributed to considerable orbital overlap. The spectra of the Ni(II) complexes exhibits two bands at about  $10256\text{ cm}^{-1}$  and  $17793\text{ cm}^{-1}$  ( $\epsilon = 0.19 \times 10^{-3}\text{ L mol}^{-1}\text{ cm}^{-1}$  and  $1.787 \times 10^{-3}\text{ L mol}^{-1}\text{ cm}^{-1}$ ) which can be assigned to allowed transition  ${}^3T_{2g}(F) \rightarrow {}^3T_{1g}(P)$  and  ${}^3T_{1g} \rightarrow {}^3A_{2g}(F)$  respectively. B values (919) found to be reduced for complexes compared to free ion value  $1041\text{ cm}^{-1}$ ,  $\beta$  value 0.88 is in good agreement with the literature value for tetrahedral Ni(II) complex [14]. The Cu(II) complex displays a broad band centered at  $19890\text{ cm}^{-1}$ .

( $\epsilon = 1.63 \times 10^{-3}\text{ L mol}^{-1}\text{ cm}^{-1}$ ) assigned to the  ${}^2E_g \rightarrow {}^2T_{1g}$  transition for Cu(II) complex due to Jahn-teller effect which removes the degeneracy of the d-orbital and the resulting distorted tetragonal geometry [15].

## 7. Magnetic Susceptibility Measurements

The magnetic moment values of the complexes are given in Table 1. For the complexes  $\mu$  values were found to be lower than the normal values indicating a dimeric or polymeric structure. Magnetic susceptibility measurements have been carried out by standard Gouy method. The magnetic moment value of 4.38 B.M. for Co (II) complex and 3.70 B.M. for Ni(II) complex suggest the tetrahedral structure [16]. The magnetic moment of Cu (II) complex is 1.80 B.M which is close to the spin only value for a tetrahedral geometry [17]. The Zn (II) and Cd (II) complexes is diamagnetic having a  $d^{10}$  system which is as per expected.

## 8. Thermo Gravimetric Study

The thermogram of 4 [2 -hydroxy salicylidene 5'(2"-thiazolylazo)] chorobenzene complexes indicate their thermal stability of up to  $200^\circ\text{C}$ . This fact is further confirmed by their DTA curves, which do not show endothermic peak in the  $150-200^\circ\text{C}$  region. The sharp decomposition associated with the loss of the ligands start above  $220^\circ\text{C}$ . A horizontal thermal curve has been observed after  $800^\circ\text{C}$ . The percent weight of the residue corresponds to metal oxide as end product. The results of thermal studies indicate the absence of coordinated water molecule [18]. The decomposition temperature of the

complexes gives their thermal stability. The kinetic parameters were determined the TG curves obtained for the complexes Coats-Redfeni [19] and Piloyan-Novikova [20] equation for the standard values of order. The value of Z increases with decrease in  $\Delta E_a$ . The values of frequency factor Z and entropy of activation  $\Delta S$  were calculated, the negative values of  $\Delta S$  indicate that the reactions are slower than normal [21].

The ESR spectra of copper (II) complex were recorded as a solid and in solution at liquid nitrogen temperature. No band corresponding to  $\Delta M_s = \pm 2$  transitions was observed in the spectrum ruling out Cu-Cu interaction. The ESR spectra of  $\text{Cu}_2[\text{IISTACB}]_2\text{Cl}_2$  exhibit a single broad signal resulting from the interaction of unpaired electron. The analysis of the spectra gives  $g_{\parallel} = 2.30, g^{\perp} = 2.08, A = 55.2 \times 10^{-4} \text{cm}^{-1}$  and  $A_{\perp} = 24.3 \times 10^{-4} \text{cm}$  respectively. The observed  $g_{\parallel} > g^{\perp} > 2.0023$  observed for the Cu(II) complex [22] indicate that unpaired electron is localized in  $d_{x^2-y^2}$  orbital of the Cu(II) ion the tetragonal elongated structure may be assumed for the Cu(II) complex [23]. The axial factor (G =3.70) calculated by using relation  $g_{\parallel} - 2/g^{\perp} - 2$ . For the complex it is found to be less than 4 indicating that the ligand forming the complex with Cu(II) is strong field ligand.  $\alpha^2\text{Cu}$  i.e. Cu-hyperfine coupling constant were calculated and found to be 0.20 which indicates that copper complex is binuclear in nature [24].

### 9. X-Ray Diffraction Study

The diffraction of IISTACB ligand consist of 9 reflections between 10 to 80° ( $2\theta$ ) with maxima reflection at  $2\theta = 18.26^\circ$  which corresponds to  $d = 4.8531 \text{ \AA}$ . The diffractogram of the coordination Cd (II) complex records 10 reflections between 10 to 80° ( $2\theta$ ) with maxima reflection at  $2\theta = 14.84^\circ$  which corresponds to  $d = 5.9646 \text{ \AA}$ . The X-ray diffraction data are given in Table-2 and Table 3.

The X-ray pattern have been indexed by using computer software (PowdMoult 2.3 version) and applying interactive trial and error method keeping in mind the characteristic of the various symmetry system, till a good fit was obtained between the observed and the calculated  $\sin^2 \theta$  values. The unit cell parameters were calculated from the indexed data [25]. The observed values for HSTACB and  $\text{Cd}_2[\text{HSTACB}]_2\text{Cl}_2$  are good fit for tetragonal system to give lattice constant that have been found to be the tetragonal type (Table- 4) . The experimental value of density of the ligand and complex determined has been found to be in good agreement within the limits of the experimental error.

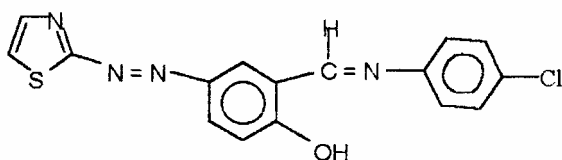
### 10. Antimicrobial Activity

The ligand and its metal complexes were screened against *Escherichia coli*, *Bacillus subtilis*, *Klebsiella pneumoniae*, *Pseudomonas aerogens*, *Salmonella paratyphi B*, *Staphylococcus aureus* and *Proteus vulgaris* by disc diffusion technique. The test solutions were prepared in DMSO and DMF at different concentrations. Nutrient agar was used as culture medium. The zones of inhibition formed were measured in mm. Cu(II) complex was found to be highly active against *Staphylococcus aureus* and Cd(II) complex exhibited moderate activity against *Bacillus subtilis*. The Co(II) and Cd(II) complexes are found to be highly active inhibitors for *Rhizopus* fungus.

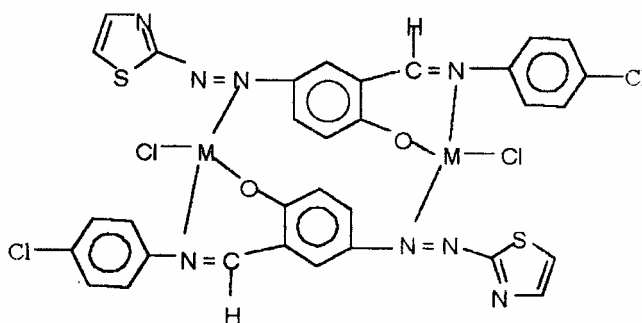
Metal complexes are more active than their ligand because the metal complexes may serve as a vehicle for activation of ligand as the principle cytotoxic species [26].

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**Fig. 1** : The structure of Ligand 4-[2'-hydroxysalicyladiene 5'-(2''-thiazolyazo)] Chlorobenzene (HSTACB).



M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

**Fig. 2** : The proposed structure for metal complex of (HSTACB) ligand.

**Table 1 : Characterization data of ligand and its metal complexes.**

Compound	Mole Formula	Found (Calcd.)%				M.P.	$\mu$ eff
	Colour	M	C	N	S	( $^{\circ}$ C)	R.M.
Ligand (HSTACB)	(C <sub>16</sub> H <sub>11</sub> N <sub>4</sub> O <sub>2</sub> Cl) Brick Red	--	56.05 (56.10)	16.34 (16.36)	9.35 (9.39)	152	--
CO <sub>2</sub> (HSTACB) <sub>2</sub> Cl <sub>2</sub>	CO <sub>2</sub> (C <sub>32</sub> H <sub>20</sub> N <sub>8</sub> O <sub>2</sub> S <sub>2</sub> Cl <sub>2</sub> )Cl <sub>2</sub> Brown Red	13.51 (13.56)	44.05 (44.07)	12.84 (12.87)	7.35 (7.41)	290	4.44
Ni <sub>2</sub> (HSTACB) <sub>2</sub> Cl <sub>2</sub>	Ni <sub>2</sub> (C <sub>32</sub> H <sub>20</sub> N <sub>8</sub> O <sub>2</sub> S <sub>2</sub> Cl <sub>2</sub> )Cl <sub>2</sub> Light Brown	13.46 (13.49)	44.08 (44.11)	12.85 (12.89)	7.35 (7.37)	>300	3.50
Cu <sub>2</sub> (HSTACB) <sub>2</sub> Cl <sub>2</sub>	Cu <sub>2</sub> (C <sub>32</sub> H <sub>20</sub> N <sub>8</sub> O <sub>2</sub> S <sub>2</sub> Cl <sub>2</sub> )Cl <sub>2</sub> Light Red	14.40 (14.44)	43.59 (43.62)	12.71 (12.76)	7.27 (7.28)	230	1.77
Zn <sub>2</sub> (HSTACB) <sub>2</sub> Cl <sub>2</sub>	Zn <sub>2</sub> (C <sub>32</sub> H <sub>20</sub> N <sub>8</sub> O <sub>2</sub> S <sub>2</sub> Cl <sub>2</sub> )Cl <sub>2</sub> Brown	14.77 (14.79)	43.41 (43.43)	12.65 (12.68)	7.24 (7.29)	250	--
Cd <sub>2</sub> (HSTACB) <sub>2</sub> Cl <sub>2</sub>	Cd <sub>2</sub> (C <sub>32</sub> H <sub>20</sub> N <sub>8</sub> O <sub>2</sub> S <sub>2</sub> Cl <sub>2</sub> )Cl <sub>2</sub> Dark Brown	22.55 (22.57)	39.24 (39.27)	11.44 (11.49)	6.54 (6.57)	280	--

**Table 2 : XRD data of 4-[2'-hydroxy salicydene – 5'(2''-thiazolylazo)] chloro benzene (HSTACB).**

Peak No.	2 $\theta$ in degree	d(obs.) $\text{\AA}$	d(calc.) $\text{\AA}$	Q(obs.)	Q(cal.)	h k l	R I
1	13.79	6.4140	6.5636	0.0243	0.0232	1 1 1	12
2	14.89	5.9427	6.2500	0.0284	0.0256	2 0 0	29
3	16.28	5.4385	5.5902	0.0338	0.0311	2 1 0	65
4.	17.62	5.0279	4.9000	0.0395	0.0416	0 0 2	46
5	18.26	4.8931	4.8557	0.0424	0.0424	2 1 1	100
6	24.25	3.6665	3.6659	0.0743	0.0744	3 1 1	90
7	25.89	3.4379	3.4669	0.0846	0.0831	3 2 0	92
8	29.48	3.0269	3.0317	0.1091	0.1087	4 1 0	32
9	47.14	1.9261	1.9281	0.2698	0.2695	4 0 4	21

**Table 3 : XRD data of Cadmium complex of Cd<sub>2</sub>[HSTACB]<sub>2</sub>Cl<sub>2</sub>**

Peak No.	2 $\theta$ in degree	d(obs.) Å	d(calc.) Å	Q(obs.)	Q(cal.)	h k l	R I
1	12.10	7.3054	7.3283	0.0186	0.0186	1 0 2	18
2	14.84	5.9646	5.9035	0.0281	0.0286	2 0 1	100
3	17.30	5.1201	5.1400	0.0381	0.0378	2 0 2	28
4	21.31	4.1660	4.1634	0.0576	0.0576	3 0 0	20
5	24.32	3.6556	3.6610	0.0747	0.0744	2 0 4	08
6	26.26	3.3909	3.4024	0.0870	0.0863	3 2 1	24
7	27.40	3.2524	3.2352	0.0945	0.0955	3 2 2	42
8	29.47	3.0279	3.0293	0.1090	0.1089	4 1 0	55
9	38.33	2.4361	2.3464	0.1816	0.1816	2 1 7	42
10	49.68	1.8336	1.8321	0.2974	0.2979	4 0 8	20

**Table 4 : X-ray parameters of HSTACB and Cd<sub>2</sub>[HSTACB]<sub>2</sub>Cl<sub>2</sub>**

Structure	Tetragonal (Ligand)	Tetragonal (Complex)
Lattice parameters	a-b-12.500 Å	a-b-12.490 Å
Bond angles	c=9.8000 Å	c=18.0992 Å
Space group	$\alpha = \beta = \gamma = 90^0$	$\alpha = \beta = \gamma = 90^0$
Symmetry of lattice	14/mmm	14/mmm
Vol. Of unit cell	Non-primitive	Non-primitive
Density $\rho$ (Experimental)	1531.25 Å <sup>3</sup>	2823.54 Å <sup>3</sup>
(Theoretical)	0.680 gr/cc	2.24 gr/cc
Pore fraction	0.678 gr/cc	2.20 gr/cc
Thickness of particle	32.43	10.43
Number of molecule per unit cell	249.05 Å	253.71 Å
	2	4



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