



**SYNTHESIS, CHARACTERIZATION, THERMAL AND ELECTRICAL STUDIES OF CO(II), NI(II), AND CU(II) COMPLEXES DERIVED FROM BIDENTATE THIAZOLE SCHIFF BASE**

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**Abstract:** The new thiazole Schiff base have been synthesized by condensing 2-hydroxy-5-chloro acetophenone and 4-(p-hydroxyphenyl)-2-aminothiazole. The metal complexes were obtained as a result of interaction of Schiff base ligand and metal ions Co(II), Ni(II), and Cu (II). The complexes have been characterized on the basis of elemental analysis, infrared, molar conductance, magnetic Susceptibilities, thermal and electrical analysis. The kinetic analysis of the thermogravimetric data was performed by using Broido, Horowitz-Metzger and Freeman-Carroll method, which confirm first order kinetics and kinetic compensation effect.

**Keywords:** Thiazole Schiff Base, Molar conductance, Thermal and Electrical.

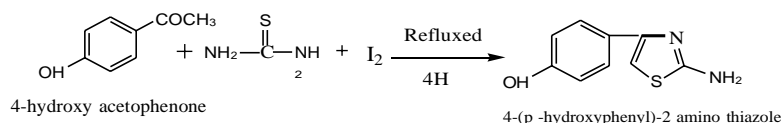
**Introduction:**

Schiff's bases are condensation products of primary amines with carbonyl compounds. Schiff bases are the most widely used organic compounds. They have been shown to exhibit a broad range of biological activities. In this research paper to studies the synthesis, characterisation and various methods of Schiff base derived from bidentate thiazole Schiff base. Data collection and recent studies on biological activities of Schiff Bases Metal Complexes [1]. Synthesis, spectral studies, antioxidant and antibacterial evaluation of aromatic nitro and halogenated tetradentate Schiff bases [2]. A review on the history, synthesis, and applications of Schiff bases and their metal Complexes [3]. There is the combination of the azo group, the imidazole unit and the Schiff base fragment to studies the synthesis, characterization, and optical properties of four different Schiff bases ligands. They are reported the possible use of such systems in biological applications for their antifungal properties and antioxidant activities [4]. Synthesis and structural diversity transition metal coordination complexes with diverse Schiff base ligands and macrocyclic systems [5]. This paper discusses the kinetic of the thermal decomposition with the accompanying compensation effect and electrical studies of Schiff base complexes of Co (II), Ni (II) and Cu (II).

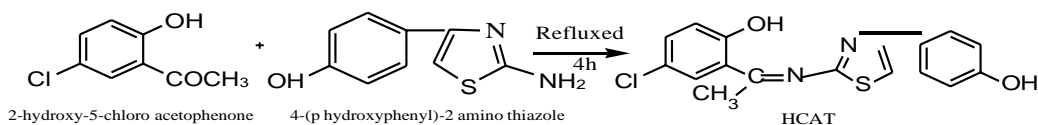
**Experimental:**

All the chemicals were of A.R. grade and used as received. 2-hydroxy-5-chloro acetophenone (HCA) and 4-(p-hydroxyphenyl)-2 amino thiazole was prepared by known methods [6-9]. The solvents were purified by standard methods [10].

Synthesis of 4-(p hydroxyphenyl)-2 amino thiazole;



Synthesis of 2-hydroxy-5-chloro acetophenone 4-(p-hydroxyphenyl)-2 imino thiazole [HCAT]: A solution of 4-(p-hydroxyphenyl)-2 imino thiazole (0.02M) in 25ml of ethanol was added to an ethanolic solution(25ml) of 2-hydroxy-5-chloro acetophenone (0.02M) and the reaction mixture was refluxed on a water bath for 4h. After cooling a pale yellow coloured crystalline solid was separated out. It was filtered and washed with ethanol, crystallized from DMF and dried under reduced pressure at ambient temperature. The purity of ligand was checked by elemental analysis shown in Table 1. and m.p. It was also characterized by IR and <sup>1</sup>H NMR spectral studies. Yield:70%; m.p. 310<sup>0</sup>C



**Table1. Analytical data of the Ligands.**

Ligand	Molecular Formula	Formula Weight	Color and nature	Elemental Analysis				
				C% found (Cal.)	H% Found (Cal.)	N% Found (Cal.)	Cl% Found (Cal.)	S% Found (Cal.)
HCAT	C <sub>17</sub> H <sub>13</sub> N <sub>2</sub> O <sub>2</sub> S Cl	344.6	Yellow Crystalline	59.38 (59.19)	03.70 (03.77)	08.5 (08.12)	10.11 (10.30)	09.22 (09.31)

**Table 2. Analytical data and molar conductance of the compounds.**

Compounds	Colour	Mol.w t.	Analysis % Found (calc.)					μ <sub>eff</sub> B.M.	ΛM (Ω <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
			M	C	H	N	Cl		
[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	Brown	800.1	7.25 (7.36)	50.86 (50.99)	3.65 (3.74)	6.86 (6.99)	8.70 (8.87)	4.48	6.9
[NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	Green	799.9	7.30 (7.33)	50.78 (51.00)	3.68 (3.75)	6.95 (7.00)	8.72 (8.87)	3.2	7.9

[CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	Brown	804.7	7.70 (7.89)	50.60 (50.70)	3.65 (3.72)	6.82 (6.95)	8.72 (8.82)	1.70	8.3
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Preparation of complexes: All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand HCAT (0.02M) in 25ml of ethanol a suspension of respective metal salts was added drop wise with constant stirring. The reaction mixture was refluxed on a water bath for 4-6 h. The precipitated complexes were filtered, washed with ethanol followed by ether and dried over fused calcium chloride. Yield : 45-50%. The complexes are soluble in DMSO and DMF but insoluble in water and common organic solvents. The metal chloride content of complexes was analyzed by standard methods [11]. The <sup>1</sup>H NMR spectra of ligand was recorded and obtained from RSIC Chandigarh. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000cm<sup>-1</sup>, carbon, hydrogen and nitrogen analysis were carried out at RSIC, Punjab University, Chandigarh. The molar conductance of the complexes at 10<sup>-3</sup>M dilution in DMF were determined using equiptronic digital conductivity meter EQ-660 with a cell constant 1.00 cm<sup>-1</sup> at room temperature. The magnetic moment measurement were made on a Gouy balance at room temperature using [HgCo(SCN)<sub>4</sub>] as the calibrant. The thermogravimetric analysis was performed on laboratory set up apparatus in air atmosphere at 10<sup>0</sup>C min<sup>-1</sup> heating rate. The molecular weights of the complexes were determined by Rast method are shown in Table 2.

### Results and Discussion:

The Schiff base ligand HCAT and its complexes have been characterized on the basis of <sup>1</sup>H NMR, IR spectral data, elemental analysis, molar conductance, magnetic susceptibility measurements and thermogravimetric analysis data. All these values and analytical data is consistent with proposed molecular formula of ligand. All the compounds are coloured solid and stable in air. They are insoluble in water but soluble in coordinating solvents like DMF and DMSO. The molar conductance values in DMF(10<sup>-3</sup>M) solution at room temperature (Table 2 ) shows all the complexes are non electrolytes<sup>11</sup> The <sup>1</sup>H NMR spectra of ligand HCAT shows signals at δ 12.09, (1H, s phenolic OH ), δ 9.51 (1H, s, phenolic OH ), δ 7.55, 7.54, 7.53 and 7.52 (4H, m, phenyl) δ 6.81, 6.80, and 6.78(3H, s Phenyl), 6.68 (1H s thiophene), and 2.56(3H, s, methyl)[12-15]. IR spectra of ligand and metal complexes shows ν(C=N) peaks at 1620cm<sup>-1</sup> and absence of C=O peak at around 1700–1750 cm<sup>-1</sup> indicates the Schiff base formation. [16-18]. IR spectra of complexes are shown in Table 3.

**Table 3. IR spectra of ligand and metal complexes.**

Compound	ν(O-H) hydrogen bonded	ν(C=N) imine	ν(C-O) phenolic	ν(M-O)	ν(M-N)	ν(C-S)
HCAT	3119	1620	1514	--	--	1122
[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	--	1608	1504	470	430	1098
[NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	--	1585	1465	468	422	1090
[CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	--	1610	1504	509	410	1110

Thermogravimetric studies: An analysis of TG curves of HCAT and its metal complexes show that the Co(II), Ni(II) and Cu(II), complexes decomposed in three stages, the ligand and Co(II), Ni(II) and Cu(II) complexes are stable upto 70°C Elimination of one water molecule from Co(II), Ni(II) and Cu(II) complexes upto 130°C have been observed (%wt loss obs./calcd. Co(II) : 2.44/2.24; Ni(II) : 2.56/2.25; Cu(II) : 2.46/2.23; In the Co(II), Ni(II) and Cu(II) complexes there is further loss in weight upto 220°C indicating the presence of two coordinated water molecule in each complex further loss in weight upto 220°C indicating the presence of one coordinated water molecule (%wt loss obs./calcd. Co(II) : 4.57/4.49; Ni(II) : 4.59/4.50; Cu(II) : 4.58/4.47; in these complexes [20] in all the complexes rapid weight-loss has been observed above 400°C, indicative of decomposition of the free part of the coordinated ligand gradual weight-loss above 400°C corresponding to degradation of actual coordination part of the ligand. In the thermograms of ligand, Co(II), Ni(II) and Cu(II), complexes The horizontal level beyond 650°C suggests the formation of final decomposition product.[21] The half decomposition temperature and the basic parameter calculated for the compounds are tabulated in Table 4 The relative thermal stability on the basis of half decomposition temperature is found to be Cu(II)>CO(II)>Ni(II)>HCAT

The Thermal activation energy (Table 4) was calculated by Freeman-Carroll,[22], Horowitz-metzger[23] and Broido[24] method

**Table 4: Thermal decomposition data of the complexes of HCAT**

Compound	Half Decomposition Temperature (°C)	Activation Energy (kJ mole <sup>-1</sup> )			Frequency Factor Z (sec <sup>-1</sup> )	Entropy Change -ΔS (J mol <sup>-1</sup> K <sup>-1</sup> )	Free Energy Change ΔF (kJ mol <sup>-1</sup> )
		B*	H-M**	F-C***			
HCAT (LH)	260.51	3.27	5.45	4.36	87.25	212.55	117.75
[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	433.50	5.73	9.55	9.55	191.11	208.24	156.67
[NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	384.17	4.13	8.26	3.30	66.03	216.60	145.64
[CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	494.86	11.28	11.28	10.16	203.31	208.54	170.28

\* Broido, \*\*Horowitz-Metzger and \*\*\*Freemenn-Carroll

Electrical Conductivity: Electrical resistivity of the different metal chelates can be measured either with a.c. or d.c. methods. However, in the present work the d.c. method is used for resistivity measurements, over a wide range of temperature. The electrical conductivity of metal complexes varies with their nature and temperature[25-29]. The variation of electrical conductivity of the metal complexes with temperature is the basis of their classification as semiconductors or metallic conductors. The electrical conductivity of metallic conductors decreases with increasing temperature (i.e., temperature coefficient is negative). their resistivity ranges from 10<sup>-6</sup> to 10<sup>-3</sup> Ω

The electrical conductivity and activation energy of HCAT complexes are cited in Table 5

1. Electrical conductivity of the complexes lies in the range of 2.10x10<sup>-9</sup> to 6.69x10<sup>-7</sup> Ω<sup>-1</sup>cm<sup>-1</sup> at 373 K.

2. The electrical conductivity of these complexes at 373 K follows the order Ni > Cu > Co.
3. The activation energy of electrical conduction of the complexes has been found to increase in the order Ni < Cu < Co.

**Table 5. Electrical Conductivity ( $\sigma$ ) at 373 K and Activation Energy ( $E_a$ ) of the complexes**

Metal		Co(II)	Ni(II)	Cu(II)
HCAT	$\sigma$ ( $\Omega^{-1} \text{ cm}^{-1}$ )	$2.10 \times 10^{-9}$	$1.28 \times 10^{-8}$	$4.10 \times 10^{-8}$
	$E_a$ (eV)	0.0824	0.0147	0.0399

### Conclusion:

The compensation effect of thermokinetic decomposition of the complexes indicate the change of sample mass and size on the estimated values of activation energy. The thermokinetic studies of the complexes involves up to three stage decomposition. It is assumed that dehydration of the complexes containing water occurs within an active reaction interface. The D.C. Electrical conductivity of the synthesized complexes were measured in the temperature range 298-423 K. All the complexes indicating their semiconducting behaviour.

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