

# Thermal and Thermokinetic Studies of Schiff Base Metal Complexes

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## ABSTRACT

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), Cu (II), Cr (III), Mn(III), Fe (III), VO (IV), Zr (IV) and UO<sub>2</sub> (VI). The complexes have been characterized on the basis of elemental analysis, infrared, molar conductance, magnetic Susceptibilities, and thermogravimetric 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:** Schiff Base, conductance, Thermal Studies.

## I. INTRODUCTION

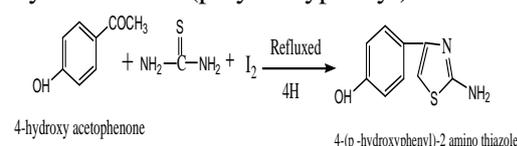
Schiff base complexes have an important and popular area of research due to their simple synthesis, versatility and diverse range of applications (Taylor and Relinski, 2004; Yamada, 1999). Schiff base and their metal complexes are becoming increasingly important in recent years due to their antiviral and biological activity.<sup>1</sup> The structural synthesis and modern application of newly synthesized Schiff bases and their coordination compounds have been largely considered in inorganic, organic and biological fields, since their structural properties nearly similar to some of the medicinal and biological systems.<sup>2</sup> A binucleating new amino schiff base ligand with a phenylene spacer afforded by the condensation of amino acids with o-phthalaldehyde has been served as an octadentate N<sub>4</sub>O<sub>4</sub> ligand Metal complexes of Schiff bases show biological activities including antibacterial, antifungal, anticancer and herbicidal<sup>3</sup>. Synthesis and spectroscopic studies on the new Schiff base derived from the 1:1 condensation of isatin with amines and its evaluating biological activity. Synthesis and characterization of new Schiff bases ligand and their complexes with Some transition metals.<sup>4,5</sup> This paper studies the kinetic of the thermal decomposition and the accompanying compensation

effect for Schiff base complexes of Co (II), Ni (II), Cu (II), Cr (III), Mn (III), Fe (III), VO (IV), Zr (IV) and UO<sub>2</sub> (VI).

## 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<sup>6-9</sup>. The solvents were purified by standard methods<sup>10</sup>

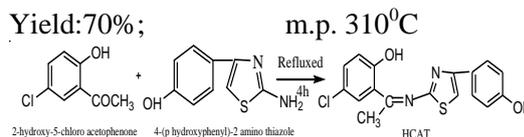
Synthesis of 4-(p hydroxyphenyl)-2 amino thiazole;



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 and m.p. It was also characterized by IR and <sup>1</sup>H NMR spectral studies.



**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> SCl	344.6	Yellow Crystalline	59.38 (59.19)	03.70 (03.77)	08.5 (08.12)	10.11 (10.30)	09.22 (09.31)

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%

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

Compounds	Colour	Mol.wt	Analysis % Found (calc.)					$\mu_{\text{eff}}$ B.M.	$\Delta M$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )
			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
[CrL <sub>2</sub> (H <sub>2</sub> O)Cl]H <sub>2</sub> O	Green	810.7	6.32 (6.41)	50.25 (50.32)	3.36 (3.45)	6.81 (6.90)	13.08 (13.13)	3.96	18.9
[MnL <sub>2</sub> (OAc)] H <sub>2</sub> O	Brown	837.1	6.40 (6.55)	51.51 (51.60)	3.60 (3.70)	6.51 (6.68)	8.32 (8.48)	4.8	18.8
[FeL <sub>2</sub> (H <sub>2</sub> O)Cl] H <sub>2</sub> O	Black	814.6	6.72 (6.86)	50.01 (50.08)	3.32 (3.43)	6.73 (6.87)	13.01 (13.07)	5.4	22.6
[VOL <sub>2</sub> ]	Green	754.2	6.63 (6.76)	54.01 (50.09)	3.05 (3.18)	7.33 (7.42)	9.32 (9.41)	1.60	12.8
[ZrL <sub>2</sub> (OH) <sub>2</sub> ] 2H <sub>2</sub> O	Yellow	848.4	10.68 (10.74)	47.93 (48.09)	3.46 (3.53)	6.52 (6.60)	8.26 (8.36)	Dia	11.7
[UO <sub>2</sub> L <sub>2</sub> ]	Orange	957.3	24.73 (24.87)	42.51 (42.61)	2.41 (2.50)	5.74 (5.84)	7.32 (7.41)	Dia	12.9

### III. 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( $10^{-3}$ 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  $\delta$  12.09, (1H, s phenolic OH ),  $\delta$  9.51 (1H, s, phenolic OH ),

$\delta$  7.55, 7.54, 7.53 and 7.52 (4H, m, phenyl)  $\delta$  6.81, 6.80, and 6.78(3H, s Phenyl), 6.68 (1H s thiophene), and 2.56(3H, s, methyl)<sup>12-15</sup> IR spectra of ligand and metal complexes shows  $\nu(\text{C}=\text{N})$  peaks at  $1620\text{cm}^{-1}$  and absence of C=O peak at around  $1700-1750\text{cm}^{-1}$  indicates the Schiff base formation<sup>16-19</sup>

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

Compound	$\nu(\text{O-H})$ hydrogen bonded	$\nu(\text{C}=\text{N})$ imine	$\nu(\text{C-O})$ phenolic	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{C-S})$
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
[CrL <sub>2</sub> (H <sub>2</sub> O)Cl] H <sub>2</sub> O	--	1590	1506	475	409	1115
[MnL <sub>2</sub> (OAc)] 2H <sub>2</sub> O	--	1562	1462	498	420	1090
[FeL <sub>2</sub> (H <sub>2</sub> O)Cl] H <sub>2</sub> O	--	1602	1504	512	440	1080
[VOL <sub>2</sub> ]	--	1598	1506	514	445	1098
[ZrL <sub>2</sub> (OH) <sub>2</sub> ] 2H <sub>2</sub> O	--	1600	1498	445	412	1108
[UO <sub>2</sub> L <sub>2</sub> ]	--	1585	1440	550	480	1082

### Thermogravimetric studies:

An analysis of TG curves of HCAT and its metal complexes show that the Co(II), Ni(II), Cu(II), Cr(III), Mn(III), Fe(III) and Zr(IV) complexes decomposed in three stages, the ligand and UO<sub>2</sub> (VI) complexes in two stages while VO(IV) complexes in one stage. The Co(II), Ni(II), Cu(II), Cr(III), Mn(III), Fe(III) and Zr(IV) complexes are stable upto 70°C Elimination of one water molecule from Co(II), Ni(II), Cu(II) Cr(III) and Fe(III) 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; Cr(III) : 2.32/2.22; Fe(III) : 4.58/4.30). The Mn(III) and Zr(IV) complexes shows percent loss corresponding to two water molecules (%wt loss obs./calcd. Mn(III) : 4.48/4.30; Zr(IV) : 4.54/4.24) upto 150°C. 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 and in each Cr(III) and Fe(III) complexes 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; Cr(III) :

2.38/2.22; Fe(III) : 2.47/2.33)<sup>20</sup> There is no weight-loss upto 250°C in VO(IV) and UO<sub>2</sub>(IV) complexes indicating the absence of any water molecules (lattice or coordinated) in these complexes<sup>21</sup> 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), Cu(II), Fe(III) and VO(IV) complexes while in case of Mn(III), Zr(IV) and UO<sub>2</sub>(VI) complexes complete decomposition has not been observed upto 800°C. The horizontal level beyond 650°C suggests the formation of final decomposition product.<sup>22</sup> The half decomposition temperature and the basic parameter calculated for the compounds are given in (Table 4) The relative thermal stability on the basis of half decomposition temperature is found to be UO<sub>2</sub>(VI)>Zr(IV)>Mn(III)>Cr(III)>Cu(II)>CO(II)>Fe(III)>VO(IV)>Ni(II) >HCAT. The Thermal activation energy (Table 4) was calculated by Freeman-Carroll,<sup>23</sup> Horowitz-metzger<sup>24</sup> and Broido<sup>25</sup> 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
[CrL <sub>2</sub> (H <sub>2</sub> O)Cl] H <sub>2</sub> O	550.45	9.08	12.98	12.98	259.74	207.11	183.52
[MnL <sub>2</sub> (OAc)] 2H <sub>2</sub> O	710.46	11.11	18.51	11.11	222.32	209.86	217.58
[FeL <sub>2</sub> (H <sub>2</sub> O)Cl] H <sub>2</sub> O	429.25	3.77	9.44	8.49	169.89	209.30	155.47
[VOL <sub>2</sub> ]	400.23	5.20	8.67	6.94	138.87	210.62	148.73
[ZrL <sub>2</sub> (OH) <sub>2</sub> ] 2H <sub>2</sub> O	711.17	7.41	18.54	11.12	222.52	209.77	217.65
[UO <sub>2</sub> L <sub>2</sub> ]	800.00	19.85	22.06	17.65	353.20	206.79	239.62

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

#### IV. CONCLUSION

The thermal decomposition of the complexes is not simple and involves up to three stage decomposition. It is assumed that dehydration of the complexes containing water occurs within an active reaction interface. The compensation effect of thermal decomposition of the complexes indicating the change of sample mass on the estimated values of activation energy.

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