

# Synthesis, Characterization, And Thermal Studies Of Co(Ii), Ni(Ii), Cu(Ii), Cr(Iii), Mn(Iii), Fe(Iii), Vo(Iv), Zr(Iv) And Uo<sub>2</sub>(Vi) Complexes Derived From Thiazole Schiff Base.

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**Abstract:** A Schiff base has been prepared by the condensation of 2-hydroxy-5-chloro-3-nitro acetophenone and thiazole. The ligand was characterized by elemental analysis and spectral methods. The coordinating ability of the ligand is investigated by preparing its metal complexes with Co(II), Ni(II), Cu(II), Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO<sub>2</sub>(VI) have been prepared and characterized by elemental analysis, conductance measurements, molecular weight determinations, spectral and thermal studies. The isolated products are coloured solids, soluble in DMF, DMSO and THF.

**Keywords:** Schiff base, Magnetic susceptibility, Thermal.

## Introduction

Schiff bases metal complexes have many applications in different fields<sup>1</sup>. The Schiff bases derived from thiazole and substituted acetophenone have been widely used as ligand for the synthesis of transition metal complexes<sup>2</sup>. Thiazole Schiff base ligands and their metal complexes are biologically active<sup>3</sup> and are known for their biological application<sup>4</sup> i.e. one of the drug in cytotoxicity of anticancer<sup>5</sup>. Due to biological potency, pharmacological properties and synthetic flexibility of thiazole Schiff bases. The aim of present investigation is to synthesize various transition metal complexes of Schiff base derived from 2-hydroxy-5-chloro acetophenone and 4-(p-hydroxyphenyl)-2 amino thiazole.

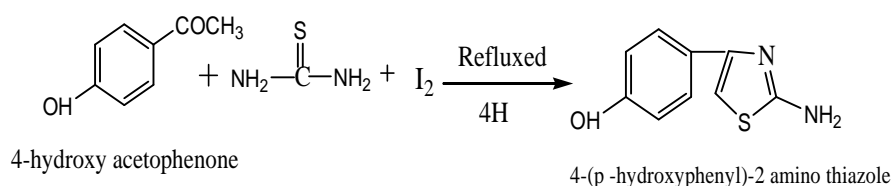
## Experimental

All the chemicals were of A.R. grade and used as received. 2-hydroxy-5-chloro-3-nitro acetophenone (HCNA) 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-(phydroxyphenyl)-2aminothiazole;**

A mixture of p-hydroxy acetophenone (12g), thiourea (15.2g), iodine (25g), and 60ml distilled water was taken in a 250ml R.B. flask. The mixture was refluxed for about 4h and poured into crushed ice to get the solid which is basify with sodium hydroxide. The product was filtered and crystallized from 70% ethanol, after several minutes the golden coloured product of 4-(p-hydroxyphenyl)-2 amino thiazole was separated out<sup>7-9</sup>. Yield: 10g (83.33%); m.p.: 216<sup>0</sup>C.



### Synthesis of 2-hydroxy-5-chloro-3-nitroacetophenone 4-(p-hydroxyphenyl)-2 iminothiazole [HCNAT]:

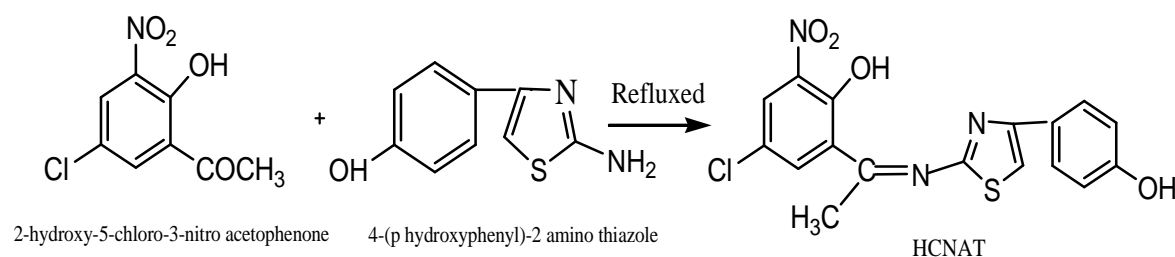
A solution of 4-(p-hydroxyphenyl)-2 iminothiazole (0.02M) in 25ml of ethanol was added to an ethanolic solution (25ml) of 2-hydroxy-5-chloro-3-nitroacetophenone (0.02M) and the reaction mixture was refluxed on a water bath for 4h. After cooling a pale yellow coloured crystalline solid was separated out. 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  $^1\text{H}$  NMR spectral studies. Yield:70%; m.p.  $310^\circ\text{C}$ .

### Preparation of complexes:

All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand HCNAT (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 4-5 h. The precipitated complexes were filtered, washed

with ethanol followed by ether and dried over fused calcium chloride. Yield : 50-55%

The complexes are soluble in DMSO and DMF but insoluble in water and common organic solvents. The metal chloride content of complexes were analyzed by standard methods<sup>12</sup> The  $^1\text{H}$  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  $400\text{-}4000\text{cm}^{-1}$ , Carbon, Hydrogen and Nitrogen analysis were carried out at RSIC, Punjab University, Chandigarh. The molar conductance of the complexes at  $10^{-3}$  M dilution in DMF were determined using equiptronic digital conductivity meter EQ-660 with a cell constant  $1.00\text{ cm}^{-1}$  at room temperature. The magnetic moment measurement were made on a Gouy balance at room temperature using  $[\text{HgCo}(\text{SCN})_4]$  as the calibrant. The thermogravimetric analysis were performed on laboratory set up apparatus in air atmosphere at  $10^\circ\text{C min}^{-1}$  heating rate. The molecular weights of the complexes were determined by Rast method.



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

Ligand	Molecular Formula	Formula Weight	Color and nature	Elemental Analysis			
				C% found (Cal.)	H% Found (Cal.)	Cl% Found (Cal.)	S% Found (Cal.)
HCNAT	$\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_4\text{SCl}$	390.6	Yellow Crystalline	52.34 (52.22)	03.26 (03.32)	9.02 (9.08)	08.12 (08.21)

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

Ligand	Formula weight g mole <sup>-1</sup>	Colour	Elemental Analysis Found (Calcd.)				$\mu_{\text{eff}}$ B. M	$\Lambda_{\text{M}}$ ( <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
			M%	C%	H%	Cl%		
[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	892.1	Brown	6.25 (6.60)	44.86 (45.73)	3.25 (3.36)	7.70 (7.95)	4.6	6.8
[NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	891.9	Green	6.30 (6.58)	45.58 (45.74)	3.16 (3.36)	7.72 (7.96)	3.1	7.6
[CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	896.7	Brown	6.90 (7.08)	45.26 (45.50)	3.12 (3.34)	7.72 (7.91)	1.6	8.2
[CrL <sub>2</sub> (H <sub>2</sub> O)Cl] H <sub>2</sub> O	902.7	Green	5.32 (5.76)	44.90 (45.19)	2.36 (2.88)	11.08 (11.79)	3.8	18.6
[MnL <sub>2</sub> (OAc)] H <sub>2</sub> O	929.1	Brown	5.40 (5.90)	46.15 (46.49)	3.16 (3.33)	7.32 (7.64)	4.6	18.4
[FeL <sub>2</sub> (H <sub>2</sub> O)Cl] H <sub>2</sub> O	906.6	Black	6.02 (6.16)	44.81 (45.00)	3.02 (3.08)	11.41 (11.74)	5.2	22.2
[VO <sub>2</sub> L <sub>2</sub> ]	846.2	Green	5.63 (6.02)	48.01 (48.21)	2.15 (2.83)	8.32 (8.39)	1.4	12.4
[ZrL <sub>2</sub> (OH) <sub>2</sub> ] 2H <sub>2</sub> O	940.4	Yellow	9.48 (9.69)	43.13 (43.38)	3.06 (3.19)	7.26 (7.54)	Dia	16.2
[UO <sub>2</sub> L <sub>2</sub> ]	1049.3	Orange	22.43 (22.69)	38.51 (38.88)	2.11 (2.28)	6.32 (6.76)	Dia	14.2

### Result and Discussion

The Schiff base HCNAT 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 (Table2) shows all the complexes are non electrolytes. The <sup>1</sup>H NMR spectra of ligand HCNAT shows signals at 12.11,(1H, s phenolic OH), 9.52 (1H, s, phenolic OH), 7.56, 7.54, 7.53 and 7.52 (4H, m, phenyl) 6.81, 6.80, and 6.78(3H, s Phenyl), 6.68 (1H s thiophene), and 2.56(3H, s, methyl)<sup>11,13-15</sup>.

IR spectra of ligand and metal complexes shows  $\nu(\text{C}=\text{N})$  peaks at 1620 cm<sup>-1</sup> and absence of  $\text{C}=\text{O}$  peak at around 1700 – 1750 cm<sup>-1</sup> 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	$\nu(\text{C=N})$ imine	$\nu(\text{C-O})$ phenolic	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{C-S})$
HCNAT (LH)	3119	1620	1514	--	--	1122
[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	--	1608	1506	472	432	1098
[NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	--	1585	1464	469	423	1090
[CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	--	1610	1503	508	412	1110
[CrL <sub>2</sub> (H <sub>2</sub> O)Cl] H <sub>2</sub> O	--	1590	1505	475	410	1115
[MnL <sub>2</sub> (OAc)] 2H <sub>2</sub> O	--	1562	1461	496	422	1090
[FeL <sub>2</sub> (H <sub>2</sub> O)Cl] H <sub>2</sub> O	--	1602	1502	510	441	1080
[VOL <sub>2</sub> ]	--	1598	1505	512	446	1098
[ZrL <sub>2</sub> (OH) <sub>2</sub> ] 2H <sub>2</sub> O	--	1600	1496	446	414	1108
[UO <sub>2</sub> L <sub>2</sub> ]	--	1585	1440	548	480	1082

**Table 4. Thermal decomposition data of HCNAT and its complexes.**

Compounds	Half Decompo- sition Tempera- ture (°C)	Activation Energy (kJ mole <sup>-1</sup> )			Frequenc y Factor Z (sec <sup>-1</sup> )	Entropy Change - S (J mol <sup>-1</sup> K <sup>-1</sup> )	Free Energy Change F (kJ mol <sup>-1</sup> )
		B*	H-M**	F- C***			
HCNAT (LH)	260.50	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	433.40	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	384.12	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	494.84	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	550.42	9.08	12.98	12.98	259.74	207.11	183.52
[MnL <sub>2</sub> (OAc)] 2H <sub>2</sub> O	710.42	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	429.22	3.77	9.44	8.49	169.89	209.30	155.47
[VOL <sub>2</sub> ]	400.20	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	711.19	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

**Thermogravimetric studies:**

Thermogravimetric study indicates all the complexes are stable up to 60-70°C. All the complexes shows half decomposition temperature (Table 4). The Thermal activation energy was calculated by Freeman-Carroll,<sup>20</sup> Horowitz-metzger<sup>21</sup> and Broido<sup>22</sup> method.

**Conclusions**

In conclusion, we have synthesized new ligand 2-hydroxy-5-chloro-3-nitro acetophenone 4-(p-

hydroxyphenyl)-2 imino thiazole and their metal complexes. Ligand was found to bind the metal ion monobasic (ON) bidentate manner.

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