

THERMOKINETIC STUDIES OF CO(II), NI(II), CU(II), CR(III), MN(III), FE(III), VO(IV), ZR(IV) AND UO₂(VI) COMPLEXES DERIVED FROM BIDENTATE THIAZOLE SCHIFF BASE

S. R. Kelode¹ and P. R. Mandlik²

1. Department of Chemistry, Arts, Commerce and Science College, Maregaon,

2. P. G. Department of Chemistry, Shri Shivaji Science College, Amravati.

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), Cu (II), Cr (III), Mn(III), Fe (III), VO (IV), Zr (IV) and UO₂ (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: Thiazole Schiff Base, Molar conductance, Thermal.

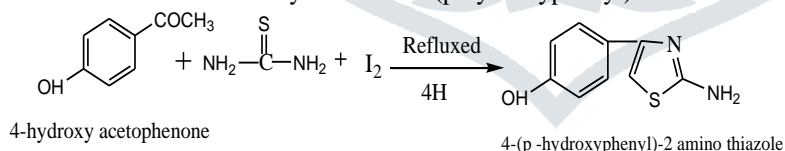
Introduction:

The present reference research paper focus on synthesis, characterisation and various methods of Schiff base derived from sulphanic acid and salicylaldehyde and Comparative study of Schiff base using various synthesis methods and their theoretical prediction of activities[1]. Synthesis, characterization and antifungal activity of manganese (II) complex with Schiff Base derived from acetylacetone and l leucine[2]. The newly synthesized Schiff bases, 2-acetylthiophene thiosemicarbazone and thiophene-2-aldehyde thiosemicarbazone and their metal complexes with Co(II), Cu(II), Zn(II) and Ni(II) complexes and Their Schiff bases metal complexes were tested for antibacterial activity[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 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 UO₂ (VI).

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 ¹H NMR spectral studies. Yield:70%; m.p. 310°C

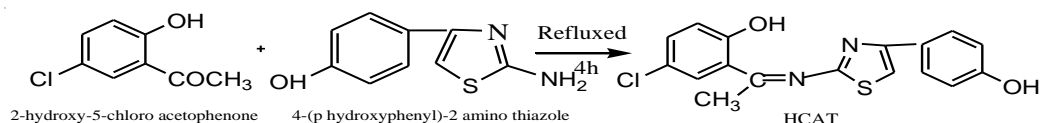


Table1. Analytical data of the Ligands.

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 ₁₇ H ₁₃ N ₂ O ₂ 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)

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

Compounds	Colour	Mol.wt.	Analysis % Found (calc.)					μ_{eff} B.M.	ΔM (Ω -1 cm ² mol ⁻¹)
			M	C	H	N	Cl		
[CoL ₂ (H ₂ O) ₂] H ₂ 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 ₂ (H ₂ O) ₂] H ₂ 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 ₂ (H ₂ O) ₂] H ₂ 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 ₂ (H ₂ O)Cl]H ₂ 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 ₂ (OAc)] H ₂ 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 ₂ (H ₂ O)Cl] H ₂ 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 ₂]	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 ₂ (OH) ₂] 2H ₂ 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 ₂ L ₂]	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

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 were analyzed by standard methods[11]. The ¹H 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⁻¹, carbon, hydrogen and nitrogen analysis were carried out at RSIC, Punjab University, Chandigarh. The molar conductance of the complexes at 10⁻³M dilution in DMF were determined using equiptronic digital conductivity meter EQ-660 with a cell constant 1.00 cm⁻¹ at room temperature. The magnetic moment measurement were made on a Gouy balance at room temperature using [HgCo(SCN)₄] as the calibrant. The thermogravimetric analysis were performed on laboratory set up apparatus in air atmosphere at 10⁰C min⁻¹ 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 ^1H 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 electrolytes¹¹ The ^1H 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 $\nu(\text{C}=\text{N})$ peaks at 1620cm^{-1} and absence of $\text{C}=\text{O}$ peak at around $1700\text{--}1750\text{ cm}^{-1}$ 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	$\nu(\text{O-H})$ hydrogen bonded	$\nu(\text{C}=\text{N})$ imine	$\nu(\text{C}-\text{O})$ phenolic	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{C}-\text{S})$
HCAT	3119	1620	1514	--	--	1122
$[\text{CoL}_2(\text{H}_2\text{O})_2] \text{H}_2\text{O}$	--	1608	1504	470	430	1098
$[\text{NiL}_2(\text{H}_2\text{O})_2] \text{H}_2\text{O}$	--	1585	1465	468	422	1090
$[\text{CuL}_2(\text{H}_2\text{O})_2] \text{H}_2\text{O}$	--	1610	1504	509	410	1110
$[\text{CrL}_2(\text{H}_2\text{O})\text{Cl}] \text{H}_2\text{O}$	--	1590	1506	475	409	1115
$[\text{MnL}_2(\text{OAc})] 2\text{H}_2\text{O}$	--	1562	1462	498	420	1090
$[\text{FeL}_2(\text{H}_2\text{O})\text{Cl}] \text{H}_2\text{O}$	--	1602	1504	512	440	1080
$[\text{VO}_2]$	--	1598	1506	514	445	1098
$[\text{ZrL}_2(\text{OH})_2] 2\text{H}_2\text{O}$	--	1600	1498	445	412	1108
$[\text{UO}_2\text{L}_2]$	--	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_2 (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)[19]. There is no weight-loss upto 250°C in VO(IV) and UO_2 (IV) complexes indicating the absence of any water molecules (lattice or coordinated) 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), Cu(II), Fe(III) and VO(IV) complexes while in case of Mn(III), Zr(IV) and UO_2 (VI) complexes complete decomposition has not been observed upto 800°C . 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 $\text{UO}_2(\text{VI}) > \text{Zr}(\text{IV}) > \text{Mn}(\text{III}) > \text{Cr}(\text{III}) > \text{Cu}(\text{II}) > \text{CO}(\text{II}) > \text{Fe}(\text{III}) > \text{VO}(\text{IV}) > \text{Ni}(\text{II}) > \text{HCAT}$

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 ⁻¹)			Frequency Factor Z (sec ⁻¹)	Entropy Change -ΔS (J mol ⁻¹ K ⁻¹)	Free Energy Change ΔF (kJ mol ⁻¹)
		B*	H-M**	F-C***			
HCAT (LH)	260.51	3.27	5.45	4.36	87.25	212.55	117.75
[CoL ₂ (H ₂ O) ₂] H ₂ O	433.50	5.73	9.55	9.55	191.11	208.24	156.67
[NiL ₂ (H ₂ O) ₂] H ₂ O	384.17	4.13	8.26	3.30	66.03	216.60	145.64
[CuL ₂ (H ₂ O) ₂] H ₂ O	494.86	11.28	11.28	10.16	203.31	208.54	170.28
[CrL ₂ (H ₂ O)Cl] H ₂ O	550.45	9.08	12.98	12.98	259.74	207.11	183.52
[MnL ₂ (OAc)] 2H ₂ O	710.46	11.11	18.51	11.11	222.32	209.86	217.58
[FeL ₂ (H ₂ O)Cl] H ₂ O	429.25	3.77	9.44	8.49	169.89	209.30	155.47
[VOL ₂]	400.23	5.20	8.67	6.94	138.87	210.62	148.73
[ZrL ₂ (OH) ₂] 2H ₂ O	711.17	7.41	18.54	11.12	222.52	209.77	217.65
[UO ₂ L ₂]	800.00	19.85	22.06	17.65	353.20	206.79	239.62

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

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..

References:

- [1] Dayma V., Sharma P., Salvi P., Rathore M. K and Baroliya P. K., Int. J. Res. Advent Technology, 2018, 6 (8), 1826
- [2] Aishatu S. M., Fatima A. and Abigail E. A., American J. Nano Res. and Appl., 2017; 5(6), 110.
- [3] Chandra Mohan, Vinod Kumar, Sarla Kumari, Int. Res. J. Pharm. 2018, 9 (7),153
- [4] Siham Slassi, Adeline Fix-Tailler, Gérald Larcher, Amina Amine and Abdelkrim El-Ghayoury, J. of Heteroatom Chem., 2019, 6862170,1
- [5] Parveez G. and Athar A. H., Asian J. Phy. and Chem. Sci. 2017, 2(4), 1.
- [6] Aswar A.S, Bahad P., Pardhi A. and Bhave N., J. Poym. Mater., 1988, 5, 232.
- [7] Pattan S., Ali M., Pattan J., Purohit S., Reddy V. and Nataraj B., Indian J. Chem., 2006, 45B, 1929.
- [8] Khrustalev D., Suleimenova A. and Fazylov S., Russian J. App. chem., 2008, 81(5), 900.
- [9] Maradiya H., and Patel V., J. Fibers and poly., 2002, 3(1), 43.
- [10] Furniss B., Hannaford A., Smith P. and Tatchell A., Vogel's practical organic chemistry 5thEd. Logman Scientific Technical, John Wiley and Sons, 1989.
- [11] Vogel AI, "A Text book of quantitative inorganic chemistry" 3rdEd., (ELBS,London,1961).
- [12] Sadigova S., Magerramov A. and Allakhverdiev M., Russian J. Org.Chem., 2008, 81(5), 900.
- [13] Campbell E. and Nguyen S., J. Tetrahedron, 2001, 42, 1221.
- [14] Pietikainen P. and Haikarainen A. J. Mole. Catalysis., 2002, 180, 59.
- [15] Kidwai M., Poddar P. and Singhal K., Indian J. Chem., 2009, 48B, 59.
- [16] Sonwane S., Srivastava S. and Srivastava S., Indian J. Chem., 2008, 47B, 633.
- [17] Patel K. and Mehata A., E. J. Chem., 2006, 3(13), 267.
- [18] Boghaei D. and Mohebi S. J. Tetrahedron, 2002, 58, 5357.
- [19] Kassem M.E., Al Kibaisi A.H., Amin R.R., J. Therm. Anal. Calorim., 1998, 51(2), 617.
- [20] Patel I.A and Thaker B.T., Indian J. Chem., 1999, 38A, 427.
- [21] Padalkar V.S., Patil V.S., Gupta V.D., Phatangare K.R., Umap P.G. and Sekar N., Int. J. Sch. Res. Net. Org. Chem., 2011, ID738361, 1.
- [22] Mallikarjun K., E. J. Chem., 2004, 1(2), 105.
- [23] Horowitz H. and Metzger G., Anal. Chem., 1963, 35, 1464.
- [24] Broido A., J. Polym. Sci., 1964, A2, 1761.