



## **THERMAL STUDIES AND APPLICATION OF TETRADENTATE SCHIFF BASE METAL COMPLEXES OF Co(II), Ni(II), Cu(II) Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO<sub>2</sub>(VI) IN ENGINEERING AND INDUSTRIES**

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### **Abstract:**

The newly synthesized tetradentate Schiff base ligand have been prepared by condensing 2-hydroxy-5-chloro acetophenone with ethylene diamine. 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, electronic spectra and thermal analysis. Thermodynamic activation parameters were computed from the thermal data using Broido, Horowitz-Metzger and Freeman-Carroll method, which confirm first order kinetics and kinetic compensation effect and the application of metal complexes with thermal and engineering industries

**Keywords:** Tetradentate Schiff base, Molar conductance, Thermal, Application.

### **Introduction**

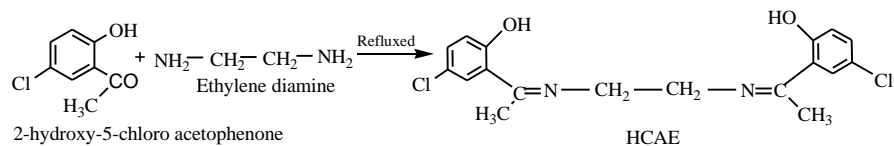
Schiff bases ligands are special ligands as they are easily prepared by condensation reaction between aldehyde derivatives and amines. Their preparation technique and their versatile applications make Schiff base unique compounds in coordination chemistry, analytical chemistry, engineering chemistry, industrial chemistry, catalysis, pharmaceutical chemistry. Data collection and recent studies on biological activities of Schiff bases metal complexes<sup>1</sup>. A review on the history, synthesis, and applications of Schiff bases and their metal complexes<sup>2</sup>. Synthesis, spectral studies, antioxidant and antibacterial evaluation of aromatic nitro and halogenated tetradentate Schiff bases<sup>3</sup>. Synthesis and structural diversity transition metal coordination complexes with diverse Schiff base ligands and macrocyclic systems<sup>4</sup>. New complexes of chelating Schiff base: Synthesis, spectral investigation, antimicrobial, and thermal behavior studies<sup>5</sup>. The thermogravimetric technique has been great significance research method on thermal stabilization and thermal decomposition. Thermogravimetric could provide theory for material heating treatment and application.<sup>6,7</sup> This paper discusses the kinetic of the thermal decomposition effect and application 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).

### **Experimental**

All the chemicals were of A.R. grade and used as received ethylene diamine and 2-hydroxy-5-chloro acetophenone (HCA) was prepared by known methods.<sup>8</sup> The solvents were purified by standard methods.<sup>9</sup>

Synthesis of 2-Hydroxy-5-chloro acetophenone-NN'-ethylenediimine (HCAE).

A hot ethanolic solution of ethylene diamine (0.05 mol) was added to an ethanolic solution of respective acetophenone (0.05 mol). The reaction mixture was refluxed in a water-bath for 4-5 h. The colour product was filtered off and recrystallised. Yield 80%. M. P. 275<sup>0</sup>C.



Preparation of complexes: All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand HCAE (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: 55-60%

**Table 1. Analytical data and molar conductance of the compounds.**

Compounds	Colour	Mol.wt.	Analysis % Found (calc.)					$\mu_{\text{eff}}$ B.M.	$\Lambda_M$ ( $\Omega^{-1}$ $\text{cm}^2$ $\text{mol}^{-1}$ )
			M	C	H	N	Cl		
$\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2\text{Cl}_2$	Yellow	367.0	--	46.84 (46.53)	3.83 (3.93)	6.17 (6.27)	--	--	--
$[\text{CoL}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	Brown	478.1	10.42 (10.45)	38.22 (38.45)	3.72 (3.89)	4.72 (4.85)	--	4.02	5.8
$[\text{NiL}] \cdot \text{H}_2\text{O}$	Black	370.7	11.12 (11.18)	40.32 (40.57)	3.44 (3.65)	5.18 (5.28)	--	Dia	6.6
$[\text{CuL}(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	Brown	500.5	10.65 (10.88)	36.71 (36.87)	3.85 (4.01)	4.60 (4.71)	--	2.12	16.8
$[\text{CrL}(\text{H}_2\text{O})\text{Cl}] \cdot 2\text{H}_2\text{O}$	Yellow	506.5	8.67 (8.78)	36.42 (36.50)	3.62 (3.70)	4.53 (4.70)	5.71 (5.92)	3.56	20.6
$[\text{MnL}(\text{OAc})] \cdot 2\text{H}_2\text{O}$	Brown	514.9	9.05 (9.15)	39.88 (39.98)	3.65 (3.82)	4.52 (4.63)	--	5.26	14.7
$[\text{FeL}(\text{H}_2\text{O})\text{Cl}] \cdot \text{H}_2\text{O}$	Green	482.4	9.11 (9.23)	37.23 (37.39)	3.35 (3.49)	4.71 (4.81)	6.01 (6.08)	5.5	15.7
[VOL]	Green	432.0	9.21 (9.53)	41.22 (41.43)	3.06 (3.09)	5.18 (5.38)	--	1.28	13.6
$[\text{ZrL}(\text{OH})_2] \cdot 2\text{H}_2\text{O}$	Yellow	526.2	14.32 (14.57)	35.18 (35.23)	3.40 (3.52)	4.32 (4.52)	--	Dia	24.7
$[\text{UO}_2\text{L}]$	Orange	635.1	32.57 (32.68)	29.52 (29.62)	2.01 (2.20)	3.73 (3.81)	--	Dia	21.5

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>8</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  $10^0 \text{ C min}^{-1}$  heating rate. The molecular weights of the complexes were determined by Rast method.

## Result and Discussion

The Schiff base ligand HCAE and its complexes have been characterized on the basis of  $^1\text{H}$  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 1) shows all the complexes are non electrolytes<sup>8</sup> The  $^1\text{H}$  NMR spectra of ligand HCAE shows signals at:  $\delta$  15.57 (1H, s, phenolic OH); 8.03(1H, s, phenyl); 7.57 and 7.41 (2H, m, phenyl), 3.23(4H, s,  $\text{CH}_2\text{-CH}_2$ ); 2.41 ppm (3H, s, methyl)<sup>10-1</sup>

**Table 2. IR spectra of ligand and metal complexes.**

Compound	$\delta$ (O-H) hydrogen bonded	$\delta$ (C=N) imine	$\delta$ (C=O) Phenolic	$\delta$ (M-O)	$\delta$ (M-N)
$\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2\text{Cl}_2$	2900	1613	1482	--	--
$[\text{CoL}(\text{H}_2\text{O})_2] \text{H}_2\text{O}$	--	1588	1442	521	456
$[\text{NiL}] \text{H}_2\text{O}$	--	1584	1461	512	496
$[\text{CuL}(\text{H}_2\text{O})_2] 2\text{H}_2\text{O}$	--	1593	1443	593	492
$[\text{CrL}(\text{H}_2\text{O})\text{Cl}] 2\text{H}_2\text{O}$	--	1598	1432	572	462
$[\text{MnL}(\text{OAc})] 2\text{H}_2\text{O}$	--	1592	1443	583	493
$[\text{FeL}(\text{H}_2\text{O})\text{Cl}] \text{H}_2\text{O}$	--	1600	1462	532	427
[VOL]	--	1600	1452	524	485
$[\text{ZrL}(\text{OH})_2] 2\text{H}_2\text{O}$	--	1602	1441	566	464
$[\text{UO}_2\text{L}]$	--	1595	1422	562	473

Thermogravimetric studies: The nature of thermograms of HCAE and its metal complexes indicates that the complexes of Co(II), Ni(II), Cu(II), Cr(III), Mn(III), Fe(III) and Zr(III) decompose in three stage the ligand and VO(IV) complex in two stage while  $\text{UO}_2$  (VI) complex in one stage. All the complexes are stable upto  $70^\circ\text{C}$ . Elimination of one water molecule from Co(II), Ni(II) and Fe(III) upto  $130^\circ\text{C}$  and two water molecules from the Cu(II), Cr(III), Mn(III) and Zr(IV) complexes upto  $150^\circ\text{C}$  have been observed (% wt loss obs./calcd. : Co(II) : 3.26/3.18; Ni(II) : 3.52/3.40; Cu(II) : 6.26/6.12; Cr(III) : 6.20/6.06; Mn(III) : 6.08/5.98; Fe(III) : 3.25/3.10; Zr(IV): 5.98/5.87). Further loss in weight upto  $220\text{-}240^\circ\text{C}$  indicating presence of two coordinated water molecule in Co(II) and Cu(II) each and one in each Cr(III) and Fe(III) complexes (% wt loss obs./calcd. : Co(II) : 6.48/6.37; Cu(II) : 6.24/6.12; Cr(III) : 3.16/3.03; Fe(III) : 3.22/3.10). There is no weight loss upto  $250^\circ\text{C}$  in VO(IV) and  $\text{UO}_2$ (VI) complexes indicating the absence of any water molecules (lattice or coordinated). In all the complexes rapid weight-loss has

been observed above 300°C, indicative of decomposition of the free part of the coordinated ligand, a gradual weight-loss above 400°C corresponding to the degradation of actual coordinated part of the ligand. The half decomposition temperature and the basic parameters calculated for the compounds are given in (Table 3). Thermal activation energy was calculated by Freeman-Carroll,<sup>20</sup> Horowitz-metzger<sup>21</sup> and Broido<sup>22</sup> method. On the basis of half decomposition temperature, the relative thermal stability order is found to be.

The relative thermal stability on the basis of half decomposition temperature is found to be Zr(IV)>UO<sub>2</sub>(VI)>Cu(II)>Cr(III)>Mn(III)>Fe(III)>VO(IV)>CO(II)>Ni(II)> HCAE.

**Table 3. Thermal decomposition data of HCAE and its complexes.**

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***			
C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub>	261.51	3.37	5.55	4.46	87.35	213.55	127.75
[CoL(H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	396.17	3.51	8.64	8.64	170.99	207.83	158.07
[NiL] H <sub>2</sub> O	266.33	2.87	5.75	4.89	98.73	213.61	128.94
[CuL(H <sub>2</sub> O) <sub>2</sub> ] 2H <sub>2</sub> O	592.16	11.51	14.37	11.51	228.43	207.62	199.78
[CrL(H <sub>2</sub> O)Cl] 2H <sub>2</sub> O	443.45	4.93	9.90	9.90	196.21	208.26	168.79
[MnL(OAc)] 2H <sub>2</sub> O	431.15	6.64	9.74	8.59	169.94	209.45	167.04
[FeL(H <sub>2</sub> O)Cl] H <sub>2</sub> O	425.27	6.61	9.40	8.47	167.59	209.36	164.35
[VOL]	416.10	8.26	9.17	8.26	163.39	209.46	162.35
[ZrL(OH) <sub>2</sub> ] 2H <sub>2</sub> O	708.21	9.29	18.49	12.97	257.64	208.61	227.35
[UO <sub>2</sub> L]	680.49	8.78	11.47	13.99	277.86	207.74	221.76

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

Application of metal Complexes in engineering and various industries: Metal complexes are applicable in catalysis, materials synthesis, photochemistry, and biological systems. Medicinal inorganic chemistry can exploit the unique properties of metal ions for the design and synthesis of new drugs in drugs industries and it also important in catalysis, materials synthesis, photochemistry, and biological systems. Medicinal inorganic chemistry can exploit the unique properties of metal ions for the design of new drugs. In analytical chemistry Complex ions are used in many analytical techniques, such as spectroscopy and chromatography, to identify and quantify different substances. Applications of Metal Complexes in Textiles<sup>23</sup> In industry Complex ions are used in the production of dyes, pigments, and catalysts. Metal complex has many applications in heat conduction, fluid flow, electrostatics, and in other areas. Metal just like Co(II), Ni(II), Cu(II), Cr(III), Mn(III), Fe(III) VO(IV), Zr(IV) and UO<sub>2</sub>(VI)



and its complexes are used extensively in manufacturing machines for industries, pharma, agriculture and automobiles which include road vehicles, railways, airplanes, rockets, construction, electronic devices, food processing, biomedical applications etc and its practical applications of metal complexes<sup>24</sup>

### Conclusion:

The compensation effect of thermal decomposition of the complexes indicating the change of sample mass on the estimated values of activation energy. 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. All above studies are applicable in analytical chemistry, engineering chemistry, industrial chemistry.

### References:

1. Maria S.S., Jessica C, Domenico I., Alessia C., Annaluisa M., Camillo R., Carmela S., Hussein E. and Pasquale L., *Int. J. Mol. Sci.* 2022, 23, 14840.
2. Cherifa B, Hana F, Amel D, Amel D, Abdesalem K, Abir B, Ahmad S. D., Tarek L, Verma R. and Yacine B, *Inorganic Chem. Communications*, 2023, 110451, , 150.
3. Bhagwat V., Kadam D and Shinde A., *J. E. Heliyon*, 2022, 8, E-09650.
4. Parveez G. and Athar A. H., *Asian J. Phy. and Chem. Sci.* 2017, 2(4), 1.
5. Al-Zaidi B. H., Hasson M. M. and Ismail A. H. *Journal of Appl.Pharm.Sci.* 2019, 9, 45.
6. Sharma, R.and Kaushik,N.K., *J. Therm. Anal. Cal.*, 2004, 78, 953.
7. Singh, B.K., Sharma, R.K. and Garg, B.S., *J. Therm. Anal.Cal*, 2006, 84, 593.
8. Aswar, A., Bahad, P.,Pardhi, A. and Bhave, N., *J. Polym. Mater*, 1988, 5, 232.
9. Furniss B., Hannaford A., Smith P. and Tatchell A., *Vogel's practical organic chemistry 5<sup>th</sup>Ed.* (Logman Scientific Technical, John Wiley and Sons), (1989).
10. Joshi, J.D., Patel, N.P. and Patel, S.D., *J. Indian Poly.*, 2006, 15(3), 219.
11. Raman, N., Raja, Y.P., Kulandaisamy, A., *J. Indian Acad. Sci.*, 2001, 113(3), 183.
12. Naik, B. and Desai, K.R., *Indian J. Chem.*, 2006, 45B, 267.
13. Campbell, E.J. and Nquyen, S.T., *J. Tetrahedron*, 2001, 42, 1221.
14. Pietikainen, P. and Haikarainen, A., *J. Mole. Catalysis*, 2002, 59, 180.
15. Gottschaldt, M., Wegner, R., Gorls, H., Klufers, P., Jager, E.G. and Klemm, D., *J. 21. Carbohydrate*, 2004, 339, 1941.
16. Matsushita, T. and Shono, T., *J. Polyhedron*, 1986, 5(3), 735.
17. Gupta, S.K., Nutchcock, P.B., Kushwah, Y.S. and Argal, G.S., *J. Inorg. Chimica Acta*, 2007, 360, 2145.
18. Cai, L.H., Hu, P.Z., Du, X.L., Zhang, L.X. and Liu, Y., *Indian J. Chem.*, 2007, 46B, 523.
19. Kidwai, M., Poddar, P.R. and Singhal, K., *Indian J. Chem.*, 2009, 48B, 886.
20. Mallikarjun, K., *E. J. Chem.*, 2004, 1(2), 105.
21. Horowitz, H. and Metzger, G., *Anal. Chem.*, 1963, 35, 1464.
22. Broido, A., *J. Polym. Sci.*, 1964, A2, 1761.
23. Shuchismita D., *Southeast Uni. Jou. of Textile Engineering*, 2021, 1(1), 30.
24. Iztok T., *Molecules*, 2015, 20, 7951.