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Synthesis and Agricultural application of Co(II), Ni(II) and Cu(II) Complexes derived from 2-hydroxy-5-chloro acetophenone 4-(p-hydroxyphenyl)-2 imino thiazole Schiff base

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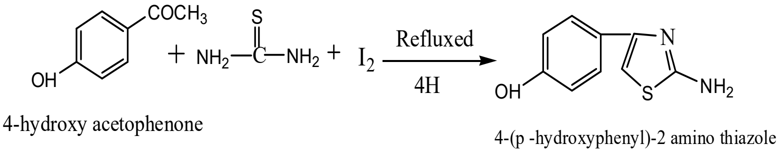
Abstract: The newly synthesized 2-hydroxy-5-chloro acetophenone 4-(p-hydroxyphenyl)-2 imino thiazole Schiff base have been synthesized by condensing 2-hydroxy-5-chloro acetophenone and 4-(p-hydroxyphenyl)-2-aminothiazole. The metal complexes were obtained as a result of interaction of Schiff base ligand 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 studies. Agricultural studies and application of given Schiff base metal complexes.

Keywords: Thiazole Schiff Base, Molar conductance, Thermal and Agricultural application.

Introduction: Synthesis of a novel Schiff base derivative with fluorescence behavior and other coordination Complexes Synthesis, characterization and anticancer potency against hepatocellular carcinoma[1]. Comprehensive review on Schiff Base heterocyclic moiety conjugates and synthesis, reactions and diverse applications[2]. Synthesis, characterisation and antimicrobial studies of Schiff base ligand derived from salicylaldehyde and 2,4-dinitrophenylhydrazine and its metals complexes[3]. synthesis, characterisation and various methods of Schiff base derived from sulphanilic acid and salicylaldehyde and Comparative study of Schiff base using various synthesis methods and their theoretical prediction of activities[4]. 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[5]. This paper discusses the kinetic of the thermal decomposition and the accompanying compensation effect for Schiff base complexes of Co(II) and Ni(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

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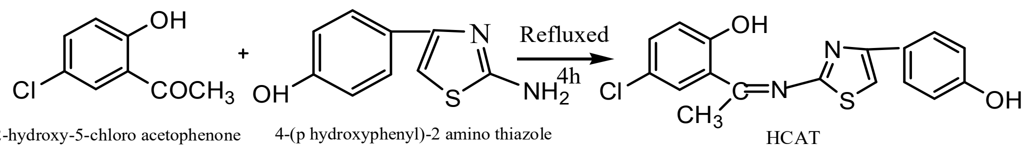
temperature. The purity of ligand was checked by elemental analysis shown in Table 1. and m.p. It was also characterized by IR and ^1H NMR spectral studies. Yield:70%; m.p. 310^{0}C



2-hydroxy-5-chloro acetophenone   4-(p hydroxyphenyl)-2 amino thiazole   HCAT

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	$C_{17}H_{13}N_2O_2SCl$	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%.

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^{-3}M 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 10^{0}C min^{-1} heating rate. The molecular weights of the complexes were determined by Rast method are shown in Table 2.

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

Compounds	Colour	Mol.wt.	Analysis % Found (calc.)					μeff B.M.	ΛM (Ω-1 cm2 mol-1)
			M	C	H	N	Cl		
$[CoL_2(H_2O)_2]\ H_2O$	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
$[NiL_2(H_2O)_2]\ H_2O$	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
$[CuL_2(H_2O)_2]\ H_2O$	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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Results and Discussion: The Schiff base ligand HCAT and its complexes have been characterized on the basis of ^{1}H NMR, IR spectral data, elemental analysis, molar conductance, magnetic succeptibility 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[11] The ^{1}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^{-} and absence of C=O peak at around 1700–1750 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	□(O□H) hydrogen bonded	□(C=N) imine	□(C□O) phenolic	□(M□O)	□(M□N)	□(C□S)
HCAT	3119	1620	1514	--	--	1122
$[CoL_2(H_2O)_2]\ H_2O$	--	1608	1504	470	430	1098
$[NiL_2(H_2O)_2]\ H_2O$	--	1585	1465	468	422	1090
$[CuL_2(H_2O)_2]\ H_2O$	--	1610	1504	509	410	1110

Thermogravimetric studies:

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
$[CoL_2\ (H_2O)_2]\ H_2O$	433.50	5.73	9.55	9.55	191.11	208.24	156.67
$[NiL_2\ (H_2O)_2]\ H_2O$	384.17	4.13	8.26	3.30	66.03	216.60	145.64
$[CuL_2\ (H_2O)_2]\ H_2O$	494.86	11.28	11.28	10.16	203.31	208.54	170.28

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

In Thermogravimetric studies 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 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;[19] In the thermograms of ligand, Co(II), Ni(II) and Cu(II) complexes[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

Agricultural application of metal complexes: A ploughshare is an cobalt Copper and nickel metal complexes used in agriculture to increase the production of crops. They are used prior to the seedling stage to loosen up the soil. Essential observed that cobalt (Co) and copper (Cu), complexes with schiff base plays a beneficial role in plant growth and development. Synthetic Action on Insecticides: Schiff base ligand was derived from the condensation of 4-(p-hydroxyphenyl)-2-aminoe thiazole and 2-hydroxy-5-chloro acetophenone. Their metal complexes show high activity against insects[25]. 4-(p-hydroxyphenyl)-2 imino thiazole acts as intermediate in synthesis of photostable pyrthriod insecticides[26]. Flourination on aldehyde part of Schiff base increases insecto acracicidal activity[27]. Schiff bases and their metal complexes with Co(II), Ni(II) and Cu(II) show insecticidal activities against bollworm[28]. Most metals complexes cause environmental and atmospheric pollution, and may be lethal to humans. Heavy metals can become strongly toxic by mixing with different environmental elements, such as water, soil, and air, and humans and other living organisms can be exposed to them through the food chain. Arsenic, cadmium, chromium, copper, nickel, lead and mercury are the most common metals which can pollute the environment. They are not all equally important but all play a role in plant growth. The heavy metals Co(II), Ni(II) and Cu(II) are micronutrients or trace elements for plants. They are essential for growth and stress resistance as well as for biosynthesis and function of different biomolecules such as carbohydrates, chlorophyll, nucleic acids, growth chemicals, and secondary metabolites. Nitrogen (N) containing Schiff base metal complexes is made available to the plant from the air and soil. But most of the needed elements that are nutrients for plants come from the soil.

Conclusions: The compensation effect of thermal studies of the complexes indicate the change of sample mass and size on the estimated values of activation energy. The Schiff bases ligand and their metal complexes shows more activity towards the agricultural Influence and applicable for plant growth

References:

1. El-Refaie K, Heikki T, Mohamed A, Samar A, Khattab M., Kenawy A., Radwan H.A. and Abosharaf, Int. J. of Biological Macromolecules, 302, 2025, 140506.
2. Harshil P.V., Shraddha A.D., Hiren V.D. and Sarita R.C., Int. J. Mult. & Res.,4(6),2024, 1
3. Shettima U.A., Ibrahim M. & Idongesit, E.E., Nigerian Res. J. of Chemical Sci, 1(12), 2024, 219.
4. Dayma V., Sharma P., Salvi P., Rathore M. K and Baroliya P. K., Int. J. Res. Advent Technology, 6(8), 2018,1826.
5. Chandra Mohan, Vinod Kumar, Sarla Kumari, Int. Res. J. Pharm. 2018, 9 (7),153
6. Aswar A.S, Bahad P., Pardhi A. and Bhave N., J. Poym. Mater., 5, 1988, 232.
7. Pattan S., Ali M., Pattan J., Purohit S., Reddy V. and Nataraj B., Indian J. Chem.,45B, 2006, 1929.
8. Khrustalev D., Suleimenova A. and Fazylov S., Russian J. App. chem., 81(5), 2008, 900.
9. Maradiya H., and Patel V., J. Fibers and poly., 3(1), 2002, 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" 3 thEd., (ELBS,London,1961).
12. Sadigova S., Magerramov A. and Allakhverdiev M., Russian J. Org.Chem., 81(5), 2008, 900.
13. Campbell E. and Nguyen S., J. Tetrahedron, 42, 2001, 1221.
14. Pietikainen P. and Haikarainen A. J. Mole. Catalysis., 180, 2002, 59.
15. Kidwai M., Poddar P. and Singhal K., Indian J. Chem., 48B, 2009, 59.
16. Sonwane S., Srivastava S. and Srivastava S., Indian J. Chem., 47B, 2008, 633.

17. Patel K. and Mehata A., E. J. Chem., 3(13), 2006, 267.
18. Boghaei D. and Mohebi S. J. Tetrahedron, 58, 2002, 5357.
19. Kassem M.E., Al Kibaisi A.H., Amin R.R., J. Therm. Anal. Calorim., 51(2), 1998, 617.
20. Patel I.A and Thaker B.T., Indian J. Chem., 38A, 1999, 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., ID738361, 2011, 1.
22. Mallikarjun K.., E. J. Chem., 1(2), 2004, 105.
23. Horowitz H. and Metzger G., Anal. Chem., 35, 1963, 1464.
24. Broido A., J. Polym. Sci., A2, 1964, 1761.
25. D.A. Laidler, D.J Milner, J. Organomet Chem., 270, 1984, 121.
26. N. S. Kozlow, G.P. Korotyshova and N.G. Rozhkova, E.I.Andreeva. Chem Abstr. 106, 1987, 155955.
27. L. Zhu, N Chen, .F. Li H, Song, X. Zhu, Chem Abstr,, 141, 2004, 374026,.
28. S. Huneck, K. Schreiber, H.D. Grimmecke , J Plant Growth Regul, 3,1984, 75.