



Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis, Characterization, Thermal and Microbiological evaluation of Thiazole Schiff Base Complexes of Co (II), Ni (II), Cu (II) and Zn (II)

S. R. Kelode and P. R. Mandlik

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

ABSTRACT

Complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff base derived from 2-hydroxy-5-chloroacetophenone and 4-(p-hydroxyphenyl)-2-aminothiazole have been synthesized and characterized on the basis of elemental analysis, Infrared, ^1H NMR, molar conductance, magnetic susceptibilities and thermogravimetric analysis. The Schiff base acts as a monobasic bidentate ligand commonly coordinates through the oxygen atom of phenolic OH group and the nitrogen atom of azomethine group, which is confirmed by IR spectral data. Thermal analysis indicates the presence of coordinated as well as lattice water molecules in the complexes which are also confirmed by IR spectral data. The analysis of diffuse reflectance spectra, magnetic susceptibility and thermal analysis data indicate distorted octahedral geometry for Cu (II) complex while octahedral geometry for the Co (II), Ni (II) & Zn (II) complexes. All the complexes have been evaluated for their antimicrobial activity by agar cup-plate method against various organisms.

Keywords: Schiff base, Magnetic, Thermo gravimetric analysis, Antimicrobial

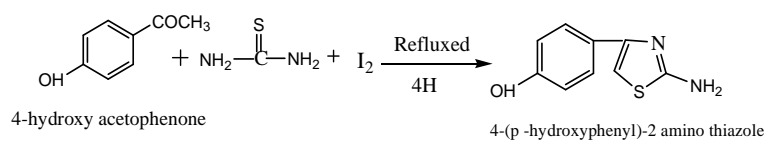
INTRODUCTION

Schiff bases are usually formed by the condensation of aliphatic or aromatic, aldehydes or ketones with primary aliphatic or aromatic amines, hydrazides, etc. The Schiff bases play a significant role in the area of Coordination Chemistry. They have widely studied because of their industrial and biological applications. Schiff bases and their metal complexes have many applications in different fields [1]. The Schiff bases derived from thiazole and substituted acetophenone have been widely used as ligand for the synthesis of transition metal complexes [2]. Thiazole Schiff base ligands and their metal complexes are biologically active [3] and are known for their biological application [4] i.e. one of the drug in cytotoxicity of anticancer [5]. 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 SECTION

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-chloroacetophenone 4-(p-hydroxyphenyl)-2-iminothiazole [HCAT]:

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-chloroacetophenone (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 ^1H NMR spectral studies.

Yield: 70%; m.p. 310°C

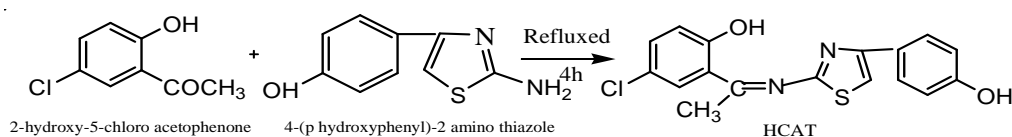


Table 1. Analytical data of the Ligands

Sr. No.	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.)
1.	HCAT	$\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}_2\text{SCl}$	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 [acetates of Co (II), Ni (II), Cu (II), and Zn (II)] 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 was 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 $400\text{-}4000\text{cm}^{-1}$, 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 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 C min^{-1} heating rate. The molecular weights of the complexes were determined by Rast method.

Table 2. Analytical data and molar conductance of the compounds

Compounds	Colour	Mol.wt.	Analysis % Found(calc.)						μ_{eff} B.M.	Δ_M ($\Omega^{-1} \text{cm}^2$ mol^{-1})
			M	C	H	N	Cl	S		
[Co(L) 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)	7.90 (8.02)	4.48	6.9
[Ni(L) 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)	7.88 (8.02)	3.2	7.9
[Cu(L) 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)	7.85 (7.97)	1.70	8.3
[Zn(L) ₂ (H ₂ O) ₂]2H ₂ O	Red	824.6	7.82 (7.93)	49.14 (49.47)	3.78 (3.88)	6.42 (6.79)	7.50 (8.61)	7.64 (7.78)	Dia	9.3

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 are 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.

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 C=O peak at around 1700–1750 cm⁻¹ indicates the Schiff base formation [16-19].

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	$\nu(\text{C-S})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
HCAT	3119	1620	1514	1122	-	-
[Co(L) ₂ (H ₂ O) ₂]H ₂ O	-	1608	1504	1098	470	430
[Ni(L) ₂ (H ₂ O) ₂]H ₂ O	-	1585	1465	1090	468	422
[Cu(L) ₂ (H ₂ O) ₂]H ₂ O	-	1610	1504	1110	509	410
[Zn(L) ₂ (H ₂ O) ₂]2H ₂ O	-	1511	1448	1106	470	425

Magnetic and electronic spectral studies:

The diffuse reflectance spectra of Co(II) complex shows three bands at 8550, 18102 and 19998cm⁻¹ which was assigned to ⁴T_{1g}(F) → ⁴T_{2g}(F), ⁴T_{1g}(F) → ⁴A_{2g}(F) and ⁴T_{1g}(F) → ⁴T_{1g}(P) transitions respectively. The observed magnetic moment 4.48 B.M. favors the high spin nature and octahedral geometry of complex [20]. The measured magnetic moment of Ni(II) complex 3.2 B.M and shows three bands at 13102, 19204 and 26998cm⁻¹ these bands are assigned to ³A_{2g} → ³T_{2g}(F), ³A_{2g} → ³T_{1g}(F) and ³A_{2g} → ³T_{1g}(P) transitions respectively. The magnetic moment and assignment of these band suggest an octahedral geometry [21]. The Cu (II) complex exhibits 1.70 B.M. magnetic moment value and two bands at 15374, 15388, 19997cm⁻¹ is assigned to ²B_{1g} → ²A_{1g}, ²B_{1g} → ²B_{2g} and ²B_{1g} → ²E_g transitions suggesting the distorted octahedral geometry of the complex [22]. The Zn(II) is found to be diamagnetic in nature and does not show any band in the electronic spectra, indicates no d-d transition as expected for d⁰ and d¹⁰ system, suggest octahedral geometry, also supported by IR, thermal and analytical data.

Thermogravimetric studies:

Thermogravimetric study indicates all the complexes are stable up to 60-70°C. All the complexes shows three stage decomposition pattern. The percentage weight loss up to 140°C indicates the loss of one water molecule from Co (II), Ni (II), and Cu (II) loss of two water molecule from Zn (II) complexes. Further loss in weight up to 220-240°C was observed. The percentage weight loss data indicates loss of two coordinated water molecule from Co (II), Ni (II), Cu (II) and Zn (II) complexes each. The Thermal activation energy (Table 4) was calculated by Freeman-Carroll [23], Horowitz-metzger [24] and Broido [25] method

Table 4: Thermal decomposition data of the complexes of HCAT

Complexes	Half decomposition Temperature(°C)	Activation energy kJmol ⁻¹			Z S ⁻¹	ΔS Jk ⁻¹ mol ⁻¹	ΔF kJ mol ⁻¹
		FC- method	HM- method	Broido- method			
Co(II)	433.50	5.73	9.55	9.55	191.11	208.24	156.67
Ni(II)	384.17	4.13	8.26	3.30	66.03	216.60	145.64
Cu(II)	494.86	11.28	11.28	10.16	203.31	208.54	170.28
Zn(II)	571	4.09	13.65	4.09	81.80	216.91	183.19

Antimicrobial activity:

The inhibition effect of the ligand and its metal complexes on the growth of various bacteria is summarized in Table 5. The synthesized complexes have been screened for the antimicrobial activity against *B. subtilis*, *P. vulgaris*, *S. aureus*, *E. coli*, *P. fluorescen*, *A. aerogenes* and *B. megatherium* strains by using agar cup-plate method .

Table 5. Antimicrobial activity [26-32]

Ligand and its complexes	<i>B. subtilis</i> (mm)	<i>P. vulgaris</i> (mm)	<i>S. aureus</i> (mm)	<i>E. coli</i> (mm)	<i>P. fluorescen</i> (mm)	<i>A. aerogenes</i> (mm)	<i>B. megatherium</i> (mm)
HCAT	S ₉	R	S ₁₆	S ₁₂	S ₁₀	R	R
Co- HCAT	S ₁₀	R	S ₉	R	S ₁₂	S ₇	R
Ni- HCAT	R	S ₈	S ₁₁	R	S ₁₄	S ₉	S ₇
Cu- HCAT	R	S ₁₂	S ₁₄	S ₇	S ₉	R	S ₉
Zn- HCAT	R	S ₇	S ₁₁	R	R	S ₈	R

CONCLUSION

All the complexes shows weight loss up to 320°C indicates decomposition of ligand molecule. On the basis of half decomposition temperature the order of thermal stability is found to be Zn (II) > Cu (II) > Co (II) > Ni (II). The analysis of thermal analysis magnetic moment, and electronic spectral data indicate distorted octahedral geometry for the Cu (II) & octahedral geometry for the Co (II), Ni (II) and Zn (II) complexes. The structural changes have marked effect on the sensitivity and sensitivity varies with organisms.

REFERENCES

- [1] M Ramesh; K Chandrashekar; K Reddy, *Indian J. Chem.*, **2000**, 39A, 1337
- [2] M Jayaramudu; K Reddy, *Indian J. Chem.*, **1999**, 38A, 1173.
- [3] S Raziya; S Mohan; S Rao, *Indian J. Chem.*, **2007**, 46B, 884.
- [4] S Kumar; D.Dhar; P.Saxena, *J. Sci.and Indu.Research*, **2009**, 68, 181.
- [5] T Reji; S Devi; K Thomas; K Sreejalekshmi; S Manju; M Francis; S Philip; A Bharathan; K Rajasekharan, *Indian J. Chem.*, **2008**, 47B, 1145.
- [6] A Aswar; P Bahad; A Pardhi; N Bhave, *J. Poym. Mater.* **1988**, 5, 232.
- [7] S Pattan; M Ali; J Pattan; S Purohit; V Reddy; B Nataraj, *Indian J. Chem.*, **2006**,45B, 1929..
- [8] D Khrustalev; A Suleimenova; S Fazylov, *Russian J. App. chem.*, **2008**, 81(5), 900.
- [9] H Maradiya; V Patel, *J. Fibers and poly.*, **2002**, 3(1), 43.
- [10] B Furniss; A Hannaford; P Smith; A Tatchell, *Vogel's practical organic chemistry* 5thEd. (Logman Scientific Technical, John Wiley and Sons),**1989**.
- [11] Vogel AI, "A Text book of quantitative inorganic chemistry" 3thEd., (ELBS,London),**1961**.
- [12] S Sadigova; A Magerramov; M Allakhverdiev, *Russian J. Org. chem.*, **2008**, 81(5), 900.
- [13] E Campbell; S Nguyen, *J. Tetrahedron*, **2001**, 42, 1221.
- [14] P Pietikainen; A Haikarainen *J. Mole. Catalysis.*, **2002**, 180, 59.
- [15] M Kidwai; P.Poddar; k Singhal, *Indian J. Chem.*, **2009**, 48B, 59.
- [16] S Sonwane; S Srivastava; S Srivastava, *Indian J. Chem.*, **2008**, 47B, 633.
- [17] K Patel; A Mehata, *E. J. Chem.*, **2006**, 3(13), 267.
- [18] R Maurya; D Antony; S Gopinathan; V Puranic; S Tavale; C.Gopinathan, *Bull. Chem. Soc. Jpn.* **1995**, 68, 2847.
- [19] D Boghaei; S Mohebi, *J. Tetrahedron*, **2002**, 58, 5357.
- [20] A Kumar; G Singh; R Handa; S Dubey, *Indian J. Chem.*,**1999**, 38A, 613.
- [21] A Syamal; M Maurya., *Indian J. Chem.*, **1985**, 42A, 836.

- [22] AK Panda; DC. Dash; P Mishra, *Indian J. Chem.*, **1997**, 36A, 712.
[23] K Mallikarjun, *E. J. Chem.*, **2004**, 1(2), 105.
[24] H Horowitz; G Metzger, *Anal. Chem.*, **1963**, 35, 1464.
[25] A Broido, *J. Polym. Sci.*, **1964**, Part A2, 1761.
[26] SD Dhumwad; KB. Gudasiand; TR Gaudar, *Indian J. Chem.*, **1994**, 33A, 320.
[27] AK Mapari; KV Mangaonkar, *Int. J. ChemTech Res.*, **2011**, 3(1), 477.
[28] IO Adeoye; OO Adelowo; OO Onawumi, *J. Chem. Pharm. Res.*, **2012**, 4(1), 1.
[29] N Chauhan; K Vyas; K Nimavat; K Joshi, *J. Chem. Pharm. Res.*, **2012**, 4(2), 1106.
[30] UI Singh; RK Singh; WR Devi; CH Singh, *J. Chem. Pharm. Res.*, **2012**, 4(2), 1130.
[31] S Prakash; VP Vaidya; KM Mahadevan; MK Shivananda1; PA Suchetan; B Nirmala; M Sunitha, *J. Chem. Pharm. Res.*, **2012**, 4(2), 1179.
[32] CI Raj; M Christudhas; GA Raj, *J. Chem. Pharm. Res.*, **2011**, 3(6), 127.