National Conference on Recent Trends and Developments in Environmental and Basic Sciences (RTDEBS-2018)
Organized by, Faculty of Science In collaboration with
Internal Quality Assurance Cell (IQAC), Dr. S. D. D. Arts College &
Commerce & Science College, Maharashtra, India. Association with
International Journal of Scientific Research in Science and Technology
© 2018 IJSRST | Volume 4 | Issue 3 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X

Thermal Studies of Thiazole Schiff Base Metal Complexes of Co(II), Ni(II), Cu(II), Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO2(IV)

S. R. Kelode
Department of Chemistry, Arts, Commerce and Science College, Maregaon, Maharashtra, India

ABSTRACT

A newly synthesize thiazole 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 newly synthesize thiazole Schiff base and metal complexes with Co(II), Ni(II), Cu(II), Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO_2(VI) have been prepared and characterized by elemental analysis, molecular weight determinations, conductance measurements, spectral and thermal studies. The isolated products are coloured solids, soluble in DMF, DMSO and THF.

Keywords: Schiff base, Magnetic susceptibility, Thermal,

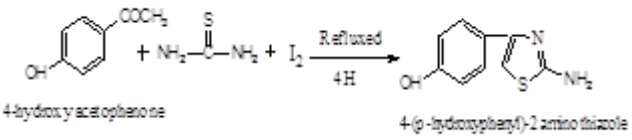
I. INTRODUCTION

Schiff's bases, widely used as analytical reactants and have been studied for chemistry.[1] Antimicrobial evaluation of 2-amino pyridine-derived Ligand Schiff base and its complexes with Cu (II), Hg (II), Ni (II), Mn (II) and Co (II)[2]. Schiff bases metal complexes have many applications in different fields. The Schiff bases derived from thiazole and substituted acetophenone have been widely used as ligand for the synthesis of transition metal complexes. 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]. 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

II. 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[6-9]. The solvents were purified by standard methods[10].

Synthesis of 4-(phydroxyphenyl)-2aminothiazole;



Synthesis of 2-hydroxy-5-chloro-3-nitro acetophenone 4-(p-hydroxyphenyl)-2 imino thiazole [HCNAT]: 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-3-nitro 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 and m.p. It was also characterized by IR and ^{1}H NMR spectral studies. Yield:70%; m.p. 310^{0}C

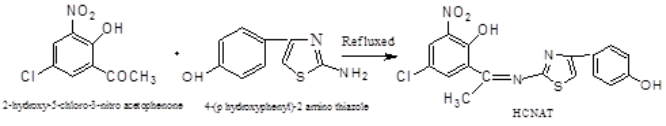


Table1. Analytical data of the Ligand.

Ligand	Molecular Formula	Formula Weight	Color and nature	Elemental Analysis			
				C% found (Cal.)	H% Found (Cal.)	Cl% Found (Cal.)	S% Found (Cal.)
HCNAT	$C_{17}H_{13}N_3O_4SCl$	390.6	Yellow Crystalline	52.34 (52.22)	03.26 (03.32)	9.02 (9.08)	08.12 (08.21)

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.

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

Ligand	Formula weight g mole^{-1}	Colour	Elemental Analysis Found (Calcd.)				μ_{eff} B.M	Λ_M (Ω^{-1} cm^2 mol^{-1})
			M%	C%	H%	Cl%		
$[CoL_2(H_2O)_2]\ H_2O$	892.1	Brown	6.25 (6.60)	44.86 (45.73)	3.25 (3.36)	7.70 (7.95)	4.6	6.8
$[NiL_2(H_2O)_2]\ H_2O$	891.9	Green	6.30 (6.58)	45.58 (45.74)	3.16 (3.36)	7.72 (7.96)	3.1	7.6
$[CuL_2(H_2O)_2]\ H_2O$	896.7	Brown	6.90 (7.08)	45.26 (45.50)	3.12 (3.34)	7.72 (7.91)	1.6	8.2
$[CrL_2(H_2O)Cl]\ H_2O$	902.7	Green	5.32 (5.76)	44.90 (45.19)	2.36 (2.88)	11.08 (11.79)	3.8	18.6
$[MnL_2(OAc)]\ H_2O$	929.1	Brown	5.40 (5.90)	46.15 (46.49)	3.16 (3.33)	7.32 (7.64)	4.6	18.4
$[FeL_2(H_2O)Cl]\ H_2O$	906.6	Black	6.02 (6.16)	44.81 (45.00)	3.02 (3.08)	11.41 (11.74)	5.2	22.2
$[VOL_2]$	846.2	Green	5.63 (6.02)	48.01 (48.21)	2.15 (2.83)	8.32 (8.39)	1.4	12.4
$[ZrL_2\ (OH)_2]\ 2H_2O$	940.4	Yellow	9.48 (9.69)	43.13 (43.38)	3.06 (3.19)	7.26 (7.54)	Dia	16.2
$[UO_2L_2]$	1049.3	Orange	22.43 (22.69)	38.51 (38.88)	2.11 (2.28)	6.32 (6.76)	Dia	14.2

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[11-12] The ^{1}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 400-4000cm^{-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.

III. RESULT AND DISCUSSION

The Schiff base HCNAT and its complexes have been characterized on the basis of ^{1}H NMR, IR spectral data, elemental analysis, molar conductance, magnetic susceptibility measurements and thermo gravimetric analysis data. All these values and analytical data is consistent with proposed molecular formula of legend. 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 (Table2) shows all the complexes are non electrolytes. The ^{1}H NMR spectra of ligand HCNAT shows signals at δ 12.11, (1H, s phenolic OH), δ 9.52 (1H, s, phenolic OH), δ 7.56, 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) [11,13-15]. IR spectra of ligand and metal complexes shows ν(C=N) peaks at 1620 cm^{-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	ν(O–H) hydrogen bonded	ν(C=N) imine	ν(C–O) phenolic	ν(M–O)	ν(M–N)	ν(C–S)
HCNAT (LH)	3119	1620	1514	--	--	1122
$[CoL_2(H_2O)_2]$ H_2O	--	1608	1506	472	432	1098
$[NiL_2(H_2O)_2]$ H_2O	--	1585	1464	469	423	1090
$[CuL_2(H_2O)_2]$ H_2O	--	1610	1503	508	412	1110
$[CrL_2(H_2O)Cl]$ H_2O	--	1590	1505	475	410	1115
$[MnL_2(OAc)]$ $2H_2O$	--	1562	1461	496	422	1090
$[FeL_2(H_2O)Cl]$ H_2O	--	1602	1502	510	441	1080
$[VOL_2]$	--	1598	1505	512	446	1098
$[ZrL_2(OH)_2]$ $2H_2O$	--	1600	1496	446	414	1108
$[UO_2L_2]$	--	1585	1440	548	480	1082

Thermogravimetric studies:

Thermogravimetric study indicates all the complexes are stable up to 60-70^{0}C. All the complexes shows half decomposition temperature(Table 4). The Thermal activation energy was calculated by Freeman-Carroll[20], Horowitz-metzger[21] and Broido[22] method.

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

Compounds	Half Decompo-sition Tempera-ture (^{o}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***			
HCNAT (LH)	260.50	3.27	5.45	4.36	87.25	212.55	117.75
$[CoL_2(H_2O)_2]\ H_2O$	433.40	5.73	9.55	9.55	191.11	208.24	156.67
$[NiL_2(H_2O)_2]\ H_2O$	384.12	4.13	8.26	3.30	66.03	216.60	145.64
$[CuL_2(H_2O)_2]\ H_2O$	494.84	11.28	11.28	10.16	203.31	208.54	170.28
$[CrL_2(H_2O)Cl]\ H_2O$	550.42	9.08	12.98	12.98	259.74	207.11	183.52
$[MnL_2(OAc)]\ 2H_2O$	710.42	11.11	18.51	11.11	222.32	209.86	217.58
$[FeL_2(H_2O)Cl]\ H_2O$	429.22	3.77	9.44	8.49	169.89	209.30	155.47
$[VOL_2]$	400.20	5.20	8.67	6.94	138.87	210.62	148.73
$[ZrL_2(OH)_2]\ 2H_2O$	711.19	7.41	18.54	11.12	222.52	209.77	217.65
$UO_2L_2]$	800.00	19.85	22.06	17.65	353.20	206.79	239.62

IV. 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. Thermogravimetric analysis concluded water loss in metal complexes from the nature of thermograms and half decomposition temperature.

V. REFERENCES

[1]. Aghera V.K. and Parsania P. H., J. Sci. and Ind. Res.,2008, 67, 1083.

[2]. Rehab K A.S., Wurood A J., and Ali N N., J. Pharma, Bio and Chem Sci., 2017, 8(3), 174.

[3]. Raziya S., Mohan S. and Rao S.,Indian J. Chem., 2007, 46B, 884.

[4]. Kumar S.,Dhar D.and Saxena P.,J. Sci.and Indu.Research, 2009, 68, 181.

[5]. Reji T., Devi S,Thomas K., Sreejalekshmi K., Manju S., Francis M.,.Philip S , Bharathan A., and Rajasekharan K.,Indian j. Chem., 2008, 47B, 1145.

[6]. Aswar A., Bahad P.,.Pardhi A. and Bhave N.,J. Poym. Mater. 5, 232 (1988).

[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 5 thEd. (Logman Scientific Technical, John Wiley and Sons), (1989).
[11]. Sadigova S., Magerramov A.and Allakhverdiev M., Russian J. Org. chem., 81(5), 2008, 900.
[12]. Vogel AI, "A Text book of quantitative inorganic chemistry"3thEd., (ELBS,London,1961).
[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]. Maurya R.,Antony D., Gopinathan S., Puranic V., Tavale S.and Gopinathan C., Bull. Chem. Soc. Jpn., 68, 1995, 2847.
[19]. Boghaei D.and Mohebi S.J. Tetrahedron, 58, 2002, 5357.
[20]. Mallikarjun K., E. J. Chem., 1(2), 2004, 105.
[21]. Horowitz H. and Metzger G.,Anal. Chem., 35, 1963, 1464.
[22]. Broido A., J. Polym. Sci. Part, A2, 1964, 1761.