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Thermal Parameter of Cr (III), Mn (III) and Fe (III) of Schiff base Complexes

S. R. Kelode[1*]

1. Department of Engg. Chemistry, Jagadambha College of Engineering and Technology, Yavatmal.
*[Email: sandeep_kelode@yahoo.co.in]

A newly synthesized Schiff base metal complexes Cr (III), Mn (III) and Fe (III) of 2-hydroxy-5-chloro acetophenone 2-imino-4-phenyl thiazole condensed from 2-hydroxy-5-chloro acetophenone and 2-amino-4-phenyl thiazole have been synthesized and characterized on the basis of elemental analysis, Infrared, ^{1}H NMR, molar conductance and magnetic susceptibilities 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. All the metal complexes have studies thermal properties and their thermal parameter.

Keyword: Schiff base, Magnetic, Thermal studies.

1. Introduction

The Schiff bases are widely used ligands due to their facile synthesis, significant versatility and good solubility in common solvents. The structure of these coordination complexes arises due to the interesting ligand systems containing different donor sites in heterocyclic rings. Schiff base have received much great interest, mainly because of their wide application in the field of synthesis and catalysis [1]. Thus, they have played a important applicable role in research and development of coordination chemistry as they readily form stable metal complexes in different oxidation states [2] Thiazole Schiff base ligands and their metal complexes are biologically active [3]. Due to its biological potency, pharmacological properties and synthetic flexibility of Schiff base derived from isonicotinic acid hydrazide [4]. Hydrazones, heteroaroyl hydrazones ligands and their metal complexes are biologically active. Heteroaroyl hydrazones forms stable metal complexes with transition metal ions and inner transition metal ions due to complexing ability of ligand through keto-enol tautomerism and availability of other donar sites in the ligand i.e. isonicotinoyl hydrazide is one of the drug in chemotherapy of tuberculosis [5].

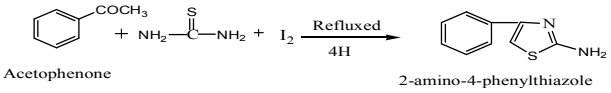
The aim of present investigation is to synthesize various transition metal complexes of Schiff base condensed from 2-hydroxy-5-chloroacetophenone and 2-amino-4-phenyl thiazole.

2. Experimental

All the chemicals were of A.R. grade and used as received. 2-hydroxy-5-chloro- acetophenone (HCA) and 2-amino-4-phenylthiazole was prepared by known methods [6-9]. The solvents were purified by standard methods [10].

2.1. Synthesis of 2-amino-4-phenylthiazole

The synthesis of 2-amino-4-phenylthiazole prepared by known method [7-9]. The product was filtered and crystallized from 70% ethanol, after several minutes the golden coloured product of 2-amino-4-phenylthiazole was separated out.
Yield: 75%; m.p.: 148-150 ^{0}C

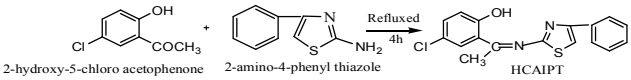


Acetophenone 2-amino-4-phenylthiazole

2.2 Synthesis of 2-hydroxy-5-chloro acetophenone 2-imino-4-phenyl thiazole [HCAIPT]

A solution of 2-hydroxy-5-chloro acetophenone (0.02 M) in 25 ml of ethanol was added to an ethanolic solution(25 ml) of 2-amino-4-phenylthiazole(0.02 M) and the reaction mixture was refluxed on a water bath for 4 h. 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: 35%; m.p. 290 ^{0}C



2-hydroxy-5-chloro acetophenone 2-amino-4-phenyl thiazole HCAIPT

Scheme 1. Synthesis of HCAIPT

Table 1: Analytical data of the Ligands.

S. No	Ligand	Molecular Formula	FormulaWeight	Color and nature	Elemental Analysis				
					C% found (Cal.)	H% Found (Cal.)	N% Found (Cal.)	Cl% Found (Cal.)	S% Found (Cal.)
1.	HCAIPT	$C_{17}H_{12}N_2OSCl$	327.6	Yellow Crystalline	61.38 (62.27)	03.10 (03.66)	08.24 (08.54)	10.21 (10.83)	09.13 (09.79)

2.3 Preparation of complexes

All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand HCAIPT (0.02 M) in 25 ml 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 (Table 2) by standard methods [11].

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		
$[CrL_2(H_2O)Cl]\ H_2O$	Green	776.7	6.32 (6.69)	52.25 (52.52)	3.36 (3.60)	6.81 (7.20)	9.08 (9.14)	3.90	18.2
$[MnL_2(OAc)]\ H_2O$	Brown	804.1	6.20 (6.82)	53.21 (53.72)	3.10 (3.48)	6.31 (6.96)	9.32 (4.41)	4.2	18.3
$[FeL_2(H_2O)Cl]\ H_2O$	Black	780.6	6.82 (7.14)	52.01 (52.26)	3.32 (3.58)	6.73 (7.17)	9.01 (9.09)	5.2	22.1

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 400-4000 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 $[HgCo(SCN)_4]$ as the calibrant. The molecular weights of the complexes were determined by Rast method. 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.

3. Result and Discussion

The Schiff base ligand HCAIPT 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 (Table2) shows all the complexes are non electrolytes.

The ^{1}H NMR spectra of ligand HCAIPT shows signals at δ 11.26, (1H, s phenolic OH), 7.41, 7.40, 7.39 and 7.38 (4H, m, phenyl) δ 6.51, 6.50, and 6.58 (3H, s Phenyl), 6.62 (1H s thiophene), and 2.16 (3H, s, methyl) [12-15].

IR spectra of ligand and metal complexes summarized in table 3. As per observation ν(C=N) peaks at 1618 cm^{-1} and absence of C=O peak at around 1700–1730 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*(C-S)	*ν* (M-O)	*ν*(M-N)
HCAIPT	3109	1618	1514	1122	-	-
[$CrL_2(H_2O)Cl$] H_2O		1590	1506	475	409	1115
[$MnL_2(OAc)$] H_2O		1562	1462	498	420	1090
[$FeL_2(H_2O)Cl$] H_2O		1602	1504	512	440	1080

3.1 Thermogravimetric Parameter

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, Frequency factor, Entropy change and Free Energy change was calculated by Freeman-Carroll, [18] Horowitz-metzger [19] and Broido [20] method.

Table 4: Thermal decomposition data of HCAIPT and its complexes.

Compound	Half Decomposition Temperature (^{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***			
HCAIPT	266.43	2.88	5.76	4.82	98.79	213.62	128.84
[$CrL_2(H_2O)Cl$] H_2O	592.66	11.52	14.39	11.56	228.46	207.66	199.68
[$MnL_2(OAc)$] H_2O	443.85	4.95	9.91	9.84	196.27	208.36	168.49
[$FeL_2(H_2O)Cl$] H_2O	431.95	6.65	9.71	8.46	169.99	209.65	167.24

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

4. Conclusions

The analysis of magnetic moment and electronic spectral data shows characterization and structural changes in metal complexes. Thermal studies concluded conformed structure of metal complexes from the study of water loss in metal complexes and other parameter.

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