SYNTHESIS AND THERMAL STUDIES OF CR(III) AND MN (III) COMPLEXES WITH DERIVED FROM THIAZOLE SCHIFF BASE WITH MICROWAVE IRRADIATION METHOD

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ABSTRACT

The newly synthesized thiazole Schiff base have been prepared by microwave irradiation method 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 Cr(III), and Mn(III), The complexes have been characterized on the basis of elemental analysis, infrared, molar conductance, magnetic Susceptibilities, and theromogravimetric analysis. The kinetic analysis of the thermogravimetric data was performed by using Broido, Horowitz-Metzger and Freeman-Carroll method, which confirm first order kinetics and kinetic compensation effect.

Keywords:*Thiazole Schiff Base, Molar conductance, Thermal.*

Introduction

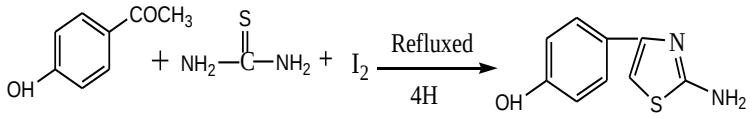
Microwave-assisted synthesis is chemical method, the application of microwave-assisted is useful technology in organic synthesis because it is simple, sensitive, reducing the hazard, often possible to reduce reaction times to a few minutes under solvent free or lower solvent and increase the yields and easier work up as compared to conventional methods. Schiff bases are chemical compounds formed from the condensation reaction of aldehydes or ketones with amines. These compounds are majorly used in industries and also have significant biological activities, including antioxidant, antibacterial, antifungal, antiviral and antitumor. There is synthesis, characterization and biological activities of new Schiff Base Compound and its lanthanide complexe[1]. Antifungal Activity of Some Mixed Ligand Complexes Incorporating Schiff Bases[2] Performance of Schiff Bases Metal Complexes and their Ligand in Biological Activity[3] Spectral and thermal characterization of Mn(II), Ni(II) and Zn(II) complexes containing schiff base ligands.[4] Compounds containing an azomethine group (CH=N), known as Schiff bases, were formed by the condensation of a primary amine with a carbonyl compound. Schiff bases of aliphatic aldehydes were relatively unstable and were readily polymerizable. Schiff bases and their complexes are shows good progress in thermal analysis[5.]

This paper discusses the kinetic of the thermal decomposition and the accompanying compensation effect for Schiff base complexes of Cr(III), and Mn(III)

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[6-8]. The solvents were purified by standard methods[9]

Synthesis of 4-(p hydroxyphenyl)-2 amino thiazole;

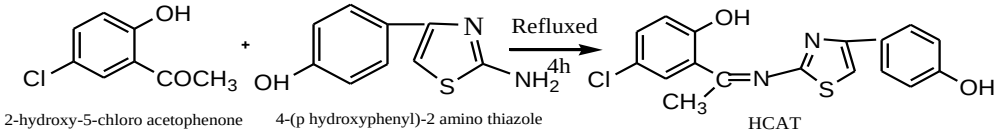


4-hydroxy acetophenone

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 heat in microwave oven for 4h[10]. 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 shown in Table 1. and m.p. It was also characterized by IR and ^{1}H 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 in microwave oven for 4-6h. 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 ^{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 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		
$[CrL_2(H_2O)Cl]H_2O$	Green	810.7	6.32 (6.41)	50.25 (50.32)	3.36 (3.45)	6.81 (6.90)	13.08 (13.13)	3.96	18.9
$[MnL_2(OAc)]H_2O$	Brown	837.1	6.40 (6.55)	51.51 (51.60)	3.60 (3.70)	6.51 (6.68)	8.32 (8.48)	4.8	18.8

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 1700–1750cm^{-1} indicates the Schiff base formation.[16-19] IR spectra of complexes are shown in Table 3.

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)
HCAT	3119	1620	1514	--	--	1122
$[CrL_2(H_2O)Cl]H_2O$	--	1590	1506	475	409	1115
$[MnL_2(OAc)]2H_2O$	--	1562	1462	498	420	1090

Thermogravimetric studies:

An analysis of TG curves of HCAT and its metal complexes show that Cr(III) and Mn(III), complexes decomposed in three stages, the ligand in two stages The Cr(III) and Mn(III) complexes are stable upto 70^{o}C Elimination of one water molecule from Cr(III) complexes upto 130^{o}C have been observed (%wt loss obs./calcd. Cr(III) : 2.32/2.22; The Mn(III) complexes shows percent loss corresponding to two water molecules (%wt loss obs./calcd. Mn(III) : 4.48/4.30 upto 150^{o}C. In the Cr(III) complexes further loss in weight upto 220^{o}C indicating the presence of one coordinated water molecule (%wt loss obs./calcd. Cr(III) : 2.38/2.22)[20&21] While in case of Mn(III) complexes complete decomposition has not been observed upto 800°C. 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 Mn(III)>Cr(III)> HCAT

The Thermal activation energy (Table 4) was calculated by Freeman-Carroll,[22] Horowitz-metzger[23] and Broido[24] method

Table 4: Thermal decomposition data of the complexes of HCAT

Compound	Half Decomposition Temperature (^oC)	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
$[CrL_2(H_2O)Cl]H_2O$	550.45	9.08	12.98	12.98	259.74	207.11	183.52
$[MnL_2(OAc)]2H_2O$	710.46	11.11	18.51	11.11	222.32	209.86	217.58

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

Conclusion

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 interface. The compensation effect of thermal decomposition of the complexes indicating the change of sample mass on the estimated values of activation energy.

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