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Thermal Observation of Zr (IV) And UO_2 (VI) Complexes Derived from Thiazole Schiff Base

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Abstract:

The innovative newly thiazole Schiff base have been synthesized 2-hydroxy-5-chloro acetophenone and 4-(p-hydroxyphenyl)-2-aminothiazole by microwave irradiation method. The metal complexes were obtained as a result of interaction of Schiff base ligand and metal ions Zr (IV) and UO2(VI). 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.

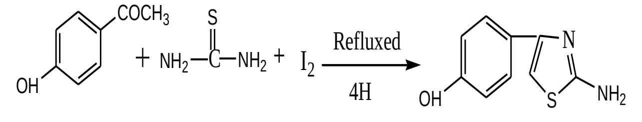
Keywords: Thiazole Schiff Base, Molar conductance, Thermal.

Introduction:

The majority of these compounds show excellent catalytic activities. Schiff bases are considered to be the most versatile ligands as they form complexes with the metal atoms. These compounds are majorly used in industries and also have significant biological activities, including antioxidant, antibacterial, antifungal, antiviral and antitumor.The mathematical calculating thermogravimetric data, thermal decomposition activation parameters studies in this paper. There is synthesis, characterization and biological activities of new Schiff Base Compound and its lanthanide complexe[1] Spectral and thermal characterization of Mn(II), Ni(II) and Zn(II) complexes containing schiff Base ligands.[2] Antifungal Activity of Some Mixed Ligand Complexes Incorporating Schiff Bases[3] They are called privileged ligands because these compounds can be synthesized simply by condensation or microwaves. Performance of Schiff Bases Metal Complexes and their Ligand in Biological Activity[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 Zr (IV) and UO_2 (VI)

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]

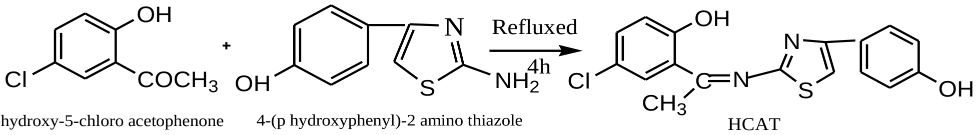
Synthesis of 4-(p hydroxyphenyl)-2 amino thiazole;



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	$C_{17}H_{13}N_2O_2S$ Cl	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 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		

[ZrL_2 $(OH)_2$] $2H_2O$	Yellow	848.4	10.68 (10.74)	47.93 (48.09)	3.46 (3.53)	6.52 (6.60)	8.26 (8.36)	Dia	11.7
[UO_2L_2]	Orange	957.3	24.73 (24.87)	42.51 (42.61)	2.41 (2.50)	5.74 (5.84)	7.32 (7.41)	Dia	12.9

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.[16-19] 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
[$ZrL_2(OH)_2$] $2H_2O$	--	1600	1498	445	412	1108
[UO_2L_2]	--	1585	1440	550	480	1082

Thermogravimetric studies : An analysis of TG curves of HCAT and its metal complexes show that the Zr(IV) complexes decomposed in three stages, the ligand and UO2(VI) complexes in two stages. 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 UO_2(VI)>Zr(IV)>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 (°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

$[ZrL_2(OH)_2]$ $2H_2O$	711.17	7.41	18.54	11.12	222.52	209.77	217.65
UO_2L_2	800.0	19.85	22.06	17.65	353.2	206.79	239.62

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

Conclusion:

The thermal decomposition in 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.

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