



ELECTRICAL CONDUCTIVITY AND BIOLOGICAL ACTIVITIES OF VO(IV), ZR(IV) AND UO₂(VI) COMPLEXES DERIVED FROM THIAZOLE SCHIFF BASE

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Abstract:

Schiff base metal complexes play an important role in many applications such as biological activity. In this Research paper the new thiazole Schiff base have been synthesized by condensing 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 VO (IV), Zr (IV) and UO₂ (VI). The complexes have been characterized on the basis of elemental analysis, infrared, molar conductance, magnetic Susceptibilities and thermal 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. And the studies of electrical and biological properties of Schiff base metal complexes.

Keywords: Thiazole Schiff Base, Molar conductance, Thermal, Electrical and Biological.

Introduction:

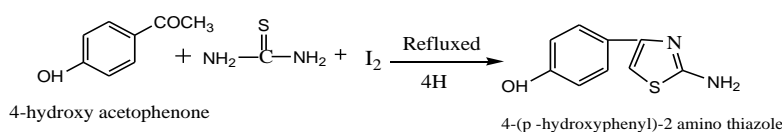
Schiff bases are synthesized compound, which is prepared for the condensation process of primary amine group and aldehyde or ketone group. Schiff base metal complexes play an important role in many biological applications. The research paper focus on the synthesis, characterisation and various methods of Schiff base derived from bidentate thiazole Schiff base and studies their properties. Performance of Schiff Bases Metal Complexes and their Ligand in Biological Activity [1]. Data collection and recent studies on biological activities of Schiff bases metal complexes [2]. A review on the history, synthesis, and applications of Schiff bases and their metal complexes [3]. Schiff base ligand derived from glycine and benzaldehyde was synthesized together with metal complexes. The bacterial assay was carried out on two pyogenic bacteria E.

coli and Staphylococci and the results showed that the complexes have high antibacterial activity [4]. Schiff base metal complexes shows dual nature as a antioxidant and antimicrobial agents [5]. This paper discusses the kinetic of the thermal decomposition and the accompanying compensation effect, electrical and biological studies for Schiff base complexes of VO(IV), Zr(IV) and UO₂(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[6-9]. The solvents were purified by standard methods[10].

Synthesis of 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 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 shown in Table 1. and m.p. It was also characterized by IR and ¹H NMR spectral studies. Yield:70%; m.p. 310⁰C

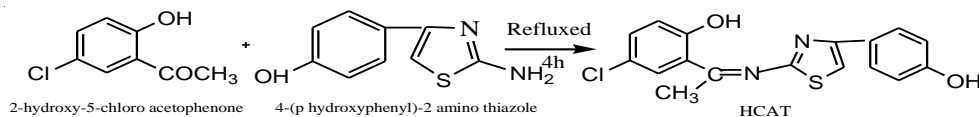


Table 1. Analytical data of the Ligands.

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 ₂ O ₂ 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)

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

Compounds	Colour	Mol.wt.	Analysis % Found (calc.)					μ_{eff} B.M.	Λ_{M} (Ω^{-1} cm ² mol ⁻¹)
			M	C	H	N	Cl		
[VOL ₂]	Green	754.2	6.63 (6.76)	54.01 (50.09)	3.05 (3.18)	7.33 (7.42)	9.32 (9.41)	1.60	12.8
[ZrL ₂ (OH) ₂] 2H ₂ O	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 ₂ L 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

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 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: 40-45%. 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 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 400-4000cm⁻¹, carbon, hydrogen and nitrogen analysis were carried out at RSIC, Punjab University, Chandigarh. The molar conductance of the complexes at 10⁻³M dilution in DMF were determined using equipronic 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 10⁰C min⁻¹ heating rate. The

molecular weights of the complexes were determined by Rast method are shown in Table 2.

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 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(10⁻³M) solution at room temperature (Table 2) shows all the complexes are non electrolytes[11] 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 ν (C=N) peaks at 1620cm⁻¹ and absence of C=O peak at around 1700-1750 cm⁻¹ indicates the Schiff base formation.[16-18]. IR spectra of complexes are shown in Table 3.

Table 3. IR spectra of ligand and metal complexes.

Compound	v(O-H) hydrogen bonded	v (C=N) imine	v (C-O) phenolic	v (M-O)	v (M-N)	v (C-S)
HCAAT	3119	1620	1514	--	--	1122
[VOL ₂]	--	1598	1506	514	445	1098
[ZrL ₂ (OH) ₂] 2H ₂ O	--	1600	1498	445	412	1108
[UO ₂ L ₂]	--	1585	1440	550	480	1082

Thermogravimetric studies: An analysis of TG curves of HCAAT and its metal complexes show that the Zr(IV) complex decomposed in three stages, the ligand and UO₂ (VI) complexes in two stages while VO(IV) complexes in one stage. The Zr(IV) complexes are stable upto 70°C Elimination of one water molecule from Zr(IV) : 4.54/4.24) upto 150°C[19]. There is no weight-loss upto 250°C in VO(IV) and UO₂(IV) complexes indicating the absence of any water molecules (lattice or coordinated) in these complexes [20] in all the complexes rapid weight-loss has been observed above 400°C, indicative of decomposition of the free part of the coordinated ligand gradual weight-loss above 400°C corresponding to degradation of actual

coordination part of the ligand. In the thermograms of ligand, VO(IV) complexes while in case of Zr(IV) and UO₂(VI) complexes complete decomposition has not been observed upto 800°C. The horizontal level beyond 650°C suggests the formation of final decomposition product.[21] 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 UO₂(VI)>Zr(IV)> VO(IV)> HCAAT. 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 HCAAT

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***			
HCAAT (LH)	260.51	3.27	5.45	4.36	87.25	212.55	117.75
[VOL ₂]	400.23	5.20	8.67	6.94	138.87	210.62	148.73
[ZrL ₂ (OH) ₂] 2H ₂ O	711.17	7.41	18.54	11.12	222.52	209.77	217.65
[UO ₂ L ₂]	800.00	19.85	22.06	17.65	353.20	206.79	239.62

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

Electrical Conductivity: The electrical conductivity of metal complexes varies with their nature and temperature [25-29]. The variation of electrical conductivity of the metal complexes with temperature is the basis of their classification as semiconductors or metallic conductors. The electrical conductivity of metallic conductors decreases with increasing temperature (i.e. temperature coefficient is negative) and their resistivity ranges from 10⁻⁸ to 10⁻⁷ Ω. The

electrical conductivity and activation energy of HCAAT complexes are cited in Table 5

1. Electrical conductivity of the complexes lies in the range 1.16x10⁻⁸ to 6.69x10⁻⁷Ω⁻¹cm⁻¹ at 373K
2. The electrical conductivity of these complexes at 373 K follows the order UO₂ > VO > > Zr
3. The activation energy of electrical conduction of the complexes has been found to increase in the order Zr < VO < UO₂.

Table 5. Electrical Conductivity (σ) at 373 K and Activation Energy (Ea) of the complexes

Metal		VO(IV)	Zr(IV)	UO ₂ (VI)
HCAAT	σ (Ω ⁻¹ cm ⁻¹)	1.16×10 ⁻⁸	2.68×10 ⁻⁸	6.69×10 ⁻⁷
	Ea (eV)	0.0791	0.0642	0.2113

Biological activity: Biological activity assay depends upon a comparison of the inhibition of growth of microorganism by measuring the concentration of the sample to be examined with

the known concentration of standard antibiotic. For the antimicrobial analysis the agar diffusion method has been employed. In this study the ligand and their metal complex were tested for

their effect on certain human pathogenic bacteria such as Gram-positive. The ligand HCAT and its complexes [30-33] are found to show considerable bacteriocidal activity against *E. coli*, *A. aerogenes*, *S. aureus* and *B. subtilis* and are almost inactive

against *B. megatherium*, *P. vulgaris* and *P. fluorescens*. The ligand inhibits the growth of *S. aureus* more than all its complexes. The results reveals that the sensitivity of the ligand HCAT and its complexes is shows in (Table 6).

Table 6. Biological activity

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. fluorescens</i> (mm)	<i>A. aerogenes</i> (mm)	<i>B. megatherium</i> (mm)
HCAT	R	R	S ₆	S ₁₁	R	R	R
VO- HCAT	R	R	S ₁₃	S ₁₂	R	S ₁₁	S ₉
Zr- HCAT	S ₁₄	S ₁₁	S ₁₁	R	R	S ₈	R
UO ₂ - HCAT	S ₆	R	S ₁₀	S ₁₂	R	S ₁₀	R

Conclusion:

The thermal studies of the complexes show three stage decomposition. The thermal decomposition of the complexes indicate the change of sample mass and size on the estimated values of activation energy. It is assumed that dehydration of the complexes containing water occurs within an active reaction interface. The D.C. Electrical conductivity of the synthesized complexes were measured in the temperature range 298-423 K. All the complexes indicating their semiconducting behaviour. The Schiff base ligand and all the metal complexes show more activity towards *S. aureus* and least activity towards *E. coli*, *A. aerogenes* and *B. megatherium*. The structural changes have marked effect on the sensitivity and sensitivity varies with organisms.

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