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Thermokinetic studies of Tetradentate Schiff base having N_2O_2 donor group with Co(II), Ni(II), Cu(II) Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO_2(VI)

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Abstract: The new tetradentate Schiff base have been synthesized by condensing 2-hydroxy-5-chloro acetophenone with ethylene diamine. The metal complexes were obtained as a result of interaction of Schiff base ligand and metal ions: Co (II), Ni (II), Cu (II), Cr (III), Mn (III), Fe (III) VO (IV), Zr (IV) and UO_2 (VI). The complexes have been characterized on the basis of elemental analysis, infrared, molar conductance, magnetic Susceptibilities, electronic spectra and theromogravimetric analysis. Thermodynamic activation parameters were computed from the thermal data using Broido, Horowitz-Metzger and Freeman-Carroll method, which confirm first order kinetics and kinetic compensation effect.

Keywords: Tetradentate Schiff base, Molar conductance, Thermal.

Introduction

The thermogravimetric technique has been great significance research method on thermal stabilsation and thermal decomposition. Thermogravimetric could provide theory for material heating treatment and application.[1,2] Schiff base and their metal complexes are becoming increasingly important in recent years due to their biological activity[3] and their used as catalysts,[4,5] photoluminescent and electroluminescent properties.[6] The Schiff base prepared by using variety of aldehydes and amines possessed antitubercular, antitumer, anticancer, fungicidal medicinal and agrochemical activities[7,8] Thermogravimetric in an easy, quick, precies measure method. The mathematical calculating thermogravimetric data, thermal decomposition activation parameters can be obtained.[9,10] Schiff bases and their complexes have a variety of applications in biological clinical and analytical fields.[11] Recently there has been a considerable interest in the chemistry of hydrazine and hydrazone compounds because of their potential pharmacological applications.[12]

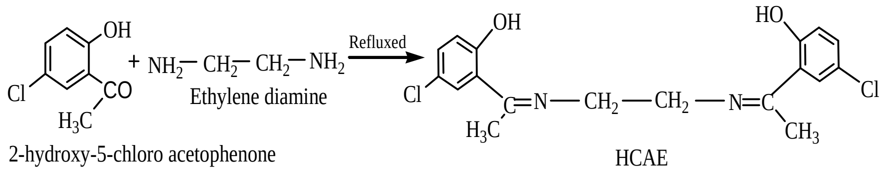
This paper discusses the kinetic of the thermal decomposition and the accompanying compensation effect for Schiff base complexes of Co (II), Ni (II), Cu (II), Cr (III), Mn (III), Fe (III) VO (IV), Zr (IV) and UO_2 (VI).

Experimental

All the chemicals were of A.R. grade and used as received ethylene diamine and 2-hydroxy-5-chloro acetophenone (HCA) was prepared by known methods.[13] The solvents were purified by standard methods.[14]

Synthesis of 2-Hydroxy-5-chloro acetophenone-N,N'-ethylenediimine (HCAE).

A hot ethanolic solution of ethylene diamine (0.05 mol) was added to an ethanolic solution of respective acetophenone (0.05 mol). The reaction mixture was refluxed in a water-bath for 4-5 h. The colour product was filtered off and recrystallised. Yield 80%. M. P. 275^0C.



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 : 55-60%.

Table 1. 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		
$C_{18}H_{18}N_2O_2Cl_2$	Yellow	367.0	--	46.84 (46.53)	3.83 (3.93)	6.17 (6.27)	--	--	--
$[CoL(H_2O)_2]\ H_2O$	Brown	478.1	10.42 (10.45)	38.22 (38.45)	3.72 (3.89)	4.72 (4.85)	--	4.02	5.8
$[NiL]\ H_2O$	Black	370.7	11.12 (11.18)	40.32 (40.57)	3.44 (3.65)	5.18 (5.28)	--	Dia	6.6
$[CuL(H_2O)_2]\ 2H_2O$	Brown	500.5	10.65 (10.88)	36.71 (36.87)	3.85 (4.01)	4.60 (4.71)	--	2.12	16.8
$[CrL(H_2O)Cl]\ 2H_2O$	Yellow	506.5	8.67 (8.78)	36.42 (36.50)	3.62 (3.70)	4.53 (4.70)	5.71 (5.92)	3.56	20.6
$[MnL(OAc)]\ 2H_2O$	Brown	514.9	9.05 (9.15)	39.88 (39.98)	3.65 (3.82)	4.52 (4.63)	--	5.26	14.7
$[FeL(H_2O)Cl]\ H_2O$	Green	482.4	9.11 (9.23)	37.23 (37.39)	3.35 (3.49)	4.71 (4.81)	6.01 (6.08)	5.5	15.7
$[VOL]$	Green	432.0	9.21 (9.53)	41.22 (41.43)	3.06 (3.09)	5.18 (5.38)	--	1.28	13.6
$[ZrL(OH)_2]\ 2H_2O$	Yellow	526.2	14.32 (14.57)	35.18 (35.23)	3.40 (3.52)	4.32 (4.52)	--	Dia	24.7
$[UO_2L]$	Orange	635.1	32.57 (32.68)	29.52 (29.62)	2.01 (2.20)	3.73 (3.81)	--	Dia	21.5

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.

Result and Discussion

The Schiff base ligand HCAE 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 1) shows all the complexes are non electrolytes[11]

The ^{1}H NMR spectra of ligand HCAE shows signals at: 15.57 (1H, s, phenolic OH); 8.03(1H, s, phenyl); 7.57 and 7.41 (2H, m, phenyl), 3.23(4H, s, CH_2 CH_2); 2.41 ppm (3H, s, methyl)[15-24].

Table 2. 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)
$C_{18}H_{18}N_2O_2Cl_2$	2900	1613	1482	--	--
$[CoL(H_2O)_2]\ H_2O$	--	1588	1442	521	456
$[NiL]\ H_2O$	--	1584	1461	512	496
$[CuL(H_2O)_2]\ 2H_2O$	--	1593	1443	593	492
$[CrL(H_2O)Cl]\ 2H_2O$	--	1598	1432	572	462
$[MnL(OAc)]\ 2H_2O$	--	1592	1443	583	493
$[FeL(H_2O)Cl]\ H_2O$	--	1600	1462	532	427
[VOL]	--	1600	1452	524	485
$[ZrL(OH)_2]\ 2H_2O$	--	1602	1441	566	464
$[UO_2L]$	--	1595	1422	562	473

Thermogravimetric studies:

The nature of thermograms of HCAE and its metal complexes indicates that the complexes of Co(II), Ni(II), Cu(II), Cr(III), Mn(III), Fe(III) and Zr(III) decompose in three stage the ligand and VO(IV) complex in two stage while UO_2 (VI) complex in one stage. All the complexes are stable upto 70°C. Elimination of one water molecule from Co(II), Ni(II) and Fe(III) upto 130°C and two water molecules from the Cu(II), Cr(III), Mn(III) and Zr(IV) complexes upto 150°C have been observed (%wt loss obs./calcd. : Co(II) : 3.26/3.18; Ni(II) : 3.52/3.40; Cu(II) : 6.26/6.12; Cr(III) : 6.20/6.06; Mn(III) : 6.08/5.98; Fe(III) : 3.25/3.10; Zr(IV) : 5.98/5.87). Further loss in weight upto 220-240°C indicating presence of two coordinated water molecule in Co(II) and Cu(II) each and one in each Cr(III) and Fe(III) complexes (%wt loss obs./calcd. : Co(II) : 6.48/6.37; Cu(II) : 6.24/6.12; Cr(III) : 3.16/3.03; Fe(III) : 3.22/3.10). There is no weight loss upto 250°C in VO(IV) and UO_2(VI) complexes indicating the absence of any water molecules (lattice or coordinated). In all the complexes rapid weight-loss has been observed above 300°C, indicative of decomposition of the free part of the coordinated ligand, a gradual weight-loss above 400°C corresponding to the degradation of actual coordinated part of the ligand. The half decomposition temperature and the basic parameters calculated for the compounds are given in (Table 3). Thermal activation energy was calculated by Freeman-Carroll,[25] Horowitz-metzger[26] and Broido[27] method. On the basis of half decomposition temperature, the relative thermal stability order is found to be The relative thermal stability on the basis of half decomposition temperature is found to be-
Zr(IV)>UO_2(VI)>Cu(II)>Cr(III)>Mn(III)>Fe(III)>VO(IV)>CO(II)>Ni(II)> HCAE.

Conclusion:

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

Table 3. Thermal decomposition data of HCAE 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***			
$C_{18}H_{18}N_2O_2Cl_2$	261.51	3.37	5.55	4.46	87.35	213.55	127.75
[CoL $(H_2O)_2$] H_2O	396.17	3.51	8.64	8.64	170.99	207.83	158.07
[NiL] H_2O	266.33	2.87	5.75	4.89	98.73	213.61	128.94
[CuL $(H_2O)_2$] $2H_2O$	592.16	11.51	14.37	11.51	228.43	207.62	199.78
[CrL (H_2O)Cl] $2H_2O$	443.45	4.93	9.90	9.90	196.21	208.26	168.79
[MnL (OAc)] $2H_2O$	431.15	6.64	9.74	8.59	169.94	209.45	167.04
[FeL (H_2O)Cl] H_2O	425.27	6.61	9.40	8.47	167.59	209.36	164.35
[VOL]	416.10	8.26	9.17	8.26	163.39	209.46	162.35
[ZrL $(OH)_2$] $2H_2O$	708.21	9.29	18.49	12.97	257.64	208.61	227.35
[UO_2L]	680.49	8.78	11.47	13.99	277.86	207.74	221.76

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

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