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THERMAL DECOMPOSITION KINETICS AND MECHANISM OF Cu(II), Zn(II) AND Cd(II) COMPLEXES DERIVED FROM FLUORENONE ANTHRANILIC ACID

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Abstract

Copper(II), zinc(II) and cadmium(II) complexes of the Schiff base, fluorenone anthranilic acid were prepared and characterized by elemental analysis, magnetic measurements, conductivity experiments and electronic and infrared spectral studies. The thermal decomposition kinetics and mechanism of these chelates was studied from TG data.

Keywords: complexes, kinetics, TG

Introduction

Transition metal complexes of Schiff bases have important technical applications. The thermal properties of metal chelates with different types of chelating ligands were studied extensively by Wendlandt and co-workers [1–5] and Hill and co-workers [6, 7]. Such studies on thermal decomposition and kinetics of metal chelates with Schiff base ligands have been done by a few workers [8–11]. In continuation of our earlier work on thermal decomposition kinetics of metal chelates of Schiff bases [12–14], we report in this paper the syntheses, characterization and thermoanalytical data of three transition metal complexes of a novel Schiff base, fluorenone anthranilic acid.

Non-isothermal methods have been widely used to study the kinetics and mechanism of thermal decomposition of solids [15–17]. This study therefore attempts to establish the mechanism of decomposition of [CuL(Ac)(H_2O)], [ZnL(Ac)(H_2O)] and [CdL(Ac)(H_2O)] from TG and DTA experiments.

Experimental

The ligand fluorenone anthranilic acid was prepared by refluxing an ethanolic mixture (1:1) of fluorenone and anthranilic acid for 5 h [18]. Yellowish brown

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crystals separated on cooling were purified by recrystallisation from methanol and characterized on the basis of analytical and spectral studies, *m.p.* 95°C.

Analytical data found: C, 80.68%, H, 4.21%, N, 5.14%

Calculated for $C_{20}H_{13}NO_2$: C, 80.27%, H, 4.35%, N. 4.68%

Samples of Cu(II), Zn(II) and Cd(II) chelates of fluorenone anthranilic acid were prepared by adding methanolic solution of the ligand to an aqueous solution of metal acetate in 1:1 ratio. The mixture was refluxed for 2 h and the precipitated complex was filtered, washed with aqueous methanol and dried in vacuum desiccator.

The complexes having general formula $[ML(Ac)(H_2O)]$ were characterized by elemental analysis, conductance and spectral data (Table 1). The infrared spectrum of the ligand shows a band of medium intensity at about 1692 cm^{-1} and a strong band at 1577 cm^{-1}. The first band may be attributed to the carbonyl stretching frequency of the carboxylate group [19] and a shift of this band to lower frequencies indicate chelation of the ligand through the carbonyl oxygen. The sharp band at 1577 cm^{-1}, assignable to $\nu(C=N)$ shifts to lower frequencies at 1542, 1536 and 1526 cm^{-1} in the complexes indicating coordination of the azomethine nitrogen [20]. The presence of coordinated water is confirmed by the observation of a broad band at 3300 cm^{-1}.

Table 1 Analytical data, magnetic susceptibility and molar conductance of $[CuL(Ac)(H_2O)]$, $[ZnL(Ac)(H_2O)]$ and $[CdL(Ac)(H_2O)]$

Substance	Colour	Metal/%		μ_{eff}	Molar conductance
		found	calculated	B. M.	$Ohm^{-1}\cdot cm^2\cdot mol^{-1}$
$[CuL(Ac)(H_2O)]$	light green	14.98	14.49	2.12	1.4
$[ZnL(Ac)(H_2O)]$	cream	15.27	14.84	D	3.7
$[CdL(Ac)(H_2O)]$	white	23.59	23.06	D	2.3

Instrumental

Thermal analysis was carried out using a Schimadzu thermal analyser system in static air atmosphere. A constant heating rate of 10 $deg\cdot min^{-1}$ and a sample mass of ~5 mg were employed for the entire study. computational work was performed with a Horizon III minicomputer using the programming Language Fortran.

Thermal behaviour

Evaluation of the mechanism of reactions from nonisothermal methods has been discussed by estak and Berggren [21] and atava [22]. For evaluating kinetic parameters from the mechanistic equations given by Satava, Coats and Redfern [23] equation was used in the general form

$$\ln g(\alpha)/T^2 = \ln AR/\varphi E - E/RT$$

and the various $g(\alpha)$ values were substituted. This has been recommended to be one of the best solutions by several authors [24, 25].

Alongwith the mechanistic equations, two non-mechanistic methods suggested by Coats and Redfern and Horowitz-Metzger [26] were also used for comparison.

Results and discussion

The TG curves of [CuL(Ac)(H_2O)], [ZnL(Ac)(H_2O)] and [CdL(Ac)(H_2O)] exhibited two-stage decomposition patterns. Mass loss considerations and X-ray diffraction data confirmed the products to be the corresponding oxides. The TG curves are represented in Figs 1, 2 and 3.

The TG curve for [CuL(Ac)(H_2O)] gives a two-stage decomposition pattern which is supported by DTA data. The first stage, which is a rapid one, represents the loss of one H_2O molecule and the fluorenone part of the ligand moiety

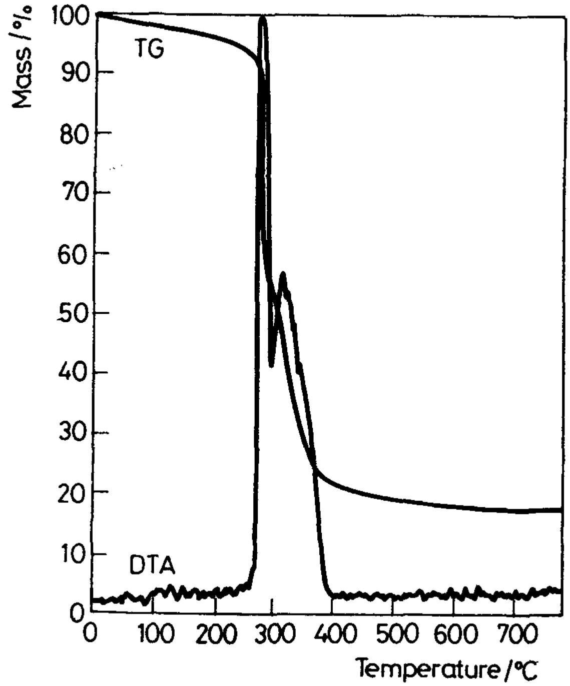

Fig. 1 TG and DTG curves of [CuL(Ac)(H_2O)]

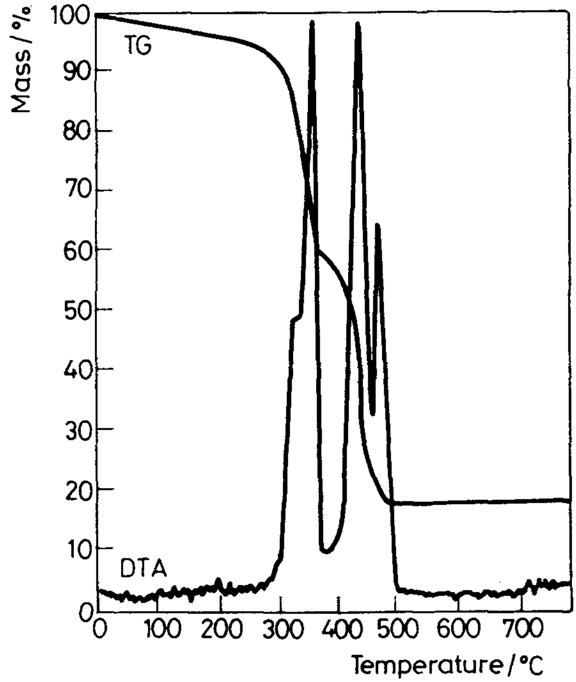

Fig. 2 TG and DTG curves of [ZnL(Ac)(H_2O)]

above 230°C. According to Nikolaev *et al.* [27], water eliminated above 150°C can be considered as coordinated water. The second stage, which consists of two sub-stages in an overlapping manner, represents the loss of anthranilic acid part of the ligand and the acetate group. DTA curve gives well-defined peaks in the appropriate region. The overall loss of mass from the curve is 82% while the theoretical loss in mass for the conversion of [CuL(Ac)(H_2O)] to CuO is 81.87%.

Zinc(II) and cadmium(II) chelates also show a two-stage decomposition pattern, although an overlapping effect is observed in the case of cadmium(II) complex. The first decomposition stage represents the loss of water molecule and fluorenone part of the ligand while the anthranilic acid part of the ligand and the acetate group are lost in the second stage.

The thermal data for the metal chelates are given in Table 2. Independent pyrolytic experimental data are also given in this table. The corresponding E, A, ΔS and r values from non-mechanistic equations (Coats-Redfern and Horowitz-Metzger) and the appropriate mechanistic equations are given in Table 3.

The activation energies obtained for the main decomposition stages of the three complexes are also comparable to those of coordination compounds of 3d transition metals having similar structures [28, 29].

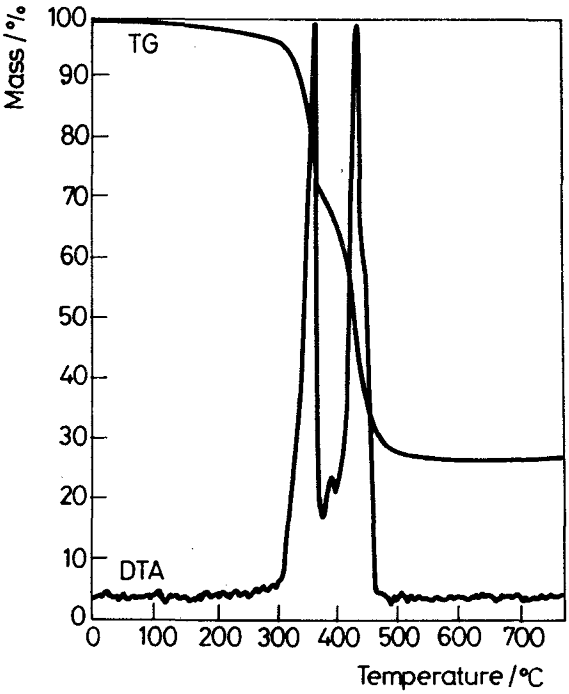

Fig. 3 TG and DTG curves of [CdL(Ac)(H_2O)]

Initial decomposition temperature and inflection temperatures have been used to determine the thermal stability of metal chelates [30, 31]. On the basis of our findings, the relative thermal stabilities of the metal chelates can be given as [CuL(Ac)(H_2O)]<[ZnL(Ac)(H_2O)]≈[CdL(Ac)(H_2O)]

Decomposition kinetics

From Table 3 it can be seen that more than one equation gives good linear curves with a high value of correlation coefficient so that it may become difficult to assign the reaction mechanism unequivocally from the linearity of the curve alone. In such cases, some authors have chosen the function $g(\alpha)$ which gives the kinetic parameters in agreement with those obtained by the numerical method. In the present case, it is observed that, for the second stage of decomposition of the Cu(II) and Zn(II) complexes, the E, A and ΔS values obtained from the Coats-Redfern equation with $n=1$ are in good agreement with E, A and ΔS values obtained from the Mampel equation which is based on random nucleation, one nucleus on each particle. For the first stage of decomposition of the Zn(II) complex and both first and second stage of decompositions of Cd(II)

Table 2 Thermal decomposition data of [CuL(Ac)(H_2O)], [ZnL(Ac)(H_2O)] and [CdL(Ac)(H_2O)]

Substances	Stage	Temp. ranges in TG/	Peak temp. in TG/	Peak temp. in DTA/	Loss of mass/%			Probable assignment
		°C			From TG	Theoretical	From pyrolysis (total mass loss)	
[CuL(Ac)(H_2O)]	I (rapid)	100–300	270	270	41.00	41.52	–	Loss of H_2O + fluorenone
	IIa	300–350	320	320				Loss of anthranilic
	IIb	350–380	370	350	41.00	40.35	–	acid + acetate
							81.34	
[ZnL(Ac)(H_2O)]	I	110–350	340	350	40.00	41.30	–	Loss of H_2O + fluorenone
	II	350–470	440	460	42.00	40.18	– 80.99	Loss of anthranilic acid + acetate
[CdL(Ac)(H_2O)]	I	140–350	340	340	30.00	37.35	–	Loss of H_2O + fluorenone
	II	350–470	420	430	43.00	36.31	– 73.06	Loss of anthranilic acid + acetate

Table 3 Kinetic parameters for the decomposition of [CuL(Ac)(H_2O)], [ZnL(Ac)(H_2O)] and [CdL(Ac)(H_2O)] from TG using non-mechanistic equations[a]

Substances	Coats-Redfern				Horowitz-Metzger			
	E	A	ΔS	r	E	A	ΔS	r
[CuL(Ac)(H_2O)]								
Stage IIa	227.26	1.83×10^{17}	79.86	0.9563	232.39	4.24×10^{17}	86.87	0.9557
Stage IIb	75.22	9.66×10^{3}	−175.09	0.9962	87.91	5.24×10^{4}	−161.06	0.9970
[ZnL(Ac)(H_2O)]								
Stage I	75.88	1.14×10^{4}	−173.32	0.9807	75.33	6.68×10^{5}	−139.46	0.9882
Stage II	193.63	1.57×10^{12}	−18.68	0.9980	221.05	7.79×10^{13}	13.79	0.9989
[CdL(Ac)(H_2O)								
Stage I	85.75	2.97×10^{4}	−165.37	0.9697	104.70	1.51×10^{6}	−132.70	0.9800
Stage II	38.15	1.07	−251.51	0.9427	52.33	1.69×10^{1}	−228.49	0.9704

[a] E/ kJ·mol^{-1}; A/s^{-1}; S/ JK^{-1} ·mol^{-1}

Table 3 continued

Substances	Mechanistic equation followed				Order of reaction/
	E	A	ΔS	r	n
$[CuL(Ac)(H_2O)]$					
Stage IIa	227.26	1.83×10^{17}	79.86	0.9563	Equation V: 1 Mampel equation
Stage IIb	75.22	9.66×10^{3}	–175.09	0.9962	Equation V: 1 equation
$[ZnL(Ac)(H_2O)]$					
Stage I	80.69	1.72×10^{4}	–169.88	0.9784	Equation VIII: 1/3 Phase boundary reaction, cylindrical symmetry
Stage II	193.63	1.57×10^{12}	–18.68	0.9980	Equation V: 1 Mampel equation
$[CdL(Ac)(H_2O)]$					
Stage I	87.32	2.12×10^{4}	–168.16	0.9694	Equation VIII: 1/3 Phase boundary reaction, cylindrical symmetry
Stage II	44.33	2.03	–246.13	0.9411	Equation VIII: 1/3 Phase boundary reaction, cylindrical symmetry

[a] E/kJ·mol^{-1}; A/s^{-1}; S/ JK^{-1}·mol^{-1}

complex, good agreement is resulted between the kinetic parameters obtained from Coats-Redfern method with $n=1/3$ and the R_2 mechanism based on a phase boundary reaction, cylindrical symmetry.

* * *

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Zusammenfassung — Kupfer(II)-, Zink(II)- und Cadmium(II)-komplexe der Schiff'schen Base Fluorenonanthranilsäure wurden hergestellt und mittels Elementaranalyse, magnetischen Messungen, Leitungsfähigkeitsexperimenten sowie Elektronen- und IR-Spektraluntersuchungen charakterisiert. Die thermische Zersetzungskinetik und der zugehörige Mechanismus dieser Chelate wurde anhand TG durchgeführt.