Physico-chemical Studies and Thermal Decomposition Kinetics of Co(II), Ni(II) and Cu(II) Complexes of Anthracene Carboxaldehyde L-Histidine

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Cobalt(II), Nickel(II) and Copper(II) complexes of the Schiff base anthracene carboxaldehyde L-histidine were prepared and characterized by elemental analysis, magnetic measurements, conductivity experiments and spectral studies. The thermal decomposition kinetics and mechanism of these chelates was studied from TG data.

Key Words: Complexes, Schiff base, Kinetics, Thermogravimetric.

INTRODUCTION

Thermal methods find widespread use for both quality control and research applications. Depending upon the properties measured and the temperature programs[1-5] more than a dozen thermal methods are recognized. Thermogravimetric method is one among them which provides primarily chemical rather than physical information about the samples. Considerable work has been done on thermal decomposition kinetics of Schiff base complexes[6-13]. We report here the preparation, characterization and thermo-analytical data of cobalt(II), nickel(II) and copper(II) complexes of the Schiff base, anthrancene carboxaldehyde L-histidine. Non-isothermal methods[14-16] are more easier to study the kinetics and mechanism of thermal decomposition of solids. This study therefore attempts to establish the mechanism of decomposition of three transition metal complexes of the Schiff base anthracene carboxaldehyde L-histidine from thermogravimetric experiments. The energy of activation E, Arrhenius factor A, and entropy of activation ΔS were calculated using mechanistic and non-mechanistic equations. Initial decomposition temperatures have been used by earlier workers[17, 18] to compare thermal stability of complexes.

EXPERIMENTAL

The ligand anthracene carboxaldehyde L-histidine was prepared by refluxing histidine in ethanolic potassium hydroxide and anthracene-9-carboxaldehyde in ethanol in the ratio (1 : 1). The mixture was refluxed on a water bath for 3 h. On cooling the mixture in ice, needle-shaped yellow crystals of potassium salt of the

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ligand were obtained. It was then filtered, washed with dilute alcohol, dried in a desiccator over anhydrous calcium chloride. The ligand obtained is recrystallized from ethanol (yield 95%, m.p. 98°C). The ligand anthracene-9-carbox-aldehyde-L-histidine was characterized on the basis of elemental analysis and spectral data.

	C %	H %	N %
Analytical data found	73.62	4.95	12.24
Calculated value for $C_{21}H_{17}N_3O_2$	73.41	4.19	11.02

The acid form of the ligand was used for CHN analysis.

Co(II), Ni(II) and Cu(II) chelates of anthracene-9-carboxaldehyde-L-histidine were prepared by adding ethanol solution of the ligand to aqueous/ethanol solution of metal acetate in 2 : 1 ratio. Sodium acetate (1 g) in ethanol was added and refluxed for 5 h. The precipitated complex was filtered, washed with 50% ethanol and dried over anhydrous calcium chloride in a desiccator.

The complexes having the general formula $[ML_2(H_2O)_2]$ were characterized by elemental analysis, conductance and spectral data (Table-1). The infrared spectroscopic results provide support for the molecular constitution of these complexes. The assignments are made on the basis of comparison with the spectra of similar type of compounds. A broad feature at 3410–3250 cm^{-1} in the spectra of these complexes is attributed to the hydroxyl-stretching mode of water molecules[19-22]. In addition a medium band approximately at 950–870 cm^{-1} suggests that water molecules are coordinated[23]. The other very strong bands are observed in the 1700–1300 cm^{-1} region, one at *ca.* cm^{-1} and the other at *ca.* 1405 cm^{-1}. These are attributed to the asymmetric and symmetric stretching vibrations respectively of carboxylate ion. Further, the separation value, $\Delta v(COO^-)$ ($v_{asym}COO^- - v_{sym}COO^-$) of *ca.* 250 cm^{-1}, rules out the possibility of a bridged or coordinated carboxylate group. A strong band approximately at 1546 cm^{-1} in the spectrum of the ligand anthracene carboxaldehyde L-histidine may be assigned to $v(C=N)$ stretch. This band shows a downward shift by about 39–19 cm^{-1} in the spectra of all the metal complexes, indicating the participation of the azomethine nitrogen in coordination with metal ions[24]. The shifted band in many cases is coincident with the $v(C=C)$ band, which then shows greater intensity or broadening.

TABLE-1

ANALYTICAL, MAGNETIC SUSCEPTIBILITY AND MOLAR CONDUCTANCE OF $[CoL_2(H_2O)_2]$, $[NiL_2(H_2O)_2]$ AND $[CuL_2(H_2O)_2]$

Metal complexes	Colour	m.p.	Metal precentage		μ_{eff} B.M.	Ω_m (ohm^{-1} cm^2 mol^{-1})
			Found	Calculated		
$[CoL_2(H_2O)_2]$	Yellow	240	8.24	7.5	4.9	5.51
$[NiL_2(H_2O)_2]$	Pale yellow	194	7.3	7.53	3.36	8.63
$[CuL_2(H_2O)_2]$	Bluish green	185	7.4	8.09	1.54	9.23

Further evidence for broadening by nitrogen and oxygen atoms is provided by far IR spectra of the complexes. Due to the interference of skeletal vibrations of the

ligands, with $\nu(M\text{---}N)$ and $\nu(M\text{---}O)$ vibrations, definite assignments of bands is difficult as a result of metal ligand vibration. Therefore only tentative assignments are made on the basis of information available in literature. Spectra of all complexes prepared in this investigation showed intense broad bands at 590–530 cm^{-1} and 510–490 cm^{-1} assignable to $\nu(M\text{---}N)$ and $\nu(M\text{---}O)$[25-27]. The aromatic out-of-plane vibration[28, 29] is seen near 810 cm^{-1} and in-plane vibrations at 770 cm^{-1} and 720 cm^{-1}.

EXPERIMENTAL

Thermal analysis was carried out using a Perkin-Elmer 7 series thermal analysis system in static air atmosphere. A constant heating rate of 10°C min^{-1} and sample mass of 2–5 mg were employed for the entire study. Computational work was performed using C++ language.

Thermal Behaviour

Evaluation of the mechanism of reactions from non-isothermal methods has been discussed by Sestak and Satava[30, 31]. For evaluating kinetic parameters from the mechanistic equations given by Satava[31], Coats and Redfern[32] equation was used in the general form $\ln \dfrac{g(\alpha)}{T^2} = \dfrac{n\,AR}{\varphi E} - \dfrac{E}{RT}$ and the various $g(\alpha)$ values were substituted. This has been recommended to be one of the best solutions by several authors[33, 34]. Along with mechanistic equations, two non-mechanistic methods suggested by Coats-Redfern[32] and Horowitz-Metzger[35] were also used for comparison.

RESULTS AND DISCUSSION

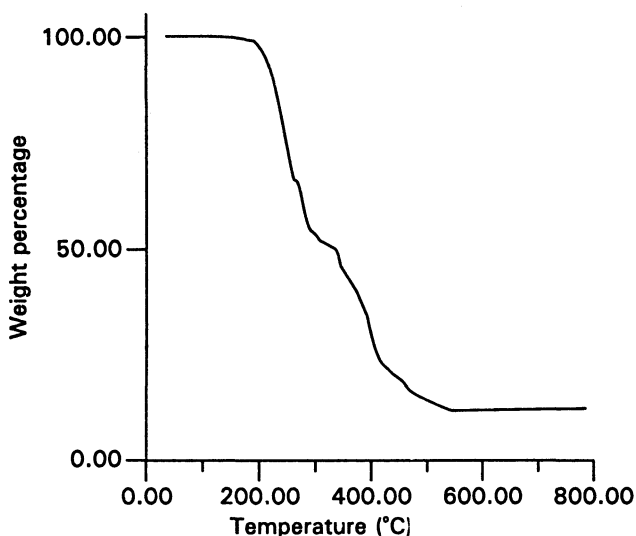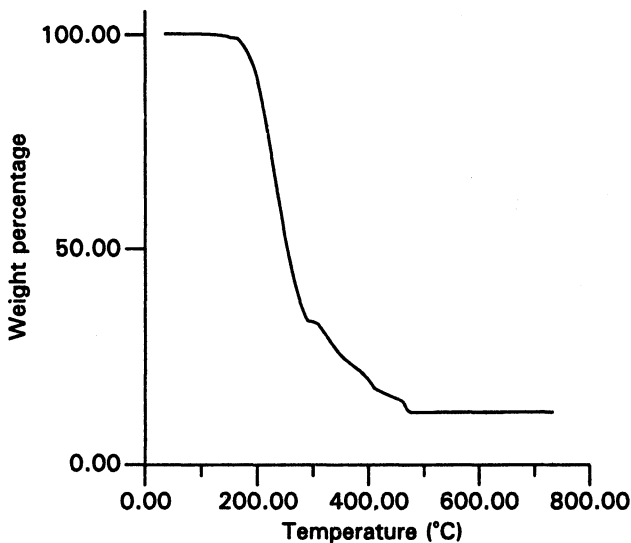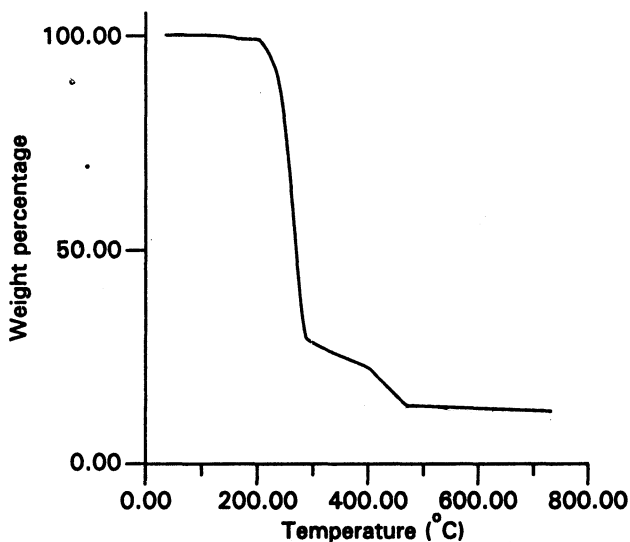TG curves are represented in Figs. 1, 2 and 3.

Fig. 1.   TG curve of [Co(ACH)$_2$(H$_2$O$_2$)]

Fig. 2.   TG curve of [Ni(ACH)$_2$(H$_2$O$_2$)]

Fig. 3.   TG curve of [Cu(ACH)$_2$(H$_2$O$_3$)]

The complexes which were subjected to thermal decomposition study were found to have the formula [ML$_2$(H$_2$O)$_2$], where M is the metal and L is the ligand anthracene carboxaldehyde-L-histidine. The TG curve of [CoL$_2$(H$_2$O)$_2$] gives a three stage decomposition pattern. The first stage represents the loss of 2H$_2$O molecules and anthracene carboxaldehyde part of the ligand moiety. According to Nikolaev *et al.*[36] water eliminated above 150°C can be considered as coordinated water. The second stage represents the loss of the second ligand. The third stage represents the loss of histidine part. The overall mass loss for the case is

88% while the theoretical loss in mass for the conversion of $[CoL_2(H_2O)_2]$ to Co_3O_4 is 90.3%.

$[NiL_2(H_2O)_2]$ gives a two stage decomposition pattern in its TG curve. The first stage represents the loss of two H_2O molecules, one ligand and one anthracene carboxaldehyde part while the second stage represents the loss of histidine part.

$[CuL_2(H_2O)_2]$ also gives a two stage decomposition pattern in its TG curve. Two water molecules, one ligand and one anthracene carboxaldehyde part are lost in the first stage, a histidine part is lost in the second stage of decomposition.

The mass loss at the end of the stage as recorded from the TG curve is 88.09% and 89.9% for Ni(II) and Cu(II) complex respectively. Initial decomposition temperature has been used to determine the thermal stability of metal chelates. In the present course of studies based on observation made by earlier workers, the relative stabilities of the three metal chelates are in the order $[CoL_2(H_2O)_2]$ $< [CuL_2(H_2O)_2] < [NiL_2(H_2O)_2]$.

The thermal data for the metal chelates are given in Table-2. Independent pyrolytic experimental data are also given in the same Table. The corresponding E, A, ΔS are r values from non mechanistic equations (Coats-Redfern[32] and Horowitz-Metzger[35]) and appropriate mechanistic equations are given in Table-3.

TABLE-2

THERMAL DECOMPOSITION DATA OF $[CoL_2(H_2O)_2]$, $[NiL_2(H_2O)_2]$ and $[CuL_2(H_2O)_2]$

Complex	Stage	Temp. range in TG (°C)	Peak temp. in TG (°C)	Loss of mass percentage			Probable assignment
				From TG	Thero-retical	Pyro-lysis	
$[CoL_2(H_2O)_2]$	I	120–240	235	30	29.0		Loss of 2 H_2O + ACA part
	II	240–380	340	43	43.9		Loss of second ligand
	III	380–520	390	15	17.4		Loss of histidine part
				88	90.3	88.8	$CoL_{\frac{1}{2}}(H_2O)_2 \rightarrow Co_3O_4$
$[NiL_2(H_2O)_2]$	I	120–290	260	70.6	72.9		Loss of 2 H_2O + 1 L + ACA part
	II	290–420	330	17.49	17.5		Loss of histidine part
				88.09	90.4	90.71	$NiL_{\frac{1}{2}}(H_2O)_2 \rightarrow NiO$
$[CuL_2(H_2O)_2]$	I	90–270	260	76.9	72.49		Loss of 2 H_2O + 1 L + ACA part
	II	270–460	450	13	17.36		Loss of histidine part
				89.9	89.85	90.3	$CuL_{\frac{1}{2}}(H_2O)_2 \rightarrow CuO$

Decomposition Kinetics

Table-3 shows that more than one equation gives good linear curves with high correlation coefficient, making the assignment of reaction mechanism a difficult task. In such cases the function (gα) which gives kinetic parameter in agreement with those obtained by non-mechanistic equation is considered.

TABLE-3

KINETIC PARAMETERS OF DECOMPOSITION OF Co(II), Ni(II) AND Cu(II)
COMPLEXES OF ANTHRACENE CARBOXALDEHYDE-L-HISTIDINE (LH) USING
NON-MECHANISTIC EQUATIONS

Complex	Para-meters	Coats-redfern	Horowitz-Metzger	Mechanical equation followed		Order of reaction
$[CoL_2(H_2O)_2]$	E	10.67	10.11	10.67	Equation 9 phase boundary reaction spherical symmetry	2/3
	A	2.937×10^3	2.206×10^3	9.79×10^2		
	ΔS	−90.01	−99.73	−92.19		
	r	0.9921	0.9832	0.9921		
$[NiL_2(H_2O)_2]$	E	14.18	19.04	14.18	Equation 8 phase boundary reaction cylindrical symmetry	1/2
	A	9.21×10^4	3.52×10^5	4.6×10^4		
	ΔS	−82.73	−80.06	−84.10		
	r	0.997121	0.99863	0.997121		
$[CuL_2(H_2O)_2]$	E	15.59	20.72	15.59	Equation 8 phase boundaryreaction cylindrical symmetry	1/2
	A	3.76×10^5	1.84×10^6	1.88×10^5		
	ΔS	−79.93	−76.78	−81.31		
	r	0.9975	0.9995	0.9975		

E: kcals mol^{-1};   A: sec^{-1}; ΔS: eu

Kinetic parameters, *viz.*, activation energy E, Arrhenius factor A, entropy of activation ΔS and order parameters n for the thermal decomposition of the three complexes were evaluated. It can be seen from the thermal data that the values of E and A from these equations are nearly the same. It is also found that greater the thermal stability of a complex, larger the activation energy for the decomposition. ΔS values in this case would be negative. The non-isothermal kinetic methods discussed by Sestak and Berggren[30] and Satava[31] have been used for deducing the mechanism of decomposition of these complexes. In the present case, it was observed that the values of E, A and ΔS for the second stage decomposition of $CoL_2(H_2O)_2$ obtained from Coats-Redfern[32] equation with n = 2/3 are in good agreement with the corresponding values obtained for R_3 mechanism based on phase boundary reaction, spherical symmetry.

For the first stage decomposition of $[NiL_2(H_2O)_2]$ and $[CuL_2(H_2O)_2]$, the values of kinetic parameters obtained for Coats-Redfern equation with n = 1/2 are in good agreement with the values obtained for equation (8). R_2 mechanism based on phase boundary reaction, cylindrical symmetry gives the maximum correlation for the first stage decomposition of Ni(II) and Cu(II) complexes. Since the values of E and A computed from the mechanistic equation agree well with those from the non-mechanistic equation (Coats-Redfern), these mechanisms are confirmed. These values are also found to give good agreement with the values obtained from Horowitz-Metzger[35] equation of the same order.

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