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Thermal decomposition Kinetics and mechanism of Co(II), Ni(II), and Cu(II) complexes derived from Anthracene carboxaldehyde L – Tyrosine

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Abstract

Cobalt(II), nickel(II), and copper(II) complexes of the Schiff base anthracene – 9 –carboxaldehyde - tyrosine were synthesized and characterized on the basis of elemental analysis, magnetic moment, molar conductance, UV- visible and IR spectra. Cobalt (II), nickel (II), and copper (II) complexes were subjected to thermal analysis to determine their thermal stability and decomposition pattern. The kinetic parameters like activation energy (ΔE), frequency factor (A), entropy of activation (ΔS), and order parameter (n) were calculated from TG curves using Coats Red fern and Horowitz Metzger equations. Evaluation of the reaction mechanism by non-iso thermal methods has been employed using the nine mechanistic equations. In all these cases the final products of decomposition were identified as respective oxides. The relative thermal stability of the chelates is in the order Co complex > Cu complex > Ni complex. The complexes of anthracene carboxaldehyde - tyrosine with Co(II) and Ni(II) having the formulae [M ACT_2 $(H_2O)_2$] exhibited a one stage decomposition pattern in its TG curve. While [Cu ACT_2 $(H_2O)_2$] gives a two stage decomposition pattern.

Keywords: Schiff base, complex, kinetics, TG, Anthracene carboxaldehyde tyrosine (ACT)

Introduction

In recent years the researches on Schiff base ligands and their transition metal complexes have come to the forefront of studies. Most of them possess apparent thermal stability and biological importance. Thermo analytical techniques provide important information in elucidating structure and bonding in complexes. A few workers[1-4] carried out studies on thermal decomposition and kinetics of metal chelates, with azomethine ligands. Dhar and Singh[5] have reported kinetics and thermal decomposition of some Schiff base complexes. Sestak and Berggren[6], and Satava[7], has been discussed the evaluation of mechanism. Heating can produce different changes in solids and depending upon properties measured, and temperature programmes, there are several thermal methods[8-10]. Fruitfull ideas about the principle, technique and instrument about thermal analysis are suggested by Smoothers[11]. Use of thermo analytical techniques for following the reaction mechanism of metal ions during the course of thermal decomposition of metal chelates has been reported by Wendlandt[12]. A study of thermal decomposition of Schiff base complexes of Co(II), Ni(II) and Cu(II) derived from salicylaldehyde and glycine have been reported by Nathmala[13]. A similar study on the Schiff base complexes of mercury and cadmium halides has been reported recently[14].

In this paper attempts have been made to establish the thermal behavior of anthracene carboxaldehyde – L – Tyrosine complexes of Co(II), Ni(II) and Cu(II) by thermo gravimetric analysis. Synthesis, spectral, electrochemical and antimicrobial studies of mixed ligand complexes of copper and cobalt with nitrogen donors have been reported recently[15,16,17]. Interpretation and mathematical analysis of thermal decomposition data, evaluation of order, entropy change, activation energy and Arrhenius factor are based on Coats – Redfern[18,19] and Horowitz – Metzger[20] methods.

Material and Methods

The ligand was prepared by treating KOH in methanol and tyrosine with hot methanolic solution of anthracene – 9 – carboxaldehyde. The orange yellow precipitate obtained was filtered and re crystallized from methanol. The reaction involved in the preparation of the ligand can be represented as follows

$$C_{14}H_9CH = O + C_9H_{10}O_3NK \longrightarrow C_{14}H_9CH = NO_3H_8C_9K + H_2O$$

Ni(II), Cu(II) and Co(II) complexes were prepared by adding methanolic solution of the metal acetate, to a refluxing solution of the ligand in methanol after adjusting its pH. Thermal decomposition study was carried out at a heating rate of 100^0 C per minute in an atmosphere of static air. A sample mass of 2 to 5 mg was used for the analysis. Calculations based on mechanistic and non mechanistic equations were performed. The instrumental T.G. curves were redrawn as mass verses temperature (TG) curves. Typical TG curves of Co (II), Ni (II),

and Cu (II), were studied in detail. Nine mechanistic equations and two non-mechanistic equations were employed to evaluate kinetic data from these T.G. Curves. Kinetic parameters like activation energy, frequency factor and entropy of activation were calculated using TG curves.

Results and Discussion

The ligand was characterized on the basis of CHN analysis and spectral data. Its melting point was found to be 79^0C. The hydrogen, carbon, nitrogen percentages were determined by micro analytical methods. All the complexes were found to posses 1 : 2 stoichiometry. Here anthracene carboxaldehyde tyrosine (ACT) act as bidentate ligand in the reaction with common transition metal ions. The calculated and observed percentages of carbon, hydrogen and nitrogen were in good agreement. The UV and IR spectra of the ligand showed the characteristic bands.

The molar conductance values of the complexes in methanol at a concentration of 1 x 10^{-4} M at 28 ± 2^0C were indicative of their non electrolytic nature. In Co (II) complex the ligand possess magnetic moment of 5.06 BM. The observed magnetic moment for the spin free octahedral Co (II) ($^4T_{1g}$) have excess of spin only value and it may be due to the orbital contribution of the ground state (t_{2g}^5 e_g^2). Octahedral high spin geometry can be assigned to Co (II) complex, because the measured μ eff value is in the range 4.7 – 5.2 BM. Ni (II) complex shows a magnetic moment value of 3.2 which is very close to the spin only value of octahedral complexes (2.9 – 3.4 BM), depending on the magnitude of the orbital contribution. Therefore an octahedral geometry can be assigned to the Ni (II) complex also. Cu (II) complex gives magnetic moment value 2.28 BM, expected for one unpaired electron of the d^9 electronic configuration indicating octahedral geometry.

The ligand anthracene carboxaldehyde – L – tyrosine shows strong bands at ≈ 1659 cm^{-1} due to carbonyl stretching frequency of carboxylate group, another band at ≈1520 cm^{-1} due to C = N and C = C stretches and a third band at ≈1440 cm^{-1} corresponding to γ sy COO- vibration. In the metal chelate, the presence of co-ordinated water is confirmed by the observation of a broad band appearing in the region 3450 – 3000 cm^{-1}. The coordinated nature of the water molecule is further supported by the appearance of a rocking mode of medium intensity at 860 cm^{-1}. The strong bands observed in the region 1700 – 1300 cm^{-1}, one at 1660 and the other at ≈ 1410 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations respectively of the carboxylate ion. The presence of monodentate carboxylate group is indicated here.

The sharp band at 1520 cm^{-1} in the infrared spectrum assignable to γ (>C = N) of the schiff base residue, shifts to lower frequencies around 1513 cm^{-1} in the complexes indicating a reduction of electron density in the azomethane linkage as the nitrogen coordinates to the metal ion. In all the above three complexes new absorption bands are observed in the regions 585 – 598 cm^{-1} and 420 – 460 cm^{-1}. These bands are assigned to γ M – N and γ M – O stretching vibrations respectively. The region 1600 – 1450 cm^{-1} also showed bands / shoulders due to the skeletal vibrations of aromatic nucleus.

The electronic spectral data was found to agree with conclusions arrived from magnetic susceptibility measurements. The spectrum of Co (II) complex with octahedral geometry was very clear in the spectrum at 20500 cm^{-1} and 13225 cm^{-1} which are assigned to the transition $^4T_{1g}$ (F) ⟶ $^4T_{1g}$ (P) and $^4T_{1g}$ (F) $^4A_{2g}$ (F) respectively of Co (II) complex. Ni (II) complex show three bands in the electronic spectrum which can be attributed to spin allowed d – d transition at 26954 cm^{-1},

25000 cm^{-1} and 17452 cm^{-1} assigned to $^3A_{2g}$ (F) ⟶ $^3T_{2g}$ (F), $^3A_{2g}$ (F) ⟶ $^3T_{1g}$ (F), and $^3A_{2g}$ (F) ⟶ $^3T_{1g}$ (P), respectively Cu(II) complex shows a strong band at 24938 cm^{-1} attributed to charge transfer transition.

Interpretation and mathematical analysis of the thermal decomposition data and evaluation of order of reaction, entropy change, energy of activation and Arrhenius factor, based on Coats Redfern and Horowitz Metzger methods are explained. Evaluation of the reaction mechanism by non-iso thermal methods has been employed using the nine mechanistic equations. Co (II), Ni (II) and Cu (II) complexes were subjected to thermal studies by non isothermal methods. Single stage decomposition is observed in Co (II) and Ni (II) complex, where as Cu (II) complex undergoes two stage decomposition. In all these cases the final products of decomposition are identified to be the oxides, Co_3O_4, Ni O and Cu O by X-ray diffraction study. The overall loss of mass from the TG curves is comparable to the theoretical loss in mass for the conversions.

		Loss % Theoretical,	TGA value
$[CoACT_2 (H_2O)_2]$ ⟶	Co_3O_4	90.4	91
$[Ni ACT_2 (H_2O)_2]$ ⟶	Ni O	91.1	91
$[CuACT_2 (H_2O)_2]$ ⟶	Cu O	90.5	90.5

The kinetic parameters namely, activation energy ΔE, Arrhenius factor A, order parameter n and entropy of activation ΔS for these decomposition reactions calculated from the TG curves, based on the nine mechanistic equations and the two non mechanistic equations are summarized in tables. On the basis of experimental findings in the present studies reveals that the relative thermal stability of the above three chelates can be written as [Co ACT_2 $(H_2O)_2$] > [Cu ACT_2 $(H_2O)_2$] > [Ni ACT_2 ($H_2O)_2$]. These complexes do not show any detectable change up to 100^0 C when heated. This shows that there is no water of hydration. At around 160^0 C a loss of mass is noted in the case of Co (II), Ni (II) and Cu (II) complexes which can be assigned to the loss of coordinated water molecules, according to Nikolaeve et al[21]

Conclusion

The kinetic parameters 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 the greater the thermal stability of a complex the larger the activation energy for decomposition. The non isothermal kinetic methods discussed by Sestak and Berggren and Satava have been used for deducing the mechanism of decomposition of these complexes. In the present case it is observed that R2 mechanism based on phase boundary reaction, cylindrical symmetry gives the maximum correlation for single stage thermal decomposition of [Co ACT_2 $(H_2O)_2$] and [Ni ACT_2 $(H_2O)_2$] obtained from Coats – Redfern with n = ½ . R3 mechanism based on phase boundary reaction, spherical symmetry gives the maximum correlation for the two stage decomposition pattern of [Cu ACT_2 $(H_2O)_2$] with n = 2/3 which is obtained from Coats – Redfern equation. Since the values of E and A computed from the mechanistic equation agree well with those from the non-mechanistic equation, these mechanisms are confirmed. The Schiff base derived from anthracene – 9 – carboxaldehyde and – L – tyrosine is found to be highly stable. The presence of - COO - group adjacent to > C = N linkage stabilizes the complex by chelation.

Table-1
Selected absorption frequencies (cm^{-1}) of transition metal chelates of Anthracene carboxaldehyde L – tyrosine (ACT)

	γ H2 O	γ asyCOO-	γ syCOO-	γ C = N	ln Plane deform	Out of plane deform	γ M - N	γ M – O
Ligand	---	1659	1440	1520	897	777 731	---	---
$CoACT_2$ $(H_2O)_2$	3443	1666	1401	1513	870	784 724	585	433
$NiACT_2(H_2O)_2$	3436	1664	1438	1518	895	781 731	593	426
$CuACT_2$ $(H_2O)_2$	3416	1660	1434	1513	890	777 731	592	425

Table-2
Micro analytical, magnetic moment and conductance data of transition metal chelates of Anthracene – 9 – carboxadehyde – L tyrosine

Metal complexes	Melting Points	color	M%	C%	H%	N%	μ eff B M	Ω^{-1} m^2 mol^{-1}
ligand	79	Orange yellow	---	78.59 (78.19)	4.41(4.89)	3.43 (3.8)	---	---
Co ACT_2 $(H_2O)_2$	95	Yellow	6.61 (7.1)	69.96 (69.29)	4.52 (4.81)	3.4 (3.37)	5.06	8.2
Ni ACT_2 $(H_2O)_2$	160	orange	6.85 (7.06)	68.84 (69.31)	4.58 (4.81)	3.91 (3.37)	3.2	12.7
$CuACT_2$ $(H_2O)_2$	104	Brown	8.8 (7.06)	69.21 (68.90)	4.52 (4.78)	3.1 (3.35)	2.28	15.51

ACT-Anthracene -9- carboxaldehyde –L-tyrosine, The calculated values are given in parentheses;

Table-3
Thermal decomposition data of Co(II), Ni(II) and Cu(II)

Complex	stage	temp range in TG (C)	peak temp in TG (C)	loss of mass percentage from TG	loss of mass percentage theoretical	loss of mass percentage pyrolysis	Probable assignment
[Co ACT_2 $H_2O)_2$]	I	120 - 320	280	91	90.4	91	loss of 2 H_2O + 2ACT
							[Co ACT_2 $(H_2O)_2$] ---> Co_3 O_4
[NiACT_2 $(H_2O)_2$]	I	170 - 320	240	91	91.1	91.29	loss of 2 H_2O + 2ACT
							[Ni ACT_2 (H_2O)$_2$] ----> Ni O
[CuACT_2 $H_2O)_2$]	I	150 - 300	260	71	71	---	loss of 2 H_2O + 1ACT +1ACA part
	II	300 - 530	500	19.5	19.5		loss of tyrosine part
				90.5	90.5	88.97	[Cu ACT_2 (H_2O)$_2$] ----> Cu O

Table-4
Kinetic parameters for the decomposition of Co(II), Ni(II) and Cu(II) complexes of anthracene carboxaldehyde - L - tyrosine (L H) from TG using mechanistic equations

Complex	para meter	mechanistic equations								
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
$[CoACT_2(H_2O)_2]$	E	34.22	35.93	37.95	36.66	19.07	19.07	19.07	17.50	17.71
	A	1.60×10^{13}	5.43×10^{13}	1.15×10^{14}	2.70×10^{13}	1.30×10^{7}	6.50×10^{6}	4.30×10^{6}	1.00×10^{6}	9.70×10^{5}
	ΔS	-45.07	-42.64	-41.14	-44.02	-72.92	-74.30	-75.10	-77.85	-78.08
	r	0.9998	0.9996	0.9982	0.9993	0.9952	0.9952	0.9952	0.9990	0.9967
$[NiACT_2(H_2O)_2]$	E	30.61	32.49	34.72	33.26	17.56	17.56	17.56	15.85	16.73
	A	8.81×10^{11}	3.75×10^{12}	1.03×10^{13}	1.98×10^{12}	4.30×10^{6}	2.20×10^{6}	1.40×10^{6}	2.90×10^{5}	5.30×10^{5}
	ΔS	-50.79	-47.91	-45.91	-49.18	-75.09	-76.46	-77.27	-80.42	-79.24
	r	0.9989	0.9990	0.9980	0.9989	0.9954	0.9954	0.9954	0.9986	0.9980
$[CuACT_2(H_2O)_2]$	E	37.22863	37.61172	39.16397	38.20961	19.05094	18.95622	19.40985	18.02664	18.60881
	A	2.93×10^{14}	2.31×10^{14}	2.92×10^{13}	9.94×10^{13}	1.08×10^{7}	4.74×10^{6}	5.24×10^{6}	1.64×10^{6}	2.093×10^{6}
	ΔS	-39.25	-39.72	-39.25	-41.40	-73.26	-74.90	-74.70	-77.00	-76.52
	r	0.9992	0.9989	0.9996	0.9992	0.9992	0.9986	0.9986	0.9992	0.9995
	E --- K cals / mol,			A --- Sec^{-1}		ΔS ---- eu				

Table-5
Kinetic parameters for the decomposition of Co(II), Ni(II), and Cu(II) complexes of anthracene carboxaldehyde - L - tyrosine (L H) using non mechanistic equations

complex	parameters	Coats Redfern	Horowitz Metziger	mechanistic equation followed		order of reaction
$[CoACT_2(H_2O)_2]$	E	17.50	23.41	17.50	equation 8 phase boundary reaction cylinderical symmetry	1/2.
	A	2.18×10^{6}	4.80×10^{7}	1.06×10^{6}		
	ΔS	-76.47	-70.33	-77.85		
	r	0.9990	0.9995	0.9990		
$[NiACT_2(H_2O)_2]$	E	15.85	21.37	15.85	equation 8 phase boundary reaction cylinderical symmetry	1/2.
	A	5.87×10^{5}	4.42×10^{6}	2.93×10^{5}		
	ΔS	-79.04	-75.03	-80.42		
	r	0.9986	0.9990	0.9986		
$[CuACT_2(H_2O)_2]$	E	18.61	24.42	18.61	equation 9 phase boundary reaction spherical symmetry	2/3.
	A	6.28×10^{6}	5.90×10^{7}	2.09×10^{6}		
	ΔS	-74.34	-69.88	-76.52		
	r	0.9995	0.9980	0.9995		

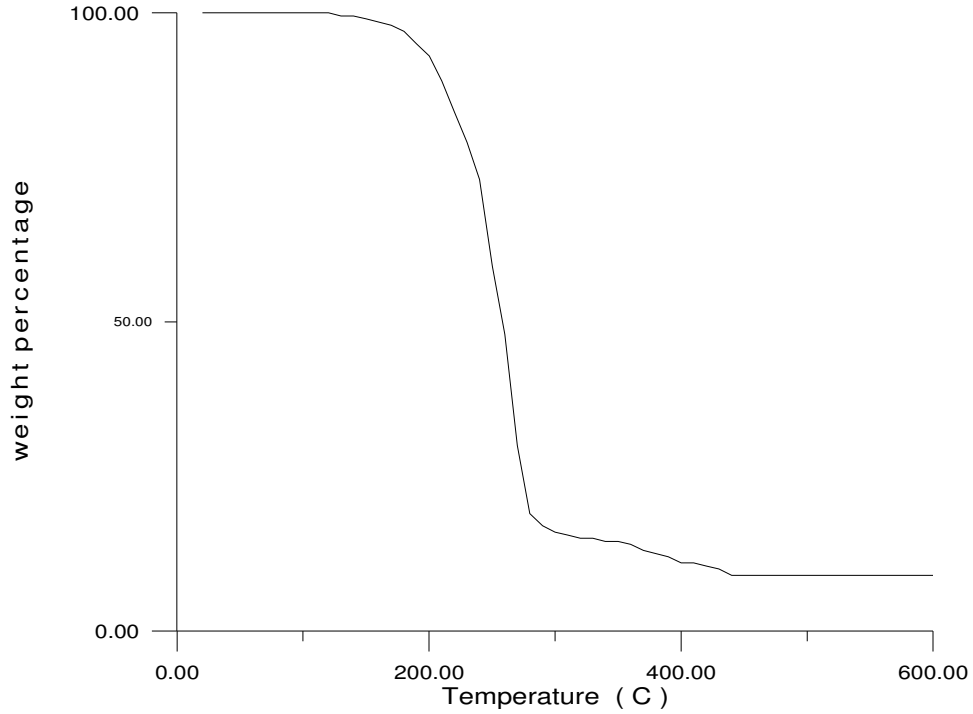

Figure-1
TG curve of Co $(ACT)_2(H_2O)_2$

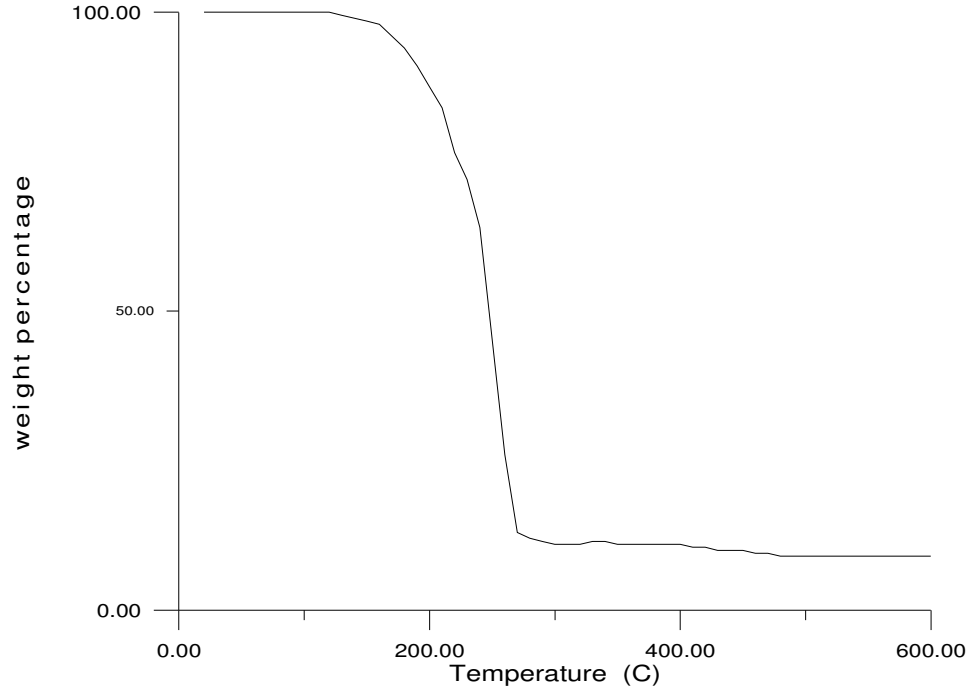

Figure-2
TG curve of Ni $(ACT)_2(H_2O)_2$

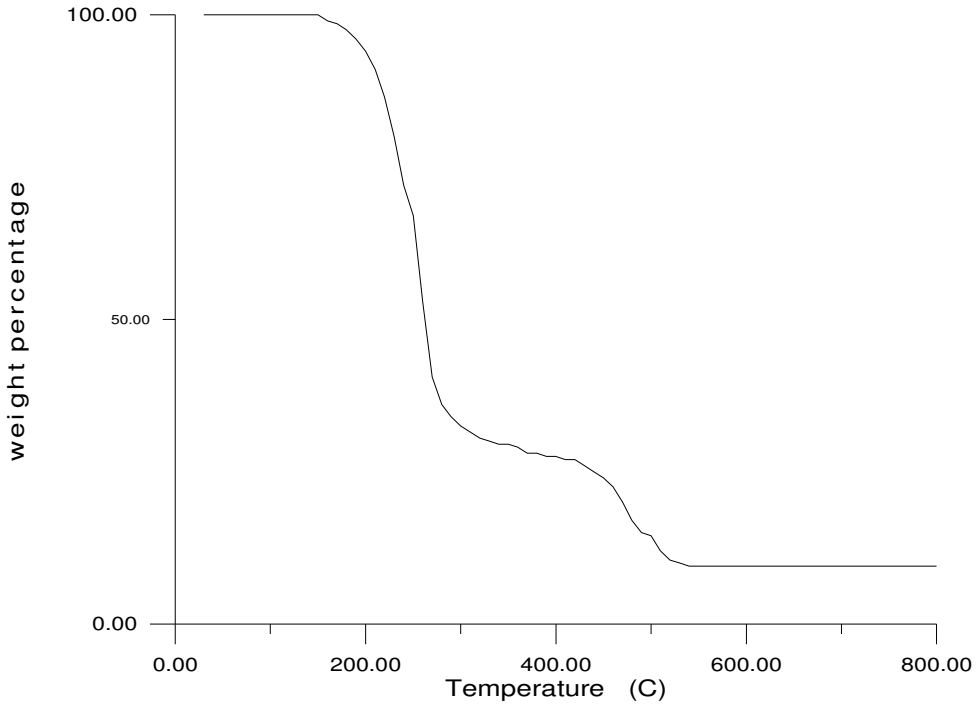

Figure-3
TG curve of Cu (ACT) $_2$ (H_2O) $_2$

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