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THERMAL DECOMPOSITION KINETICS AND MECHANISM OF Mn(II), Ni(II) AND Cu(II) COMPLEXES OF 3-FORMYLINDOLE-2-AMINO-5-BROMO BENZOICACID

Aby Paul*
Joby Thomas K**
Reeja Johnson***

Abstract

Manganese(II), Nickel(II) and Copper(II) complexes of the Schiff base, 3-formylindole-2-amino-5-bromobenzoicacid were prepared and characterized by various analytical techniques such as ^{1}Hnmr, ^{13}Cnmr, infrared, mass, electronic spectroscopy, elemental, magnetic and conductance studies. Structural evalution established that a stoichiometry exists between the metal and ligand and the Chelates possess general formula $[ML(Ac)(H_2O)_3]$. Geometry of all the complexes was found to be octahedral Thermal decomposition kinetics and mechanism of the metal chelates were studied by TGA and DTA techniques. The TG curves of Mn(II) and Ni(II) showed a three stage decomposition pattern and Cu(II) complex showed a two stage decomposition pattern, which is supported by DTA data.

Keywords:

Complexes;
Kinetic;
Themogravimetric studies.

Author correspondence:

Joby Thomas K,
Research Division
Department of Chemistry,
St.Thomas College (autonomous),Thrissur

1. Introduction

Transition metal complexes of Schiff bases have important technical applications. The thermal properties of metal chelates of a wide variety of chelating ligands were studied extensively by Wendlandt and co-workers[1-3] and Hill and co-workers[4,5]. Such studies on thermal decomposition and kinetics of metal chelates with Schiff bases have been done by many researchers[6-9]. In the present course of studies, synthesis, characterization and thermoanalytical data of three transition metal complexes of a novel potential Schiff base, 3-formylindole-2-amino-5-bromobenzoicacid (3FI2A5BBA) were carried out.

Non –isothermal methods have been widely used to study the kinetics and mechanism of thermal decomposition of solids[10,11]. This study therefore attempts to establish the mechanism of decomposition of $[MnLAc(H_2O)_3]$, $[NiLAc(H_2O)_3]$ and $[CuLAc(H_2O)_3]$ from TGA and DTA experiments.

2. Research Method

The ligand 3-formylindole-2-amino-5-bromobenzoic acid (3FI2A5BBA) was prepared by refluxing an ethanolic mixture(1:1) of 2-amino-5-bromobenzoic acid and 3-formylindole for five hours. Yellowish crystals separated on cooling were purified by recrystallization from ethanol and characterized on the basis of analytical and spectral studies, mp 155^0C. Samples of Mn(II), Ni(II) and Cu(II) chelates of 3-formylindole-2-amino-5-bromobenzoic acid(3FI2A5BBA) were prepared by adding ethanolic solution of the ligand to an aqueous solution of metal acetate in 1:1 ratio. The resulting solution was refluxed for about 3 hours, concentrated and cooled in an ice bath. The complex formed was filtered, washed with ethanol and dried in a vaccum desiccator.

Physicochemical techniques such as solution conductance, magnetic susceptibility measurements and spectral studies like ^{1}Hnmr, ^{13}Cnmr, infrared, mass and UV-Visible have been used to elucidate the structure and geometry of the complexes.

Thermogravimetric and differential thermal analysis curves were traced using a Shimadzu DT40 thermobalance in an atmosphere of static air. A constant heating rate of 10^0Cmin^{-1} and a sample mass of 5-10 mg were employed for the entire study. The mass loss considerations and X-ray diffraction data confirmed the products to the corresponding oxides. Mechanistic and non mechanistic calculations were performed with a Pentium IV computer using EXCEL and origin softwares. Evaluation of the mechanism of reactions from nonisothermal methods has been discussed by Sestak and Berggren[12] and Satava[13]. For evaluating kinetic parameters from mechanistic equations given by Satava, Coats and Redfern[14] following equation was used in the general form and the various g(α) values were substituted. This has been recommended to be one of the best solutions by several authors[15,16]. Along with the mechanistic equations, two non mechanistic methods suggested by Coats and Redfern and Horowitz[17] were also used for comparison.

$$\text{In}\,(\alpha)/T^2 = \text{In}AR/\varphi E - E/RT$$

where α= fraction of the compound decomposed at time T, φ, rate of heating in deg.min-^{1}, R= Universal gas constant, A= frequency factor and E =activation energy

3. Results and Analysis

Molar conductance, magnetic susceptibility and analytical data are presented in Table 1. The complexes exhibit molar conductance in the range 2-10($\Omega^{-1}cm^2mol^{-1}$) indicating the non electrolytic nature.

Table 1 Microanalytical, magnetic and conductance data of transition metal complexes of 3-formylindole-2-amino-5-bromobenzoic acid (3FI2A5BBA)

Compound	Colour	M.P (^0C)	Metal% (Cald)*	C %	H %	N%	μ_{eff} (BM)	Ω **
3FI2A5BBA (LH)	Yellow	155	-	52.3 (56.14)	3.88 (3.21)	8.66 (8.18)	-	-
$[MnLAc(H_2O)_3]$	Grey	240	10.65 (10.81)	44.23 (44.44)	3.34 (3.73)	5.21 (5.50)	6.10	18
$[NiLAc(H_2O)_3]$	Grey	278	11.85 (11.50)	42.47 (42.10)	3.19 (3.70)	5.51 (5.46)	2.58	4
$[CuLAc(H_2O)_3]$	Green	340	12.37 (12.36)	41.28 (41.60)	2.01 (2.89)	5.02 (5.40)	2.00	15

*(Calculated values are given in parenthesis) ** Molar conductance in ($\Omega^{-1}cm^2mol^{-1}$)

In the infrared spectrum of the ligand, the significant absorption frequencies appeared at $1610cm^{-1}$and $1446cm^{-1}$ can be attributed to the stretching frequencies of the carbonyl bond of the carboxylic acid group. A strong band displayed at $1570cm^{-1}$ is a clear evidence for –C=N group. All the C-H vibrations of ligand appeared in the range $3050\text{-}3100cm^{-1}$. The complexes exhibited slight deviations from the IR spectrum of the free Schiff base ligand. All the symmetric and asymmetric stretching vibrations of the carboxylate group in metal chelates changed into the lower frequency regions indicates chelation of the ligand to the metal atom through the carboxylate moiety[18]. All the studied metal chelates exhibited their characteristic stretching frequency for C=N group in the region $1540\text{-}1550cm^{-1}$ which falls to the lower region compared to the azomethine stretching frequency of the free Schiff base ($1570cm^{-1}$). These results also support the argument that one of the coordination sites of the bidentate Schiff base ligand is the azomethine nitrogen[19]. New bands appeared in the IR spectrum of the metal chelates at ~ 510cm^{-1}and 640-670cm^{-1} can be regarded as the presence of newly formed metal-nitrogen and metal-oxygen coordinate bonds respectively. In chelates, the presence of coordinated water is confirmed by the observation of a broad band at 3300cm^{-1}[20].

The sites of coordination of the Schiff base to the metal ions were further confirmed by recording the ^{1}Hnmr and ^{13}Cnmr spectra of the metal chelates. In the ^{1}Hnmr spectra of all the metal complexes, the signal due to the carboxylic acid proton was absent, showing that one of the linkages by the ligand to the metal ion is through the carboxylate part of the Schiff base, after deprotonation. Also a noticeable shift for the azomethine proton peak to the downfield regions, suggests that second coordinating moiety of the ligand is the azomethine nitrogen. In the ^{13}Cnmr spectra of all complexes, the peak due to the azomethine carbon atom in the metal chelates are shifted to downfield region which is an indication of the coordination through the C=N moiety. Even though two different carboxylate groups were present in the metal chelates, which originated from the ligand and the acetate respectively, considerable downward shift was noticed only for the signal of carboxylic acid carbon of the chelated ligand.

In the mass spectrum of the Schiff base, the M^{+} peak was absent. The base peak observed at m/z 144 can be assignable to the fragment $[C_9H_8N_2]^{+}$ formed by the loss of bromobenzoic acid part of the ligand.

Electronic spectrum of the Schiff base was characterized by two intense bands lying at 27548cm^{-1} and 37735cm^{-1}. The intense peak observed at 28571cm^{-1} can be attributed due to $\pi\rightarrow\pi^*$ transition. The electronic spectrum of the Mn(II) complex revealed a band at 24800 cm^{-1} which support the presence of Mn(II) in an octahedral geometry [21]. The effective magnetic moment value of Cu(II) chelate was 2.0 BM, which is in agreement with the value found for octahedral copper complexes [22]. The electronic transitions in the Ni(II) complex gave three intense bands at 14200, 18864 and 24243cm^{-1}, which can be assigned to $^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}$, $^{3}A_{2g}(F) \rightarrow {}^{3}T_{1}g(F)$ and $^{3}A_{2g}(F)\rightarrow{}^{3}T_{1g}(P)$ transitions respectively. In the octahedral field, Cu(II) chelate is expected to display a band in the electronic spectrum which can be assigned due to $^{2}E_{g}\rightarrow{}^{2}T_{g}$ electronic transition. In the present case, the same signal appeared at 20100cm^{-1}. In addition to this, a band with high molar extinction coefficient was observed at 27640cm^{-1}, assignable to the Laporte forbidden LMCT band. The magnetic moment value and the electronic spectral data thus confirmed the octahedral geometry of the Cu(II) chelate. On the basis of the above results, the structure of the ligand 3FI2A5BBA was confirmed and shown in the Fig.1. From the spectroscopic and magnetic studies octahedral geometry can be assigned to all these complexes of 3FI2A5BBA (Fig. 2)

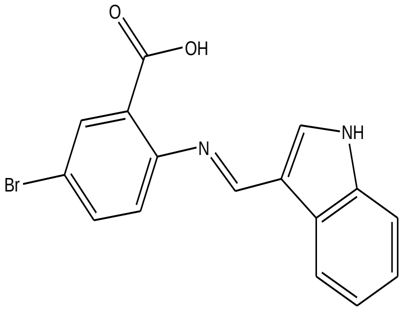

Fig. 1 Structure of 3FI2A5BBA

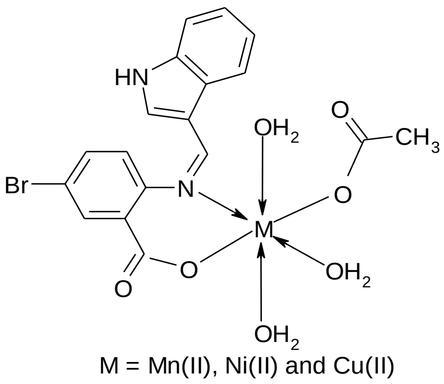

Fig.2 Structure of the metal complexes

3.1 Thermal studies

The TG curves of Mn(II) and Ni(II) complexes show a three stage decomposition pattern which is supported by DTA data (Fig.3 and Fig.4) . The first stage decomposition of both the Mn(II) and Ni(II) complexes consist of the removal of the coordinated water molecules. The second stage in both cases has two sub stages. The two sub stages of second stage decomposition of Mn(II) complex is quite overlapping and overall mass loss may due to the removal of indole and bromo parts of the ligand. In the case of Ni(II) complex the first substage(IIa) is due to the loss of indole and azomethine moieties of the Schiff base. The bromine part of the ligand is lost in the second substage(IIb). The loss of three water molecules and acetate part, indole and bromo part of the ligand takes place in the first stage decomposition pattern of the copper complex (Fig.5). The Cu(II) complex exhibits a well clear two stage decomposition pattern where the second stage may be due to the loss of the rest part of the ligand. In the third stage decomposition pattern of both Mn(II) and Ni(II) complexes there is a loss of acetate part and the rest of the ligand moieties.

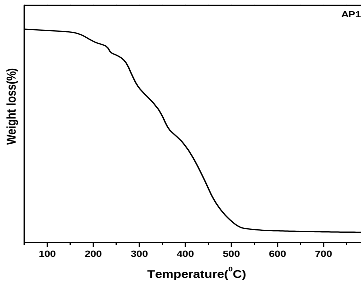

Fig.3 TG curve of $[MnLAc(H_2O)_3]$

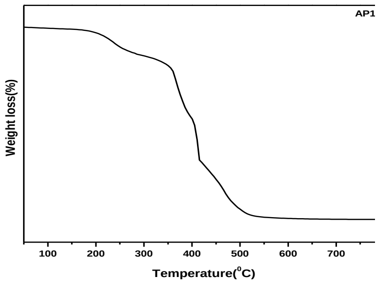

Fig. 4 TG curve of $[NiLAc(H_2O)_3]$

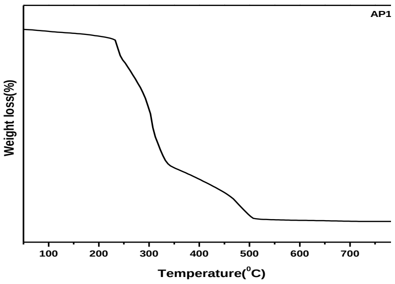

Fig. 5 TG curve of $[CuLAc(H_2O)_3]$

3.2 Decomposition Kinetics

Thermal decomposition data of the three metal chelates are represented in Table 2. Data from independent pyrolytic experiments are also given in this table. The non-isothermal TG curves have been subjected to mathematical analysis using the integral method of Coats-Redfern and the activation parameters have been evaluated for all these complexes. The most suitable parameters were selected with the aid of correlation coefficient which is shown in Table 3 and 4. The mechanism of decomposition has been established from the TG data using the nine mechanistic equations in comparison with the integral method (Coats and Redfern).The kinetic parameters obtained show maximum correlation between F_1 mechanism, (Mampel equation i.e. $-\ln(1-\alpha) = kt$) based on random nucleation with one nucleus at each particle and the Coats-Redfern equation with n=1, for the second and third stage decomposition pattern of manganese complex. Similarly the values of kinetic parameters obtained from various mechanistic and non mechanistic equations, particularly the Coats-Redfern equation, revealed that IIa and III stages of decomposition of Ni(II) chelate follows R_2 mechanism, phase boundary reaction, cylindrical symmetry (n=1/3), whereas IIb stage of decomposition obeys equation V; Mampel equation with random nucleation. It is observed that the F_1 mechanism based on Mampel equation gives maximum correlation for the first and second stage decomposition of $[CuLAc(H_2O)_3]$. Thermal decomposition studies established the relative stability of these complexes follows the order $[MnLAc(H_2O)_3] < [NiLAc(H_2O)_3] < [CuLAc(H_2O)_3]$.

Table 2 Thermal decomposition data (^{0}C) of Mn(II), Ni(II) and Cu(II) complexes of 3FI2A5BBA

Complex	Stage	Temp range in TG	Peak temp in TG	Peak temp in DTA	Loss of mass %		
					From TG	Cald.	From Pyrolysis
$[MnLAc(H_2O)_3]$	Ia	76-231	194	199			
	Ib	231-241	233	237	10.35	10.61	-
	IIa	241-301	276	281			
	IIb	301-396	346	350	38.09	38.31	-
	III	396-531	416	425	35.71	35.57	
					84.15	84.49	84.5
$[NiLAc(H_2O)_3]$	I	120-255	220	222	10	10.53	-
	IIa	255-385	365	370	27.35	27.88	-
	IIb	385-410	405	408	15.09	15.39	-
	III	410-505	465	472	33.12	31.64	-
					85.56	85.43	85.37
$[CuLAc(H_2O)_3]$	I	6-352	280	287	58.85	59.46	-
	II	352-987	422	428	22.41	22.01	-
					81.26	81.47	81.41

Table 3 Kinetic parameters of the decomposition of Mn(II) and Ni(II) complexes of 3FI2A5BBA from TG using non-mechanistic equation (Coats-Redfern) and its correlation with mechanistic equation

Complex (Stage)	Non-mechanistic/ mechanistic equation	Kinetic parameters*				Order (n)	Mechanism of decomposition
		E	A	ΔS	r		
$[MnLAc(H_2O)_3]$ Stage IIa	Coats-Redfern	185.11	$1.51\text{x}10^{15}$	40.6	0.9982	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	185.11	$1.51\text{x}10^{15}$	40.6	0.9982		
Stage IIb	Coats-Redfern	133.46	$7.69\text{x}10^{8}$	-80.86	0.9963	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	133.46	$7.69\text{x}10^{8}$	-80.86	0.9963		
Stage III	Coats-Redfern	140.16	$4.53\text{x}10^{7}$	-105.29	0.9800	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	140.16	$4.53\text{x}10^{7}$	-105.29	0.9800		
$[NiLAc(H_2O)_3]$ Stage IIa	Coats-Redfern	60.24	$1.34\text{x}10^{2}$	-210.48	0.9686	1/3	R_2 mechanism. Phase boundary reaction. Cylindrical symmetry
	Equation VIII	62.10	$1.03\text{x}10^{2}$	-212.64	0.9658		
Stage IIb	Coats-Redfern	390.36	$1.54\text{x}10^{28}$	287.88	0.9974	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	390.36	$1.54\text{x}10^{28}$	287.88	0.9974		
Stage III	Coats-Redfern	57.48	$1.2\text{x}10^{8}$	-97.79	0.9993	1/3	R_2 mechanism. Phase boundary reaction. Cylindrical symmetry
	Equation VIII	64.22	$2.63\text{x}10^{8}$	-91.258	0.9984		
$[CuLAc(H_2O)_3]$ Stage I	Coats- Redfern	109.7	$4.99\text{x}10^{7}$	-102.66	0.997	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	109.7	$4.99\text{x}10^{7}$	-102.66	0.997		
StageII	Coats-Redfern	93.98	$1.71\text{x}10^{4}$	-170.9	0.985	1	F_1 mechanism. Mampel equation. Random nucleation. One nucleus at each particle
	Equation V	93.98	$1.71\text{x}10^{4}$	-170.9	0.985		

*E in $kJmol^{-1}$; A in s^{-1}, ΔS in $JK^{-1}mol^{-1}$

4. Conclusion

- Novel heterocyclic Schiff base 3-formylindole-2-amino-5-bromobenzoic acid (3FI2A5BBA) and its metal chelates were synthesized
- Structures of the ligand and chelates were established by various analytical methods and it was proved that 1:1 stoichiometry exists between the ligand and the metal ion. Octahedral geometry was suggested for these chelates
- The thermal behavior of metal complexes shows that the lose of hydrated water molecules occurs in the first step, immediately followed by decomposition of ligand molecules in the subsequent steps.
- Thermal data showed degradation pattern of the complexes. TG and DTA studies also guided to derive the thermodynamic, kinetic and reactivity behavior of these materials and metal-ligand interaction.
- Thermal decomposition studies established the relative stability of these complexes follows the order $[MnLAc(H_2O)_3]$ < $[NiLAc(H_2O)_3]$ < $[CuLAc(H_2O)_3]$.

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