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Studies on the Thermal Decomposition of Copper (II) Fluoride Complexes with Various Amino Acids in Nitrogen Atmosphere

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Thermal decomposition reactions of various copper (II) fluoride complexes of the general type $\text{Cu}(\text{L})\text{F}\cdot x\text{H}_2\text{O}$ (L= asparagine(asp), arginine (arg), methionine (meth) and proline (pro), $x = 3$ to 4) have been studied in nitrogen atmosphere using TG and DTA techniques. A possible mechanism of decomposition is suggested on the basis of the reactions of their pyrolysis. The residues obtained at the end of various decomposition processes were identified through IR spectrometry. The kinetic parameters such as energy of activation (E°) and order of reaction (n) were also determined.

Introduction

In the literature, complexes of transition metal containing BF_4^{-1} ions have been reported for numerous ligands¹. Fluoride complexes of divalent transition-metal ions, on the other hand, are hardly known, in sharp contrast to the many formed by the corresponding chloride, bromide and iodide². Copper complexes, in which fluoride is either attached to the metal ion or uncoordinated as a counter anion, are still relatively rare³⁻⁵ and very few have been reported so far, without any thermal studies⁶⁻¹¹.

In the present work, Cu (II) complexes with various amino acids containing fluoride, were prepared and characterized by elemental analysis, infrared and electronic spectroscopy and magnetic susceptibility

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techniques. In this paper, we probe the thermal behavior of Cu (II) fluoride complexes with various amino acids, with the aim of discussing the possibilities of a correlation between the stability and stepwise analysis of their thermal decomposition.

Experimental

The complexes were prepared by the methods reported previously¹². All the chemicals used in this work were of Aldrich, Merck and BDH analytical reagent grade and were used as such.

Preparation of Complexes

Cu (II) fluoride complexes of amino acids were obtained by mixing 10 mmol of various amino acids with 10 mmol of corresponding metal fluoride hydrate dissolved in water (50 cm³). In all cases the final metal/ligand ratio was 1 : 1. The resulting solutions were stirred for one hour, filtered and evaporated on a rotary evaporator until dryness. The colored crystals were dried over silica gel.

The complexes, synthesized as above, were then analyzed by microanalytical method (C, H and N), IR spectrometry, magnetic moments and electronic spectra to ensure their purity. The analytical data are given in Tables 1, 2 and 3, respectively. The concentration of copper was estimated by Atomic Absorption Spectrophotometer and fluoride was determined spectrophotometrically using alizarine fluorine-blue reagent after destruction of the complex by fusion with NaOH⁵.

Table 1. Chemical analyses of the complexes

Compound	Color	Carbon% Found	Hydrogen% Found	Nitrogen% Found	Metal% Found	Fluorine% Found
I Cu (asp) F.3H ₂ O	Dark blue	11.2 (11.27)*	5.11 (5.23)	20.1 (21.32)	25.5 (25.55)	7.6 (7.65)
II Cu (arg) F.4H ₂ O	Light blue	16.1 (17.1)	6.9 (6.41)	22.3 (21.98)	19.01 (19.39)	5.2 (5.8)
III Cu(meth)F.3H ₂ O	Sky blue	4.9 (4.92)	4.92 (5.62)	21.3 (21.09)	22.31 (22.32)	6.09 (6.68)
IV Cu (pro)F.4H ₂ O	Sky blue	5.3 (5.21)	6.35 (5.96)	21.3 (22.35)	22.9 (23.65)	7.7 (7.08)

*Calculated values are given in parentheses

Table 2. Values of magnetic moments, molar conductance and absorption maxima (or absorption bands in electronic (d-d) spectra)

Complex	μ_{eff} B.M.	M^a	ϵ (cm ⁻¹)
I	1.75	16	14190
II	1.90	12	14090
III	1.95	16	14090
IV	1.99	12	14280

a = ohm⁻¹ cm² mol⁻¹ 10⁻³ in deionized water

Table 3. Maxima of absorption band in IR spectra

Complexn	ν NH	δ NH ₂	ν COO ⁻¹	ν CuO	ν CuN	ν CuF
I	3290 s 3280 s	1600 m	1385 m	580 m	290 m	500 s
II	3300 s 3260 s	1605 m	1390 m	610 s	270 m	435 m
III	3230 s 3200 s	1610 m	1375 m	580 s	300 s	460 m
IV	3270 s 3200 s	1600 m	1370 m	610 m	290 m	500 m

s = strong, m = medium

Apparatus

The microanalyses of C, H and N were carried out on a Coleman automatic analyzer. Metal ions were determined with an Atomic Absorption Spectrophotometer (Hitachi, Model AA-670). Infrared spectra were recorded in the range of 4000-200 cm⁻¹ using a Hitachi Infrared Spectrometer, Model 290-50, in KBr pellets.

The magnetic moments and electronic spectra were obtained using a Newport variable temperature balance and a Beckman ACTA MIV spectrophotometer, respectively.

The thermal analyses were carried out using NETZSCH Simultaneous Thermal Analyzer STA 429 in an atmosphere of nitrogen, in the temperature range of ambient to 1100°C, at a heating rate of 20°C min⁻¹ using Kaolin as reference material. The thermal reactions were studied with samples varying from 40 to 44 mg.

Determination of activation energy and reaction order

The activation energy (E°) and order of reaction (n) were evaluated using the Horowitz-Metzger method¹³. For $n = 1$, a plot of $\ln \ln w_o - w/w - w_f$ against θ resulted in a straight line (Fig. 1). The activation energy was calculated from its slope, which was equal to $E/2.303 RT_s^2$. For $n \neq 1$, a plot of $\log [1 - (w - w_f/w_o - w_f)^{1-n}/1 - n]$ vs. θ was drawn and a straight line of the same slope as in the previous case was obtained.

Results and Discussion

The results of chemical analyses (Table 1) reveal the the composition of solid complexes corresponds to 1 : 1 (M : L) molar ratios and almost all the prepared complexes have more than two water molecules either coordinated to the central metal atom or hydrogen bonded to the ligand fluoride.

Magnetic and Spectral Properties

On the basis of the magnetic moments (Table 2), it can be concluded that all the complexes under study are paramagnetic and the values are in the range usually found for octahedral geometry¹⁴. The complexes exhibit only a single band in their electronic spectra, which is typical of mono-molecular octahedral complexes with ligand coordinated through a nitrogen atom^{14,15}. The broad absorption bands in the range 14280 to 14090 cm⁻¹ can be assigned to the transition ${}^2E_g \longrightarrow {}^2T_{2g}$. The broadness of the bands is due to Jahn-Teller distortion which results from an odd number of electrons in the E_g orbitals¹⁶.

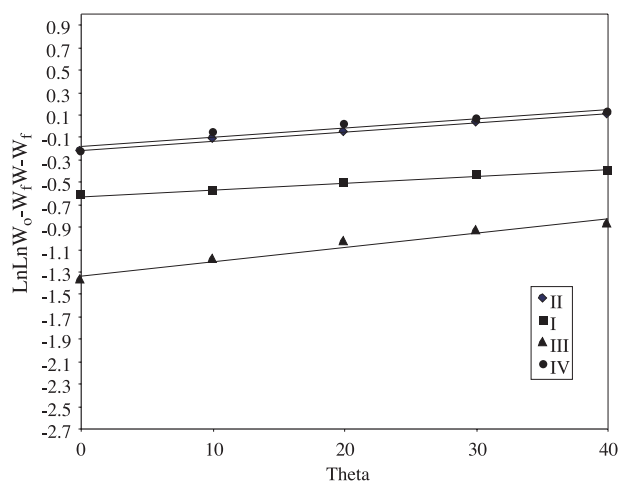


Figure 1. Determination of Activation Energy from Thermogravimetry

In infrared spectra (Table 3), the bands at $3390\text{-}3350\text{ cm}^{-1}$ and $1625\text{-}1615\text{ cm}^{-1}$ which are assigned to ν N-H group stretching and δ (NH_2) group bending frequencies in the ligands, respectively, shift toward lower values in all the complexes ($3270\text{-}3230\text{ cm}^{-1}$), indicating that the amino nitrogen is coordinated to the copper atom. The bands in the region of $1375\text{-}1390\text{ cm}^{-1}$ (sym COO^{-1} stretching vibration) suggest that the amino acids' carboxyl group is involved in the complex formation¹⁷. In the far infrared region, the complexes show bands around $620\text{-}560\text{ cm}^{-1}$ and $320\text{-}270\text{ cm}^{-1}$ that may be assigned to n Cu-N⁴. A new strong metal dependent absorption is found at about $500\text{-}435\text{ cm}^{-1}$. This band may probably be assigned to the ν Cu-F stretching vibration¹⁰⁻¹¹.

Thermal Properties

The thermal decomposition curves (TG and DTA) are given in Figs. 2-5, while the TG weight loss data and DTA peak temperatures are presented in Table 4. The complex, Cu (asp) F.3H₂O (I), begins to lose weight around 100°C and, up to 200°C , 10.45% weight loss is observed. This is the dehydration stage in which two water molecules are eliminated. No stable intermediate is formed between the first and second stages as the second stage starts at 200°C . Around 200°C , a sharp decrease in weight is noted and the subsequent slow weight loss occurs until 340°C . This stage shows a 47.74% weight loss, which is attributed to the breakage of the amino acid molecule. The last stage, that starts around 360°C , exhibits a 6% weight loss and suggests the elimination of a water molecule. The residue is CuF_2 , which is stable even above 800°C ¹⁸.

TG of the complex Cu (arg) F.4H₂O (II) starts to decompose around 180°C . This stage continues until 240°C and one water molecule is eliminated. The weight loss recorded for this stage was 5.5%. The main degradation step starts around 240°C and ends at 270°C with an overall weight loss of 50.48%. The whole segment of the amino acid is broken. The last step is ascribed to the elimination of the remaining three molecules of water, which commences at 270°C and until the end (450°C) shows a weight loss of 13%. Residue, in this case, is again CuF_2 .

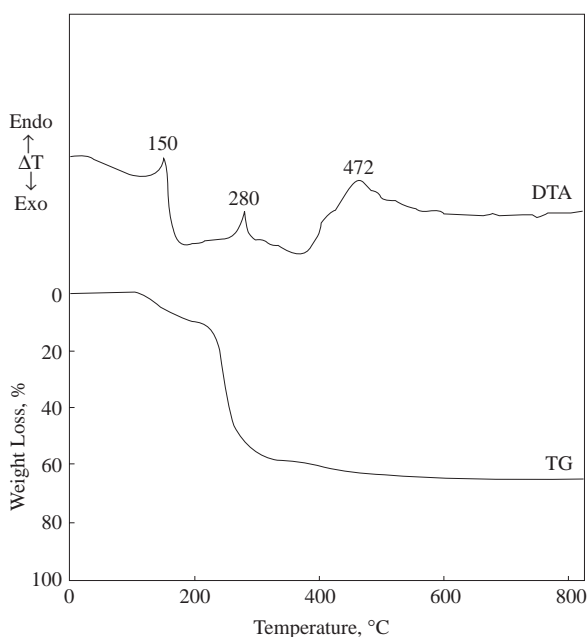


Figure 2. TG and DTA Curves of Cu(asp)F.3H₂O in Nitrogen

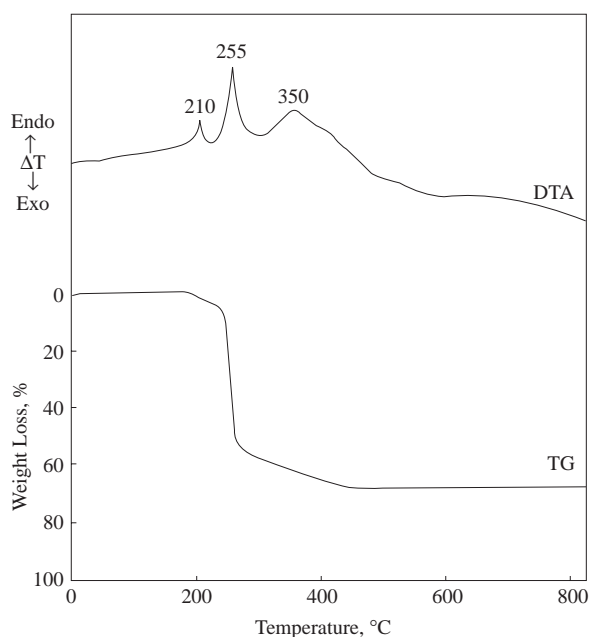


Figure 3. TG and DTA curves of Cu(arg)F.4H₂O in Nitrogen

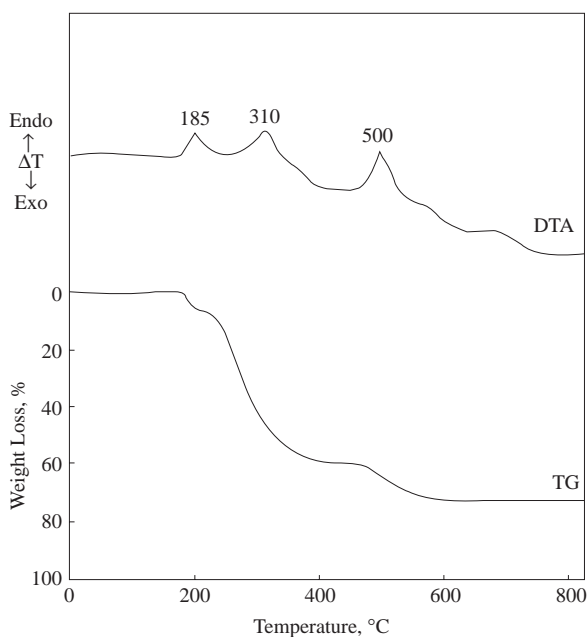


Figure 4. TG and DTA Curves of Cu(meth)F.3H₂O in Nitrogen

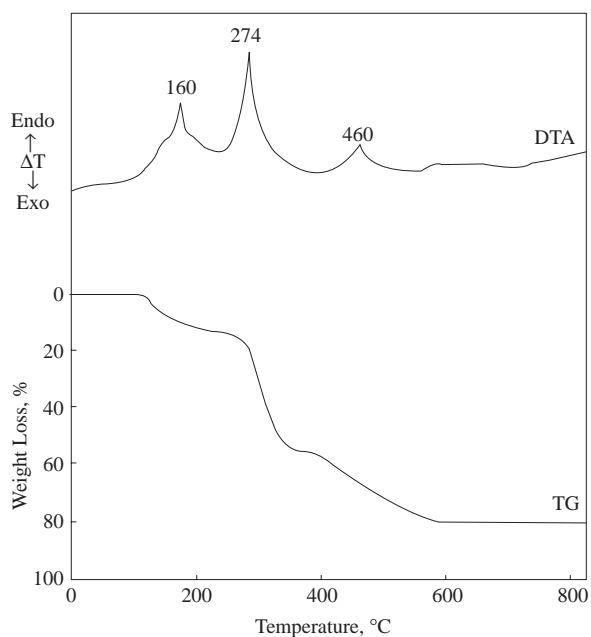


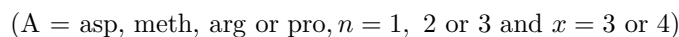
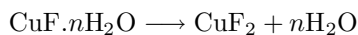
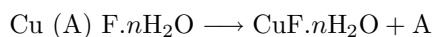
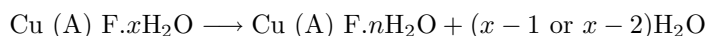
Figure 5. TG and DTA Curves of Cu(pro)F.4H₂O in Nitrogen

The decomposition of the complex, Cu (meth) F. 3H₂O (**III**), starts around 170°C and, up to 200°C, a weight loss of 5.6% is recorded. Dehydration takes place and one molecule of water is eliminated. The second stage, which starts at 200°C, shows a weight loss of 54.80% corresponding to the loss of methionine. The third stage starts at 450°C and exhibits a weight loss of 12%, which is attributed to the elimination of two water molecules. The residue is identified as CuF₂.

Table 4. Thermal behavior of Copper (II) Fluoride Complexes of Amino Acids

Compound	Temperature range, °C	Stage	TG Wt. Loss, % Found	DTA Temperature Peak, °C	Evolved Moiety	
					Formula	Mass Calcd.%
I	100-200	1	10.45	150(endo)	2H ₂ O	13.35
	200-340	2	47.74	280(endo)	asp	49.35
	360-600	3	6	472(endo)	H ₂ O	6.67
II	180-240	1	5.5	210(endo)	H ₂ O	5.47
	240-270	2	50.48	255(endo)	arg	52.43
	270-450	3	13	350(endo)	3H ₂ O	16.43
III	170-200	1	5.6	185(endo)	H ₂ O	6.3
	200-450	2	54.8	310(endo)	meth	52.18
	450-600	3	12	500(endo)	2H ₂ O	12.6
IV	100-200	1	13	160(endo)	2H ₂ O	13.34
	220-360	2	43	274(endo)	pro	42.67
	360-600	3	13	460(endo)	2H ₂ O	13.34

The complex, Cu (pro) F.4H₂O (IV), starts decomposing around 100°C and a 13% weight loss is observed in this step. Two water molecules are eliminated. At 220°C the second step begins and shows the loss of an amino acid molecule with a weight loss equal to 43%. This stage ends at 360°C. The third stage starts at 360°C with a weight loss of 13% corresponding to the elimination of two water molecules. Residue is CuF₂ as was the case for previous complexes. In general, the thermal decomposition of complexes may be described by the following equation:



With the initial decomposition temperature as the criterion of thermal stability, it can be inferred that the thermal stability of these complexes decreases in the following order:

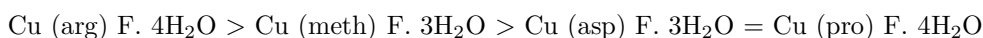


Table 5 gives the values of activation energy (E°) and order of reaction (n) for the thermal decomposition of the complexes under study. The highest thermal stability is displayed by the complex, Cu (arg) F. 4H₂O, on the basis of activation energy.

Table 5. Kinetic Parameters of the Thermal Decomposition of Copper (II) Fluoride Complexes of Amino Acids

Compound	Temperature range °C	Activation Energy E° KJ/mol	Order of Reaction, n
I	110-410	29.24	0.5
II	190-380	61.44	0.5
III	170-430	30.92	0.5
IV	100-360	47.47	0.5

Conclusions

In conclusion, (i) all the amino acid complexes of copper show three stage degradation, which also indicates the similarity of the mode of degradation, (ii) the intermediates for different stages are not stable and start decomposing immediately after their formation, (iii) the ligands appear to be more stable than their corresponding metal complexes¹⁹, (iv) in all cases, CuF₂ is the residue, which is stable even above 800°C, (v) the elimination of water molecules above 300°C, suggests that these are strongly coordinated in the crystal lattice of complexes and (vi) the results of the present study reveal that thermal analysis could be useful for differentiating between the coordinated water molecules and hydrogen bonded water molecules.

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