

Note

THERMAL DECOMPOSITION OF COPPER(II) GLUTAMATES

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Glutamic acid is potentially a terdentate ligand capable of bonding through the amino and carboxylato groups in its metal complexes. In aquo-glutamato-copper(II) monohydrate, a water molecule and a nitrogen and two oxygen atoms of the carboxyl groups of the glutamate constitute a plane, and the distorted octahedral coordination around Cu(II) is completed by the slightly weaker bonding of the glutamate oxygen atoms in the apical positions [1]. In Cu(II) glutamate adducts of N-donor ligands, the bases replace the water in the equatorial position and the Cu(II) retains the tetragonally distorted octahedral configuration. The electronic spectral data of the adducts suggest that the order of stability of the Cu(II) adducts follows the basicity of the ligands [2]. It was thought worthwhile to study the thermal stabilities of these complexes and to correlate them with the base strengths of the ligands. This paper reports the results of the thermal decomposition of copper(II) glutamate and its adducts with ammonia, morpholine, β - and γ -picolines and pyridine.

EXPERIMENTAL

Copper(II) glutamate dihydrate, Cu glut \cdot 2 H₂O was obtained by the interaction of aqueous solutions of lithium glutamate and copper(II) chloride. The precipitated complex was filtered, washed with acetone and dried. The adducts with ammonia, morpholine, β - and γ -picolines and pyridine formulated, respectively, as Cu glut \cdot NH₃, Cu glut \cdot morph, Cu glut \cdot β -pic, Cu glut \cdot γ -pic and Cu glut \cdot py, were prepared by dissolving Cu glut \cdot 2 H₂O in the respective 1 : 1 aqueous bases. The resultant solutions were stirred and diluted with acetone, producing blue complexes which were filtered, washed with acetone and dried. All the complexes gave satisfactory analytical results.

The TG studies were made in air on a Stanton thermobalance at a heating rate of 6°C min⁻¹, whereas the DTA runs were carried out on a Netzsch differential thermal analyzer at a heating rate of 10°C min⁻¹.

RESULTS AND DISCUSSION

The TG and DTA plots of the copper glutamates are given in Figs. 1 and 2. The decomposition temperatures, observed weight losses, calculated weight losses based on the formation of CuO, and the DTA peak temperatures, are tabulated in Table 1. Cu glut \cdot 2 H₂O starts to lose weight at 110°C due to dehydration, which is followed by the decomposition of the glutamate moiety. The two processes apparently seem to overlap under the experimental conditions. Similarly, there is no indication in the TG curves of the adducts, the stepwise decomposition of the base and glutamate. The DTA curve shows an endothermic effect around 260°C for Cu glut \cdot 2 H₂O which is attributed to the decomposition of water and glutamate, whereas for the adducts an exothermic effect appears which is immediately followed by endothermicity. The exothermic reaction is probably due to breakage of the Cu-N bond and the subsequent expulsion of the base from the coordination sphere. The other exothermic effects at higher temperatures are due to the oxidation of the organic matter as well as the oxidation of the lower valent copper formed [3] during the decomposition.

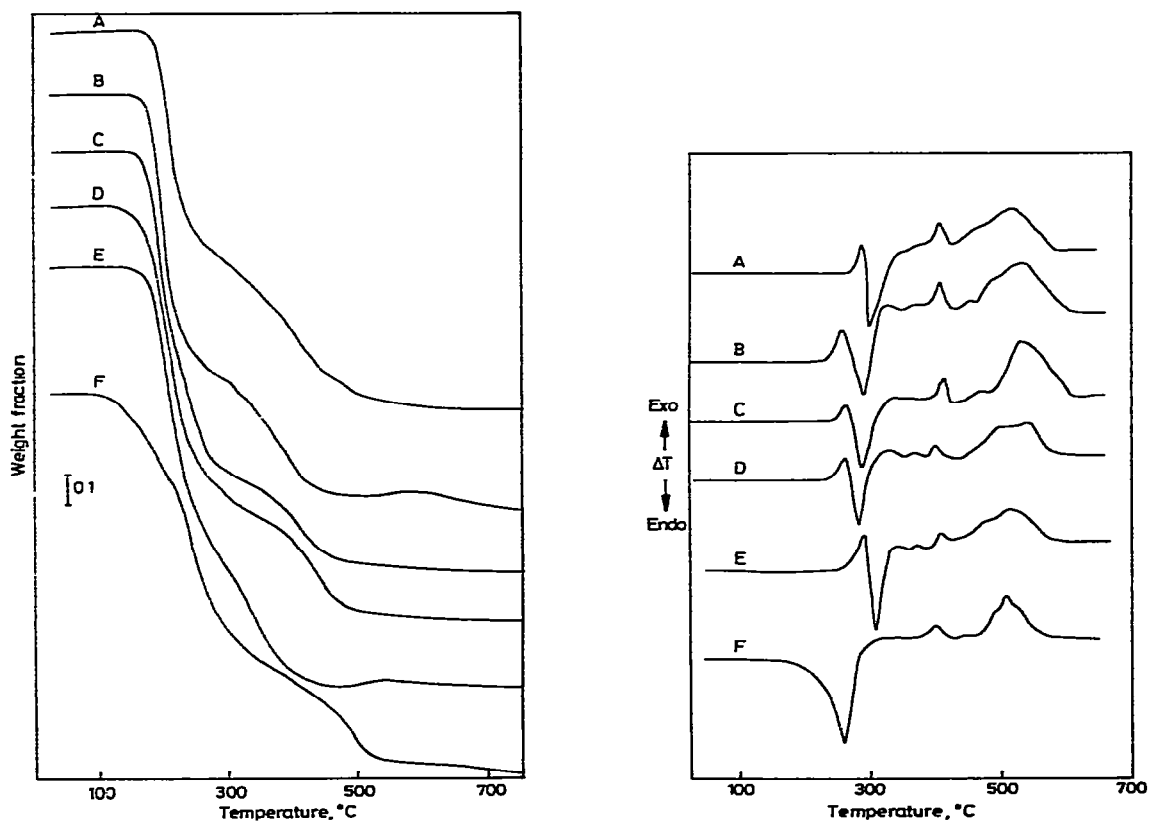


Fig. 1. TG plots of Cu glut \cdot NH₃(A), Cu glut \cdot γ-pic (B), Cu glut \cdot β-pic (C), Cu glut \cdot py (D), Cu glut \cdot morph (E), and Cu glut \cdot 2 H₂O (F).

Fig. 2. DTA plots of Cu glut \cdot morph (A), Cu glut \cdot py (B), Cu glut \cdot β-pic (C), Cu glut \cdot γ-pic (D), Cu glut \cdot NH₃ (E), and Cu glut \cdot 2 H₂O (F).

TABLE 1

TG and DTA data of copper(II) glutamates

Complex	Decomp. temp. (°C)	Wt. loss (%)		DTA peak temp. (°C)	
		Found	Calcd.	Endo	Exo
Cu glut · 2 H ₂ O	110	32.0	32.5	260	400, 510
Cu glut · NH ₃	225	35.0	35.2	300	290, 400, 520
Cu glut · morph	220	27.0	26.9	290	280, 400, 540
Cu glut · γ -pic	215	26.0	26.4	280	260, 400, 540
Cu glut · β -pic	210	26.0	26.4	280	260, 400, 560
Cu glut · py	190	27.0	27.6	270	210, 400, 550

On the basis of the decomposition temperatures, the thermal stability order is given as NH₃ > morph > γ -pic > β -pic > py > H₂O. The order resembles that obtained [2] from the crystal field spectra of the complexes and is related to the pK_a values of the bases [4]. Among the bases employed, ammonia is the strongest and pyridine is the weakest. Thus, it is seen that as the base strength increases, the thermal stability increases. The poor base strength probably makes a weaker contact with the Cu(II) in the equatorial position and hence is the source of initiation of the decomposition. Bowman and Rogers [5] have reported that as the base strength of the ligand is increased, the thermal stability decreases due to the oxidation–reduction reaction occurring during the decomposition. In the present case, however, it is primarily the rupture of the Cu–N bond and the subsequent expulsion of the base, and hence the reverse trend is probably justified.

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