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Note

THERMAL DECOMPOSITION OF BIS[μ-(β-ALANINE)-O,O']-DISILVER(I) DINITRATE

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The thermal decomposition of the metallic salts of organic acids has been widely studied [1–5]. However, there is little information concerning the thermal behaviour of complex metallic salts with amino acids. During the thermal degradation analysis of this type of compound, it is interesting to investigate $[Ag_2(C_3H_7NO_2)_2](NO_3)_2$, bis[$\mu$-($\beta$-alanine)-$O,O'$]-disilver(I) dinitrate [6].

The alanine residue is of particular interest because of the great variety of conformations in which it is bonded, especially in peptides [7]. In the structure of the studied compound, two alanine groups and two Ag^+ ions form a centro-symmetric dimer. Within the dimer, the Ag–Ag distance of 2.85 Å is comparable to the small distance of 2.88 Å found in metallic silver [6]. The NO_3 groups are in a *trans* configuration and are bonded to the alanine moiety by N–O–H–N hydrogen bonds. Likewise, the Ag–O distances are comparable to those reported for silver oxalate [6]. So, the NO_3^- and NH_3^+ groups (from the zwitterionic form of alanine) are structural neighbours and the alanine carboxylic residue is bonded to the Ag ions. The thermal behaviour of this salt shows some relation with the thermal results observed in other related compounds, such as silver carboxylates and squarate as well as NH_4NO_3 [2–5,8–10].

EXPERIMENTAL

As has been previously reported, pure samples of the studied compound were prepared by slow evaporation of an aqueous solution containing a stoichiometric proportion of silver nitrate and β-alanine [6]. Chemical analysis, XRD, electron microprobe and IR spectroscopy were used to characterise the original sample and the heated sample. Thermogravimetric and differential thermal analysis were carried out on a Rigaku thermoanalyser (type YLDG/CN 8002 L2) using a chromel–alumel thermoelement and working under a constant flux of N_2 (0.4 l min^{-1}). Parallel experiments

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were carried out in air and in N_2 atmospheres in a furnace under identical experimental conditions. The heating rate was 10 °C min^{-1} and α-Al_2O_3 was used as a DTA standard. The sample weight ranged between 15 and 20 mg and the maximum heating temperature was 700 °C.

RESULTS AND DISCUSSION

Typical TG and DTA curves for the sample heated in flowing N_2 are shown in Fig. 1. The results obtained in air differ only in the weight loss because the DTA curve is similar. The decomposition is complete at 230 °C in both types of atmospheres (N_2 or air). The thermal residue in air is pure metallic silver. In N_2 atmosphere, the residue is metallic silver embedded in a carbonaceous matrix. This was also observed in the decompositions of silver malonate and silver squarate [10,11].

In the first step of the DTA curve, an endothermic peak without weight loss is observed at 150 °C. The X-ray diffraction analysis of the original sample and of the one heated to 150 °C show different patterns. Thus, it may be inferred that a new phase has formed at this temperature. Likewise, the orientational disorder of NO_3 and NH_4 groups, in relation to the polymorphism of nitrates and ammonium salts is very well-known [12]. For this reason, it is possible to expect a phase change due to the motion of the NO_3^- or NH_3^+ groups.

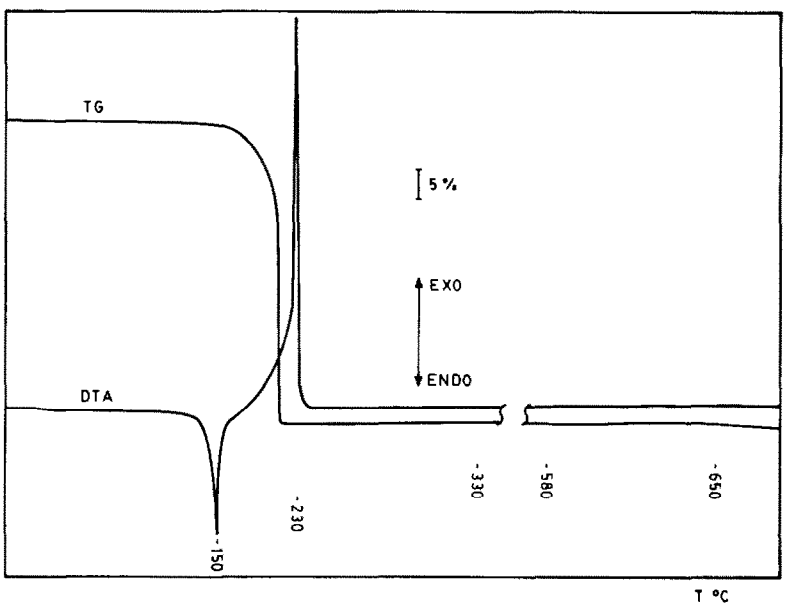

Fig. 1. Typical TG and DTA plots of bis[μ-(β-alanine)-O,O']-disilver(I) dinitrate.

On the other hand, some slight differences are apparent in the IR spectral region between 1200 and 1800 cm^{-1} where the characteristic vibrations for the NO_3^-, NH_3^+ and COO^- stretchings (the latter two from the zwitterionic form of β-alanine) can be observed. These also suggest the presence of two different crystalline phases.

The breakdown of the structure occurs at 230 °C, where there is an abrupt weight loss together with a strong exothermic peak (experimental weight loss, 46.28%; theoretical weight loss, 46.78%).

According to the experimental results, the following overall decomposition scheme can be formulated

$$[Ag_2(C_3H_7NO_2)_2](NO_3)_2 \xrightarrow{N_2} 2Ag + 5C + CO + 2N_2O + 7H_2O \quad (1)$$

It is remarkable that the degradation step in air, unlike that in N_2 produces elemental silver (experimental weight loss, 58.33%; theoretical weight-loss, 58.34%) together with the evolution of CO_2.

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