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COORDINATION COMPOUNDS OF BIOLOGICAL INTEREST

THERMAL PROPERTIES OF GLYCINATE AND GLUTAMATE CHROMIUM(III) COMPLEXES

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ABSTRACT

The thermal properties of the Cr(III) complexes with the ligands glycine and glutamic acid were determined using TG, DTG and DTA techniques.

The chromium(III)–glycine complex is more stable than the chromium(III)–glutamate complex. This behaviour is discussed in terms of different structures by IR and reflectance spectra as well as thermal data.

INTRODUCTION

The complexes of chromium(III) with ligands as pyridinic acids, glycine and glutamic acid show biological activity in the maintenance of normal glucose tolerance in experimental animals and, probably, in man[1]. Compounds of this type have been the subject of some our previous investigations[2–5]. It is the purpose of this paper to present the thermal properties, as determined by thermogravimetry (TG), differential thermogravimetry (DTG), differential thermal analysis (DTA) of the chromium(III) complexes with glycine and glutamic acid.

EXPERIMENTAL PART

Instrumentation

The TG, DTG and DTA curves of the solid complexes were obtained using a DuPont Model 990 DTA cell and a Model 951 thermobalance. The heating rate used was 10°C min^{-1} on samples whose mass ranged from 1 to 10 mg. The furnace atmosphere consisted of either dry nitrogen or air, at flow-rates of 50–100 ml min^{-1}. All temperatures were corrected for thermocouples non linearity and are, of course, procedural temperatures.

Preparation of complexes

Glycine and glutamic acid were from Fisher Chemical Co. The other chemicals employed were all of reagent grade quality. The complexes were prepared by refluxing for many hours an aqueous solution of the aminoacid with an excess of chromium(III) hydroxide. After 1 h the solution becomes colored. The obtained colored solution was filtered and then allowed to stand at room temperature until a precipitate was obtained. The precipitate was separated from the mother liquor, washed with water, alcohol and ether and then dried in a vacuum dessiccator at room temperature for 48 h.

Thin-layer chromatography was used to check the purity of the compounds when to determine the water content and residual oxide thermogravimetry was used.

Reflectance and IR spectra

The diffuse reflectance spectra of the complexes were obtained by using a Beckman Model DK-2A spectroreflectometer.

The IR spectra were recorded by means of a Perkin-Elmer Model 257 instrument.

RESULTS AND DISCUSSION

Chromium(III) glycinate

The obtained crystals were pale red.

The TG, DTG and DTA curves of chromium(III)glycinate CrGly$_2$OH are given in Figs. 1 and 2.

All the thermal analysis curves show that the compound is anhydrous and dissociates in air in two steps, between 275 and 345 °C to give a residual metal oxide Cr_2O_3 (35.3% found; 35.03% calc.). In air the decomposition reactions are exothermic .In nitrogen the decomposition takes place in one step and the DTA in nitrogen reveals only one endothermic peak.

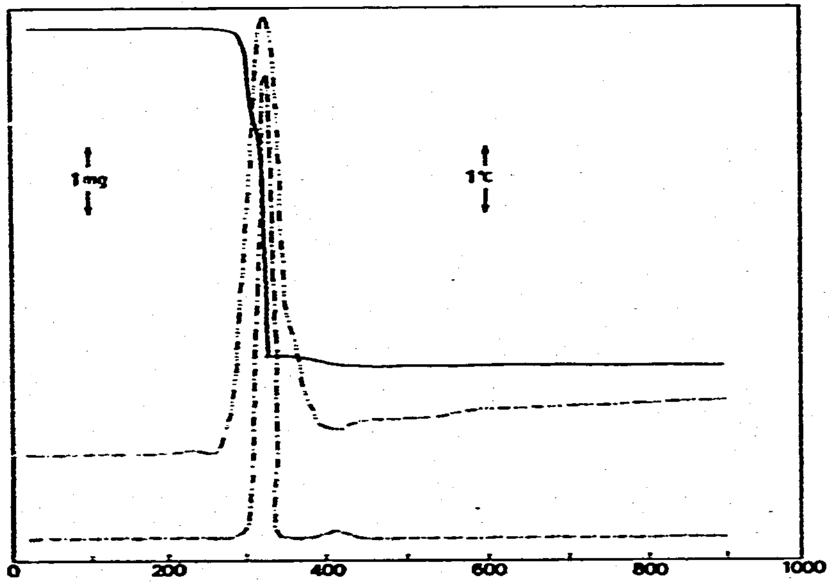

Fig. 1. TG, DTG and DTA curves of CrGly$_2$OH. ———, TG; —·—·, DTG; and —··—, DTA curves in air atmosphere.

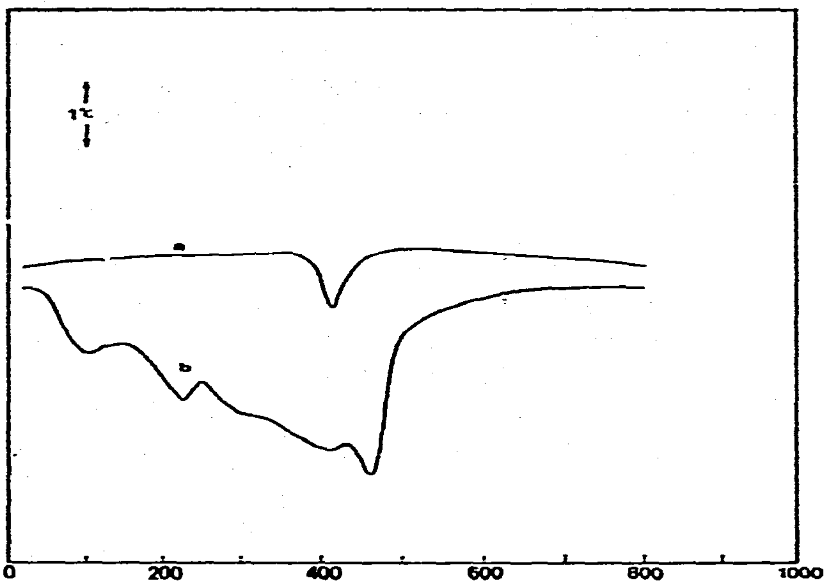

Fig. 2. DTA curves of complexes in a nitrogen atmosphere. (a), Chromium(III)-glycinate; (b) chromium(III)-glutamate.

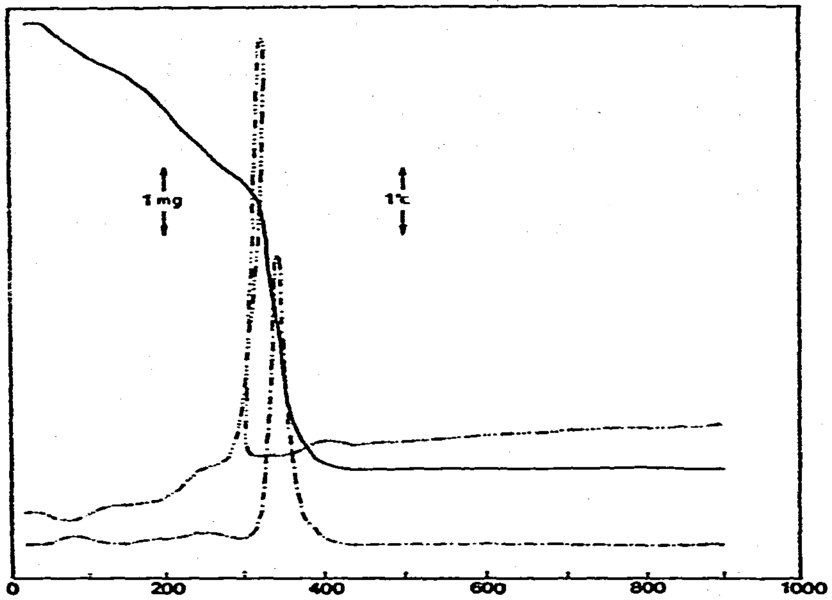

Fig. 3. TG, DTG and DTA curves of Cr Glu$_2$OH·H$_2$O. ———, TG; —·—·, DTG; and —··—, DTA curves in air atmosphere.

Chromium(III) glutamate

The TG, DTG and DTA curves of chromium(III) glutamate, CrGlu$_2$ OH·H$_2$O are shown in Figs. 3 and 2. The pale-green crystals evolved water of hydration over the temperature interval of 40 to 100°C (4.7 % found; 4.75% calc.), then the anhydrous complex decomposes, in air, in two steps to give the oxide Cr_2O_3 (20.0% found; 20.05% calc.). The DTA in air reveals a single endothermic peak for the dehydration followed by two largely overlapped exothermic peaks for the decomposition.

In nitrogen the decomposition of the anhydrous compound is a multi-step process as shown also from the DTA curve.

DISCUSSION

The TG, DTG and DTA curves show that chromium(III) glycinate is more stable than chromium(III) glutamate and also from the shape of the curves, it is possible, to see that the decomposition takes place in different ways to give for both compounds the oxide Cr_2O_3.

This behaviour can be explained on the basis that chromium(III) binds to the aminoacid in a different way.

Peaks, assigned to the N–H stretching vibration[6], are observed at 3300, 3250 and 3140 cm^{-1} in the 3 μ region of the IR spectra of chromium(III)glycinate. The N–H frequencies are lower for chromium(III)glycinate than for the sodium and potassium salts, indicating the presence of a metal–nitrogen bond. The antisymmetric carbon–oxygen stretching vibration in the carboxylate ion gives, as shown by the spectrum of potassium glycinate, a peak at about 1600 cm^{-1}. The asymmetric band situated near 1700 cm^{-1} for the –COOH group is shifted at about 1600 cm^{-1} and indicates the presence of the carboxylate ion in the chromium(III) glycinate complex.

The IR spectrum of anhydrous chromium(III)glutamate in the 3 μ region does not give any shift corresponding to the metal–nitrogen bond, while between 1700 and 1600 cm^{-1} there is the concomitance of the –COOH and $-COO^-$ band indicating the presence of the carboxyl and the carboxylate group together in the complex.

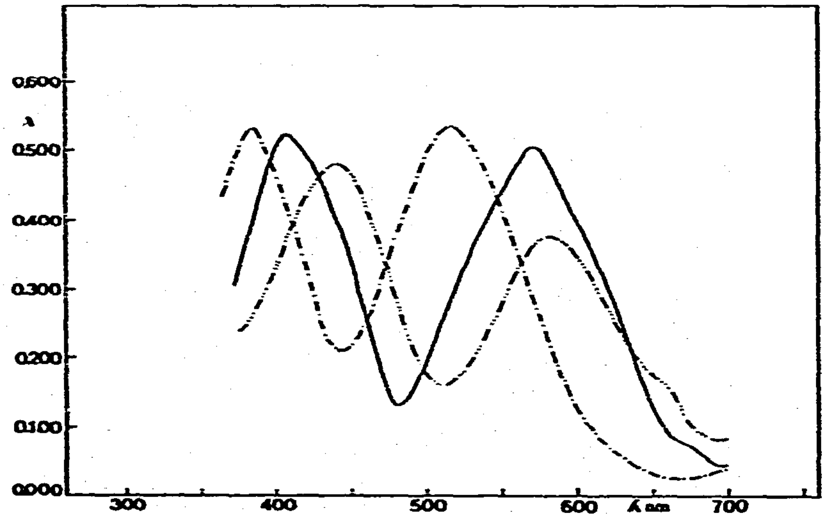

Fig. 4. Diffuse reflectance spectra of: ———, chromium(III)-nitrate; —·—·, chromium(III)-glycinate; and —··—, chromium(III)-glutamate.

The spectrum of chromium(III)glycinate (Fig. 4) shows two maxima at 515 and 385 nm, respectively, ipsochromically shifted with respect to chromium(III) nitrate alone, indicating that nitrogen binds to chromium. The spectrum of chromium(III)glutamate shows two maxima at 585 and 440 nm, respectively, batochromically shifted with respect to chromium(III) nitrate indicating that glutamic acid binds to chromium only through the carboxylate oxygen.

From the obtained data one can see that the two glycine molecules bind to chromium(III) either through the amino-group or through the carboxyl group to give a chelate structure, when an $-OH^-$ group completes the electroneutrality of the compound.

All data are in agreement with the structure determined from three-dimensional single-crystal X-ray data from Veal et al.[7]. This consists of $[Cr(gly)_2OH]_2$ dimeric units where the $-OH^-$ acts as a bridging group, so increasing the thermal stability of the compound.

Glutamic acid binds to chromium(III), as shown by IR and reflectance spectra only through a carboxyl oxygen and only one of the two carboxyl groups present in the molecule acts as a ligand, while the other is protonated at the operational pH (about 4.5) according with the stability constants of this acid[8]. The carboxyl group involved in the chromium(III)-aminoacid bond is that far from the aminogroup. This hypothesis is supported by the behaviour of the chromium(III)glutamine reaction. In fact working under the same conditions used to prepare chromium(III)-glutamate, glutamine reacts very slowly giving a red solution whose spectrum shows two maxima ipsochromically shifted with respect to the chromium(III) maxima. Then when the $-COOH$ far from the amino group is substituted with a $-CONH_2$ group, the spectrophotometric behaviour changes giving a spectrum of the same type as that of chromium(III)glycinate. This implies that in chromium(III)glutamate there is no chelation in agreement with the lower thermal stability of this compound. The electroneutrality of the compound is completed by a $-OH^-$ group.

ACKNOWLEDGEMENT

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