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Note

THERMAL AND CHROMATOGRAPHIC BEHAVIOUR OF METAL COMPLEXES. PART II. COMPLEXES OF PLATINUM(II) WITH DIPEPTIDE ESTER *

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Studies on the thermal decomposition of metallic ion complexes with aminocarboxylic acid as ligands are still scarce in the literature, especially if compared with those related with other techniques and other ligands [1]. As we have previously shown [2], the combination of differential thermal analysis (DTA) and gas chromatography (GC) allows us to obtain very important physical data that helps in discerning some properties of the complexes, to detect decarboxylation processes and to study the gases liberated during these processes. The thermal behaviour is influenced by many factors, for example, the different kinds of bond, the existence or not of coordinated carboxylic groups, so leading to the conclusion that there are very important differences in the thermal stability of the metal complexes.

In order to study the thermal evolution of the products evolved in the above mentioned compounds, DTA and GC techniques were used. At the end of the tube where the decomposition gases passed through, an outlet valve joined to a gas chromatograph was connected. The combination of both techniques enables the simultaneous investigation of the thermal behaviour of the complexes and the nature of the gaseous products from the decomposition reactions.

In this paper we study the DTA diagram of the evolution of the gases generated during the heating process of the complexes

trans-$PtCl_2[NH_2CHRC(O)NHCH(CH_3)COOC_2H_5]_2$

where $R = H$ (I): α-glycine (Gly) and $R = CH_3$ (II): L-alanine (Ala), as well as the curves obtained by thermogravimetric analysis.

MATERIALS AND METHODS

The DTA and TG curves were obtained in an Aminco 4-4442 A unit and a Cahn electrobalance, respectively. The experiments were performed under an atmosphere

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* For Part I, see ref. 2.

of helium with a flow rate of 60 ml min^{-1} and a heating rate of 10°C min^{-1}. Chromel–alumel and Pt/Pt/Rh thermocouples were used to measure temperature changes and α-Al_2O_3 was employed as reference material in the DTA measurements. The employed Hewlett-Packard gas chromatograph was connected with the DTA and TG instruments, also using helium as carrier gas. The metallic columns were filled with Porapak "Q" (80–100 Mesh, 2 m in length and 1/8 in diameter). The retention indexes for GC columns have been given in a previous paper [2].

RESULTS AND DISCUSSION

The characterization by IR spectroscopy and nuclear magnetic resonance of the coordination compounds

trans-$PtCl_2(Gly\text{-}AlaOEt)_2$ (I)

trans-$PtCl_2(Ala\text{-}AlaOEt)_2$ (II)

has been shown previously [3]. Because of their structural analogy these two compounds have been studied together.

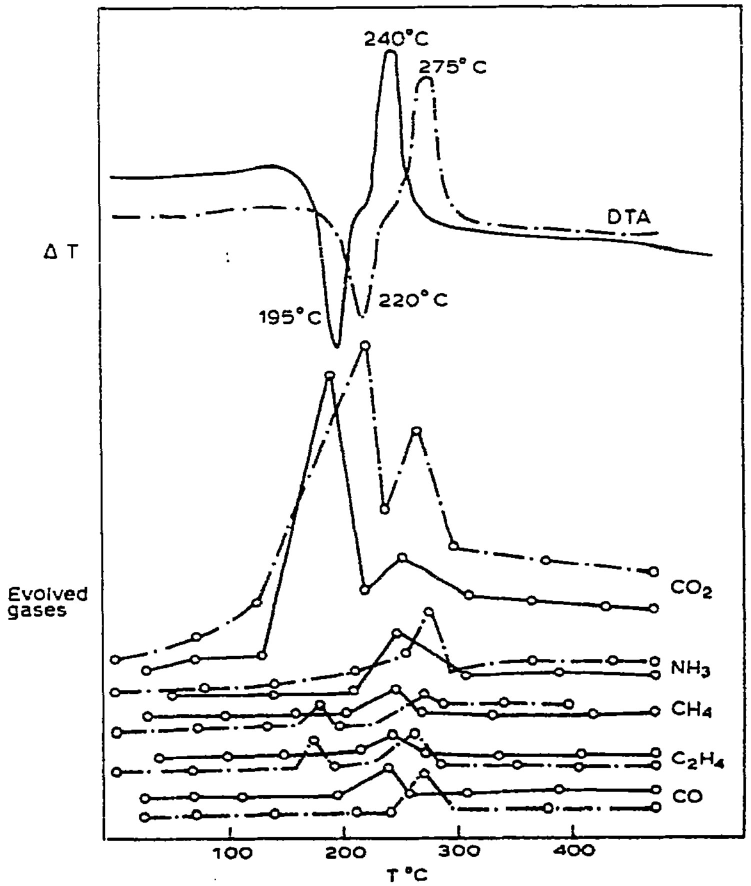

Fig. 1. Thermal and chromatographic study of *trans*-$PtCl_2(Gly–AlaOEt)_2$ and $PtCl_2(Ala–AlaOEt)_2$. ———, Compound I; -·-·-, compound II.

The DTA curves of these compounds, plotted in Fig. 1, were obtained under an atmosphere of helium and are composed of two effects, one exothermic and the other endothermic, that take place between 195 and 275°C. The first observed endothermic effect appears at 195 and 220°C for compounds (I) and (II), respectively. Both of them are sharp, intense peaks corresponding to the first decarboxylation process.

Around 240°C for compound (I) and 275°C for compound (II), a sharp exothermic effect appears, which is in agreement with the analysis by gas chromatography of the gases generated in this decomposition. In both compounds (I) and (II) another process of change or structural rearrangement occurs at the same time as the decarboxylation process.

In order to determine the nature of the phenomenon observed in the DTA study, the gases liberated during the thermal decomposition were studied simultaneously. This technique was prepared in our laboratories, and enabled us to obtain very good results and to formulate some interpretations of the thermal decomposition process of those compounds [4].

The evolution of the gases liberated during the decomposition vs. temperature is shown in Fig. 1. The evolution of CO_2 during the thermal decomposition of compounds (I) and (II) shows that the maximum release of CO_2 occurs at 195 and 220°C, respectively, and coincides with endothermic effects, followed by a sharp decrease in the amount released at 240°C (I) and 275°C (II) which is related to the strong exothermic maximum shown in the DTA curves.

The chromatographic study of the nature of the gases liberated during the heating process shows the existence of gases such as ammonia, methane and ethylene with maximum releases according to the exothermic effect. We have observed that, at temperatures up to 200°C in coordination compounds with aminoacids, the chlorine ligand atoms are liberated according to the following reaction

$$\textit{trans}\text{-}PtCl_2(LH)_2 \rightarrow \textit{trans}\text{-}PtL_2 + 2\,HCl$$

(LH = α-glycine or L-alanine)

Through the thermal treatment, the following process has been elucidated by IR spectroscopy and elemental analysis:

(a) in compounds (I) and (II) there is first decarboxylation with a simultaneous

TABLE 1

Theoretical and experimental weight losses in the decarboxylation process

Compound	First stage 160–210°C		Second stage 220–260°C	
	Theor. (%)	Exptl. (%)	Theor. (%)	Exptl. (%)
I	45.96	45.10	24.59	23.70
II	44.91	43.80	28.64	27.60

break of the ligands
$-NH_2-CH(R)-CONH-CH(CH_3)-COOC_2H_5$

(b) at the same time as process (a) liberation of two coordinated chlorine atoms has been detected;

(c) in both compounds a structural rearrangement takes place and *trans*-$Pt(NH_2-CH(R)-CONH)_2$ has been found.

Beyond these three processes the total decomposition of the substances has been observed.

Kaushik et al. [5] and Kabesova et al. [6] have studied the thermic behaviour of many complexes, and have observed that the ligands (a) break away and a structural rearrangement, as postulated in this work, appears.

The thermogravimetric curve was studied and a weight loss coinciding with the percentage and temperature intervals of the detected gases and also coinciding with the results obtained from the DTA studies was found. The theoretical and experimental percentage for first and second stages of the decarboxylation process are shown in Table 1.

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