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THERMAL STUDY OF PALLADIUM COMPLEXES WITH *trans*-1,2-DIAMINECYCLOHEXANETETRAACETIC ACID

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ABSTRACT

Thermal decomposition processes for cyclohexanediaminetetraacetic acid (CDTA-H_4) complexes of palladium, [Pd(CDTA-H_2)] and [Pd(CDTA-H_4)Cl_2]·2 HCl·2 H_2O have been studied using TG–DTA techniques. Infrared spectroscopy and X-ray diffraction have been also used for the characterization of intermediate and final products. In the decomposition of the dichloro complex, chloride ions are released simultaneously to a ring closure reaction in which CDTA becomes tetradentate. For both compounds, the final product in the decomposition is PdO, as confirmed by the X-ray difraction pattern of a sample heated at 600°C.

INTRODUCTION

In recent papers, we have studied the thermal decomposition of several chelating agents [1] and some of their complexes with palladium [2]. An interesting observation is that the decarboxylation process takes place in two stages, the first one being associated with the release of free carboxylic groups and the second one with that of saline or coordinated carboxylate groups. However, we had not yet studied the process for a compound with carboxylic groups only, in which the decarboxylation can take place at a single step or can be more complex due to changes in the dentate character of the ligand [2]. In this sense, it is interesting to note that ring closure reactions in the solid phase of square-planar complexes of platinum [3] and palladium [4] are well known.

In this paper, we report the thermal study of two palladium complexes with *trans*-1,2-diaminecyclohexanetetraacetic acid (CDTA-H_4). Both complexes, [Pd(CDTA-H_2)] and [Pd(CDTA-H_4)Cl_2]·2 HCl·2 H_2O, were first prepared by Ezerskaya et al. [5] and the latter contains the ligand linked in a bidentate way without Pd–O bonds.

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EXPERIMENTAL

[Pd(CDTA-H_2)] was prepared by the method of Ezerskaya et al. [5], but for [Pd(CDTA-H_4)Cl_2]·2 HCl·2 H_2O, a new synthetic procedure has been used. Solid CDTA-H_4 (Merck) was added in equimolecular amounts to a solution of $PdCl_2$ (Fluka) in 2 M HCl. The resulting solution was concentrated in a water bath until precipitation began to occur and was then stored overnight. The precipitate was recrystallized from 2 M HCl and washed with ethanol. Both complexes were characterized by infrared spectra, potentiometric titration and elementary analyses. [Pd(CDTA-H_2)] can be also obtained by recrystallization from aqueous solutions of the dichloro complex.

DTA and TG curves were obtained in an atmosphere of static air with a Mettler TA-HE-20 system filled with Pt/Pt–10% Rh thermocouples. α-Al_2O_3 was used as reference material and the heating rate was 10°C min^{-1}. A sample weight of 10 mg was used for every measurement.

In separate experiments, several samples of the two compounds were heated in a Heron furnace at different temperatures chosen from characteristic points of DTA and TG curves. The samples were allowed to reach constant weight before their IR spectra were recorded as KBr pellets using a Pye Unicam SP3-300 spectrophotometer. For the case of the dichloro complex, samples were also dissolved in hot water to determine chloride ion conductimetrically with $AgNO_3$ solution. Conductivity measurements were performed with a Philips PW 9505 conductimeter provided with a 95W cell. All chloride ions were titrated simultaneously, as can be expected from the literature data [6]. No data could be obtained from samples corresponding to temperatures greater than 225°C because of their low solubility. The nature of these samples also made the recording of IR spectra difficult.

X-Ray powder diagrams were recorded in a 114.93 mm diameter Debye–Scherrer camera using a Siemens D-500 generator with Cu-K radiation and Ni filter.

RESULTS AND DISCUSSION

Thermal decomposition of [Pd(CDTA-H_2)]

Figure 1 shows the TG and DTA curves for this compound and Fig. 2 shows the infrared spectra of some intermediate products at different temperatures. As we pointed out for PDTA complexes of palladium [2], there is a small but significant difference in the temperature ranges observed in the DTA–TG curves and those of static heating. So, the values of temperature used in this paper are based mainly on the thermal curves, IR spectra being used only to elucidate the sequence in which the several groups are released during the decomposition process.

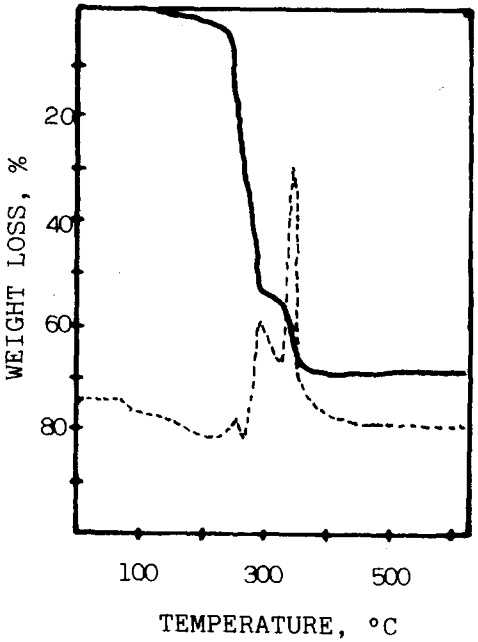

Fig. 1. DTA and TG curves for [Pd(CDTA-H_2)].

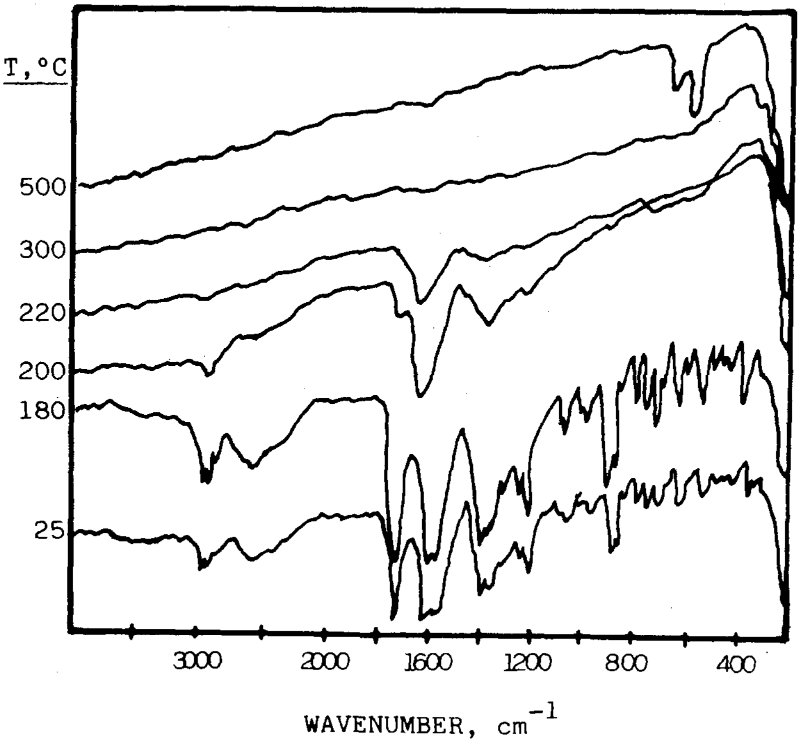

Fig. 2. IR spectra of some intermediate products in the decomposition of [Pd(CDTA-H_2)].

The first stage in the decomposition occurs between 145 and 255°C with a weight loss of 5%. It is an endothermic process in which carboxylic groups progressively disappear, as shown in the infrared spectra of the intermediate products at 180, 200 and 220°C by the relative intensities of ν_{COOH} and ν_{COO} bands at ca. 1700 cm^{-1} and 1600 cm^{-1}, respectively. Moreover, the loss of COOH groups also causes the disappearance of ν_{OH}(COOH) bands at 3600 and 3500 cm^{-1}. However, the nature of the gaseous products evolved at this stage is not clear.

The temperature range in which decarboxylation of free carboxylic groups takes place is rather similar to that observed for PDTA complexes of palladium [2,7]. In this step, a displacement of the ν_{COO} band at higher wavenumber is also observed. It can be interpreted in terms of an increase in covalent character of the Pd–O bonds [8] and changes in hydrogen bonding involving C=O groups.

The following stages in the decomposition are much more difficult to determine because of the great complexity of the compound and the pronounced weight loss between 255 and 295°C, in which 53% of the total weight is lost. This step includes the release of carboxylate groups and the pyrolysis of an important part of the CDTA molecule, this being completed in the following step that takes place at 350°C accompanied by a great exothermic effect. The total weight loss is 70%, the theorethical value for PdO formation being 72.8%. The IR spectrum of a sample heated at 600°C shows two bands at 650 and 590 cm^{-1}. PdO has been also identified as the decomposition product by recording the X-ray powder diagram of a sample heated at 600°C. There is further weight loss at 870°C associated with an endothermic effect in DTA, both corresponding to PdO decomposition with O_2 release [9].

Thermal decomposition of $[Pd(CDTA\text{-}H_4)Cl_2] \cdot 2\ HCl \cdot 2\ H_2O$

TG–DTA curves and infrared spectra of some intermediates in the thermal decomposition of this compound are shown in Figs. 3 and 4. The first endothermic effect at 105°C corresponds to the release of water of crystallization. The weight loss associated with this effect (6%) is consistent with the theoretical value for two molecules (5.7%). This temperature is lower than those observed for most of PDTA complexes of palladium, although it is in the range expected for a weak interaction with the complex [7].

The pronounced weight loss observed from 200°C is associated with a second endothermic effect in DTA centered at 210°C. This is the most interesting stage in the decomposition because it is here where decarboxylation processes take place. Two bands in the $\nu_{C=O}$ zone are observed in the infrared spectrum of the intermediate at 190°C, showing the formation of carboxylate groups from free carboxylic groups. The spectra of the inter-

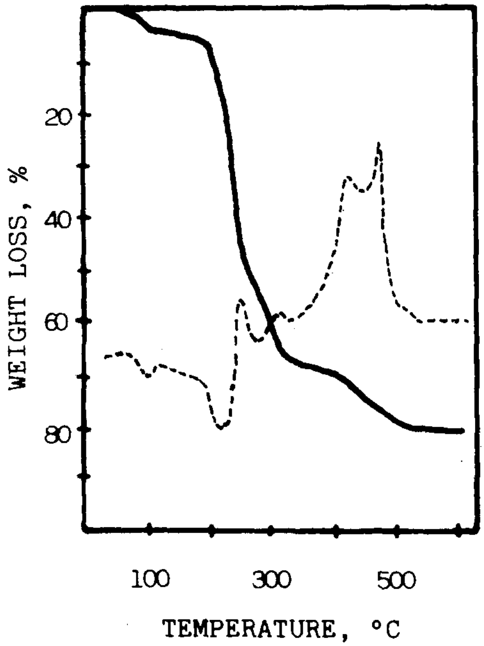

Fig. 3. DTA and TG curves for [Pd(CDTA-H_4)Cl_2]·2 HCl·2 H_2O.

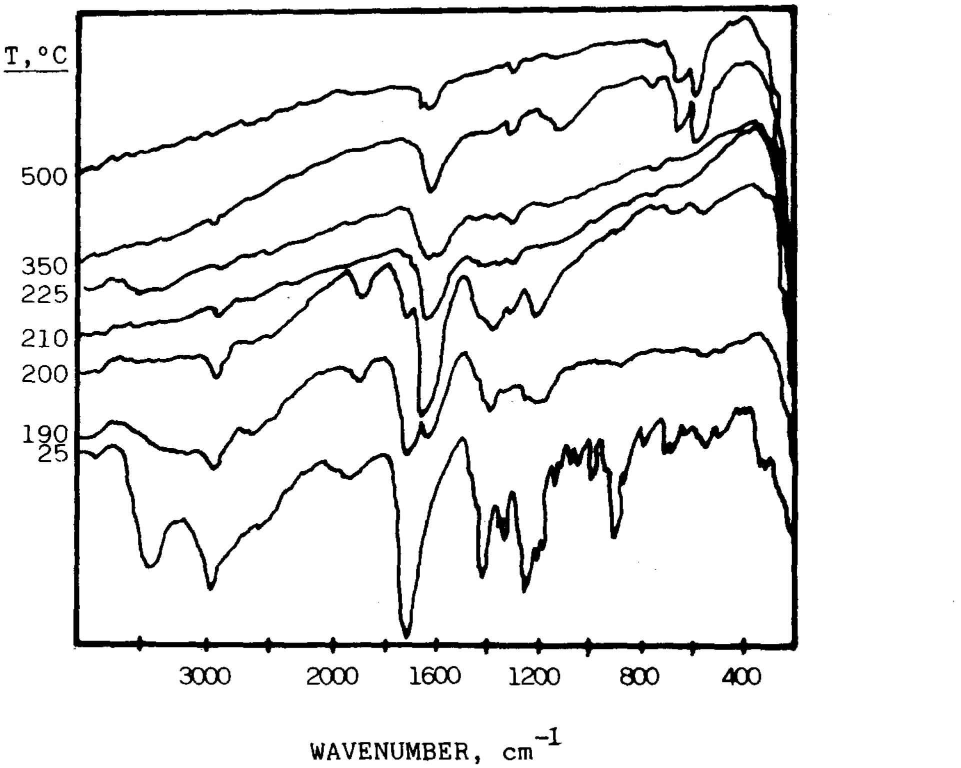

Fig. 4. IR spectra of some intermediate products in the decomposition of [Pd(CDTA-H_4)Cl_2]·2 HCl·2 H_2O.

mediates at higher temperatures show the progressive disappearance of ν_{COOH} band as the intensity of ν_{COO} band increases. To determine the role of chloride ions in this stage of the thermal decomposition, they were titrated with $AgNO_3$ solution. The results indicated that they are completely released at 225°C and that there is only 13% of the initial chloride content in the intermediate solid at 200°C. It is evident that these temperatures, and those of Fig. 4, are lower than those of the thermal curves. So, it is more interesting to consider the corresponding weight losses in order to avoid the differences between programmed and static heating experiments. In this way, for a sample with a total weight loss of 39.6% there is only 13% of the initial chloride content and there is no chloride in a sample with a total weight loss of 65.9%. No difference was observed in any case between coordinated and crystallization chloride because of the low stability of Pd–Cl bonds in aqueous solutions [6], and so all the results correspond to the total content of chloride in the sample. These data are similar to those obtained by other authors [3,4] for dichloroaminoacid compounds and suggest that in the decomposition stage starting at 200°C (lower for static heating experiments) there is an initial step in which HCl and coordinated chloride are released with simultaneous formation of coordinated carboxylate groups. Later, the remaining carboxylic groups are also released previous to the decarboxylation of coordinated groups, in a similar way to that observed for analogous complexes [2]. Additional evidence for the proposed sequence is the dissappearance of the ν_{Pd-Cl} bands at 344 and 322 cm^{-1} simultaneously with carboxylate group formation, as shown in the infrared spectrum of the intermediate product at 190°C.

The following stages in the thermal decomposition of the dichloro complex are similar to those observed for related compounds, with exothermic effects leading to PdO formation. As we pointed out for palladium complexes of PDTA, the shape and the temperature at which these effects appear are variable depending on the nature of the complex [2].

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