

THERMAL AND CHROMATOGRAPHIC BEHAVIOUR OF METAL COMPLEXES. PART III. COMPLEXES OF PALLADIUM(II) WITH IMINODIACETIC ACID *

M. CASTILLO MARTOS **, F. GONZALEZ VILCHEZ † and E. RAMIREZ CARRASCO

Departamento de Química Inorgánica, Facultad de Química, Universidad de Sevilla, Sevilla (Spain)

(Received 3 June 1982)

ABSTRACT

A study of the thermal properties of the complexes formed between Pd(II) and iminodiacetic acid (IDA) and the chromatographic analysis of their thermal decomposition products have been carried out. The dehydration of the isolated compounds is detected above 100°C. The decarboxylation process of the COO⁻ groups takes place yielding CO₂ and CO simultaneously or consecutively if they are not coordinated, respectively. The formation of gases (methane, ethane, etc.) is also observed.

INTRODUCTION

In recent years the synthesis and characterization of coordination compounds formed between platinum group metals and polycarboxylic acid type ligands have been carried out. In a previous paper [1] related to the study of the thermal properties of Ru(III) and Rh(III) complexes with iminodiacetic acid, a method was developed for the study of the thermal and chromatographic behaviour (DTA, GC) of these compounds. By simultaneously combining both techniques it was possible to obtain data to discern some properties such as dehydration temperature, position of water molecules, pyrolysis and decarboxylation process. Due to the thermal decomposition process of this type of coordination compound, the use of DTA is not sufficient because of the uncertainty in the composition of the gases liberated during the heating process. Likewise, it is not possible to assign with certainty the weight loss observed in the TG curve. Therefore a combination

* For part II, see ref. 8.

** To whom correspondence should be addressed.

† Permanent address: Departamento de Química Inorgánica, Facultad de Química, Universidad de Cadiz, Cadiz, Spain.

of both techniques, DTA and GC, is required to obtain information about the nature of gases liberated. The usefulness of this method has been shown in a previous paper [1] as well as in 3d transition metal complexes with 1,2-diamino-cyclohexanetetraacetic acid (DCTA) [2].

In the present paper the thermal and chromatographic behaviour of two complexes of palladium(II) with iminodiacetic acid (IDA), here (HY), of formulae $\text{Na}_3[\text{PdYCl}_3] \cdot 2 \text{H}_2\text{O}$ and $\text{Na}_2[\text{PdY}_2] \cdot 5 \text{H}_2\text{O}$ are studied.

EXPERIMENTAL

The two complexes between Pd(II) and IDA (HY) were prepared according to the method described previously [3]. The spectroscopic and analytical characterization of these complexes have been shown elsewhere [3]. The following apparatus was used to study the thermal decomposition (DTA, TG). The DTA curves were obtained in an Aminco 4-4442 A unit. A Cahn electrobalance was used for the thermogravimetric curves. The experiments were performed under an atmosphere of helium at a flow rate of 60 ml min^{-1} , and a heating rate of $10^\circ\text{C min}^{-1}$. Chromel-alumel and Pt/Pt/Rh thermocouples were used to measure temperature changes, and $\alpha\text{-Al}_2\text{O}_3$ 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 are given in ref. 1.

RESULTS AND DISCUSSION

$\text{Na}_3[\text{PdYCl}_3] \cdot 2 \text{H}_2\text{O}$

The DTA curve of $\text{Na}_3[\text{PdYCl}_3] \cdot 2 \text{H}_2\text{O}$ (Fig. 1) shows a strong endothermic effect at 120°C due to the elimination of the water of hydration. This has been confirmed by heating the compound at this temperature and studying the IR red spectra in which the band at 3440 cm^{-1} disappeared [3], and other characteristic bands corresponding to the same molecule.

In the TG diagram of this substance a gap between 117 and 122°C , probably due to the elimination of the hydration water molecules is observed. The experimental weight loss of 7.98% is in good agreement with the theoretical value of 8.02%.

The chromatographic profile of H_2O (Fig. 1) shows a maximum release around $300\text{--}350^\circ\text{C}$. This temperature is abnormally high for the elimination of hydration water molecules, as is the case for every complex studied in our laboratories, so it was assumed to be due to the high retention index for

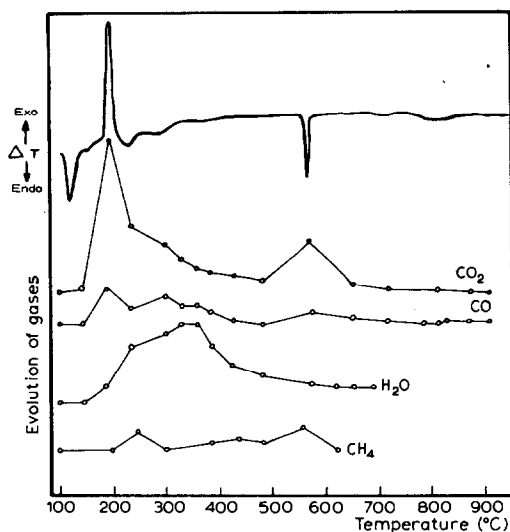


Fig. 1. DTA diagram and evolution of gases for GC against temperature for the compound $\text{Na}_3[\text{PdYCl}_3] \cdot 2\text{H}_2\text{O}$.

water of Porapak-“Q” used in the chromatographic columns.

The existence of a strong, sharp exothermic effect at 200°C is of special interest since, as will be seen later, it coincides with the release of CO_2 and CO in a smaller quantity. This phenomenon has not been observed in other transition metal complexes with iminodiacetic acid, as for example Ru(III) compounds with complexones [1], but it has been recorded in other Pd(II) compounds with the same ligand [4] and with other ligands [5], because these complexes of Pd(II) have not coordinated the group carboxylate.

As has been pointed out, the exothermic peak at 200°C coincides with a sudden decarboxylation of the substance, as seen in the chromatographic profiles of CO_2 and CO (Fig. 1) that show maxima near 200°C. The release of CO_2 decreases regularly from 200 to 650°C where it is practically zero. Also, there is another weak maximum at 300°C due to the liberation of CO that corresponds to a weak endothermic effect in the DTA diagram.

These facts suggest that a structural rearrangement takes place at the same time as the decarboxylation of the carboxylate groups not coordinated to the metal, whose structure was shown in a previous paper [3]. Around 550–600°C an endothermic effect appears which is probably due to the total decomposition of the substance. Jona et al. [6] and Bernard and Decker [7] have studied the thermic decomposition of many coordination compounds and they obtained results in agreement with our conclusions.

$$\text{Na}_2[\text{PdY}_2] \cdot 5 \text{H}_2\text{O}$$

The DTA of the complex is presented in Fig. 2, which shows quite an irregular shape. The first endothermic effect appears around 80°C and is probably due to the elimination of hydration water molecules. The TG curve shows a weight loss of 17.5% between 80 and 185°C which corresponds to the elimination of water molecules. There is good agreement between the theoretical result calculated from the proposed formula (17.84%) and that obtained using the Karl–Fischer reaction (17.70%).

At 210–215°C only an exothermic effect appears, followed by a sharp endothermic effect with a minimum at 270°C. Both of which are related to a wide release of CO_2 , as may be verified by the gas chromatographic study showing the evolution of gases liberated during the thermal decomposition of the substance (Fig. 2). A large amount of carbon dioxide is liberated at 210°C, which coincides with the exothermic effect of the DTA curve. The low temperature of the decarboxylation process suggests that there are several types of carboxylate groups in the compound.

At 270 and 370°C there is further release of CO_2 and these temperatures correspond to the endothermic effect mentioned above, and to another weaker effect that appears around 370°C in the DTA curve. The CO liberation takes place above 500°C and the maximum is recorded at 770°C,

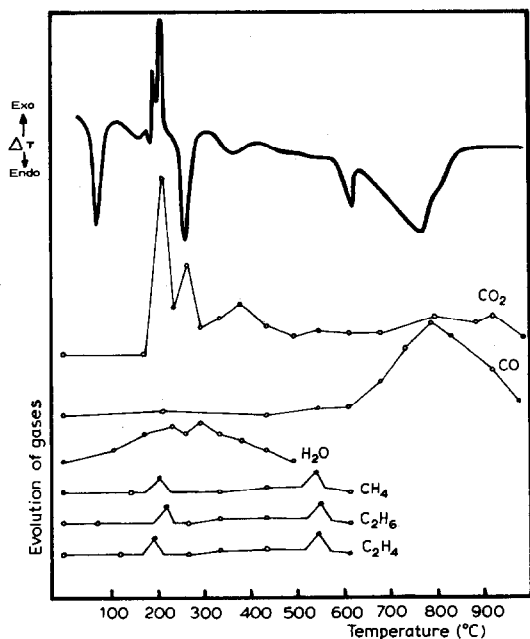


Fig. 2. DTA diagram and evolution of gases for GC against temperature for the compound $\text{Na}_2[\text{PdY}_2] \cdot 5 \text{H}_2\text{O}$.

at the same temperature as the appearance of the last endothermic effect in the DTA diagram.

A comparison of the results obtained from the DTA curve and those from the chromatographic profiles of CO_2 and CO suggests a decarboxylation process in two distinct steps, due to the existence of two types of carboxylic groups in the complex. Between 210 and 400°C several releases of CO_2 take place, probably due to the decomposition of the uncoordinated carboxylate groups.

The decomposition of the coordinated $-\text{COO}^-$ groups takes place above 500°C and that is checked by weak releases of CO_2 and a strong liberation of CO at 770°C . The high temperatures where this decomposition takes place suggests that these carboxylic groups are strongly bonded to the metal. In the chromatographic profiles of methane, ethane and ethylene several releases are recorded between 250 and 550°C , with a maximum at 420°C . Traces of hydrogen are detected in the same temperature range.

CONCLUSIONS

From the present study it may be concluded that:

- (1) the dehydration process of the coordination compounds studied is characterized by a sharp endothermic effect at temperatures near $100\text{--}120^\circ\text{C}$;
- (2) the decarboxylation process depends fundamentally on the number of coordinated carboxylate groups. Thus, in compounds where these groups predominate, losses of CO_2 and CO are usually detected at higher temperatures than when the carboxylate groups are uncoordinated;
- (3) in cases where there are both coordinated and uncoordinated carboxylate groups, the formation of methane, ethane and ethylene is observed, while in compounds with only uncoordinated carboxylate groups, only methane is detected.

REFERENCES

- 1 F. Gonzalez Vilchez and M. Castillo Martos, *Thermochim. Acta*, 21 (1977) 127.
- 2 F. Gonzalez Garcia and E. Carmona Guzman, *An. Quim.*, 72 (1976) 768.
- 3 F. Gonzalez Vilchez, M. Castillo Martos and M.F. Gargallo Esteban, *Transition Met. Chem.*, 2 (1977) 67.
- 4 F. Gonzalez Vilchez and M. Castillo Martos, *An. Quim.*, 70 (1974) 342.
- 5 F. Gonzalez Vilchez and S. Gonzalez Garcia, *An. Quim.*, 66 (1970) 875.
- 6 E. Jona, T. Sramko and J. Gazo, *J. Therm. Anal.*, 16 (1979) 213.
- 7 M.A. Bernard and N. Decker, *Bull. Soc. Chim. Fr.*, (1972) 3721.
- 8 M. Castillo Martos and E. Ramirez Carrasco, *Thermochim. Acta*, 54 (1982) 361.