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THERMAL BEHAVIOUR OF Pd(II) COMPLEXES OF *N*-ARYLGLYCINE DERIVATIVES

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ABSTRACT

The thermal properties of Pd(II) complexes of some *N*-arylglycine derivatives were determined using TG, DTG and DSC techniques. IR spectroscopy was applied to clarify the decomposition steps.

INTRODUCTION

Although the interaction between glycine and its derivatives with metal ions has been the subject of numerous studies [1–3], relatively limited information is available on metal complexes of arylglycine derivatives. For this reason, and following the thermal studies of several arylglycine derivatives and some of their metal complexes [4–6], in the present paper, we report the thermal behaviour of four new compounds of Pd(II) with *N*-(2,3-dimethylphenyl)glycine (2,3-PGH), *N*-(2,4-dimethylphenyl)glycine (2,4-PGH), *N*,*N*-(4-ethylphenyl(carboxymethyl)) glycinato Na salt (4-EPAGHNa) and *N*-*N*-(2,6-dimethylphenyl)(carboxymethyl)glycine (2,6-PAGH$_2$) (Fig. 1).

EXPERIMENTAL

TG studies were made using pure air at a flow rate of 100 ml min^{-1} on a Mettler thermobalance (model TG-50), using samples varying in weight from 3.95 to 12.75 mg, and a heating rate of 10°C min^{-1}. The DSC curves were recorded on a Mettler differential scanning calorimeter (model DSC-20) at a

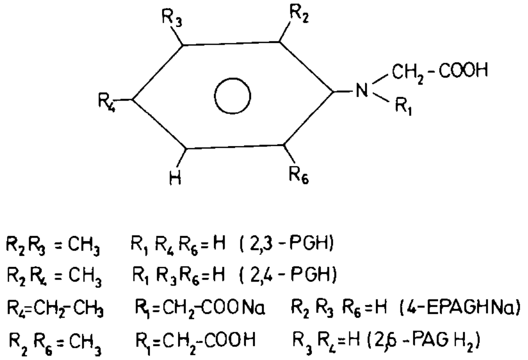

Fig. 1. Structure of the arylglycine derivatives.

heating rate of 5°C min^{-1}, in the temperature range 40–560°C, using samples varying in weight from 1.36 to 3.03 mg.

The synthesis and characterization of the compounds studied in this paper have been previously reported [7].

RESULTS AND DISCUSSION

Figures 2 and 3 show TG and DSC plots of Pd(II) complexes.

Pd(2,3-PG)$_2$(I) and Pd(2,4-PG)$_2$(II)

These complexes present the same structure [7] (Fig. 4) which makes their DSC curves similar. Thus, above 200°C they show an exothermic effect centered at 272 (**I**) and 224°C (**II**), probably due to the elimination of the COO^- group coordinated to the Pd(II) ion and pyrolysis of a part of the ligand. This exothermic behaviour has also been observed in complexes of the type ML_2 (L = iminodiacetate or glycinate anion) [8]. The decarboxylation tempeatures indicate that in complex **I** the carboxylato anion is more strongly bonded to the Pd(II) ions than in compound **II**. On further heating, the pyrolysis of the organic moiety takes place, as can be observed in the respective DSC curves, by the exothermic effect in the range 300–450 (**I**) and 360–460°C (**II**).

The TG curves of these complexes present a fast decomposition between 180 and 260°C, followed by a slow decomposition from around 360°C to the end of the pyrolysis around 470°C, which is in accordance with the DSC data above. At this point, the residual weight (25.8 (**I**) and 26.3% (**II**)) is in good agreement with the theoretical value required for PdO (26.47%).

Pd(4-EPAGH)$_2$ · 2H$_2$O (III)

The TG curve of Pd(4-EPAGH)$_2$ · $2H_2O$ (structure given in Fig. 4) shows that this compound becomes completely dehydrated in the temperature

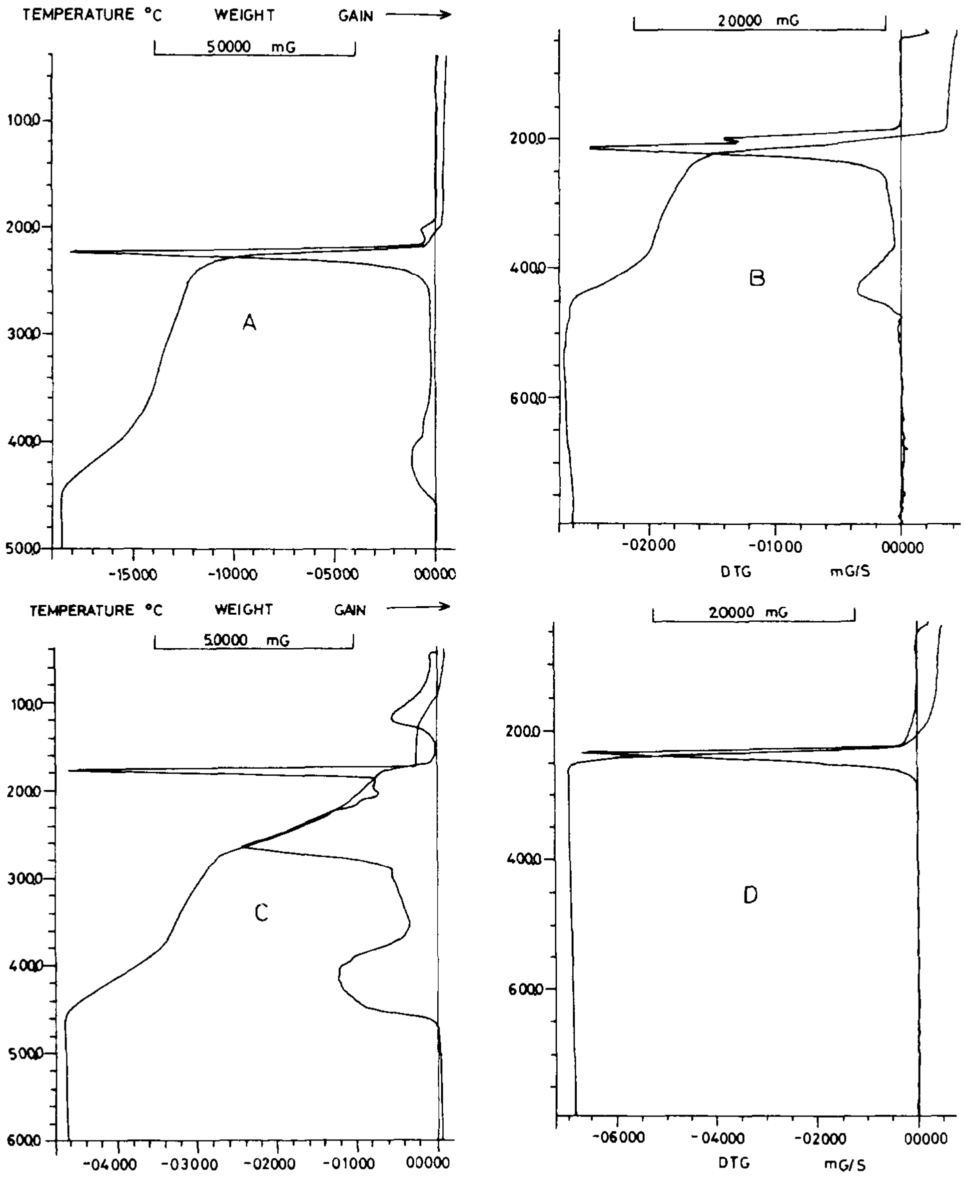

Fig. 2. TG curves of **I** (A), **II** (B), **III** (C) and **IV** (D).

range 80–140°C. The calculated weight loss for the dehydration process (5.86%) is in good agreement with the observed value (5.7%). The DSC curve shows an endothermic effect corresponding to this process at 123°C. The dehydration enthalpy was 37 kJ mol^{-1} H_2O.

Anhydrous Pd(4-EPAGH)$_2$ is stable from 140 to 170°C. Above this temperature the TG curve of this complex shows a strong weight loss effect between 175 and 190°C. The observed weight loss (7.7%) is in accordance

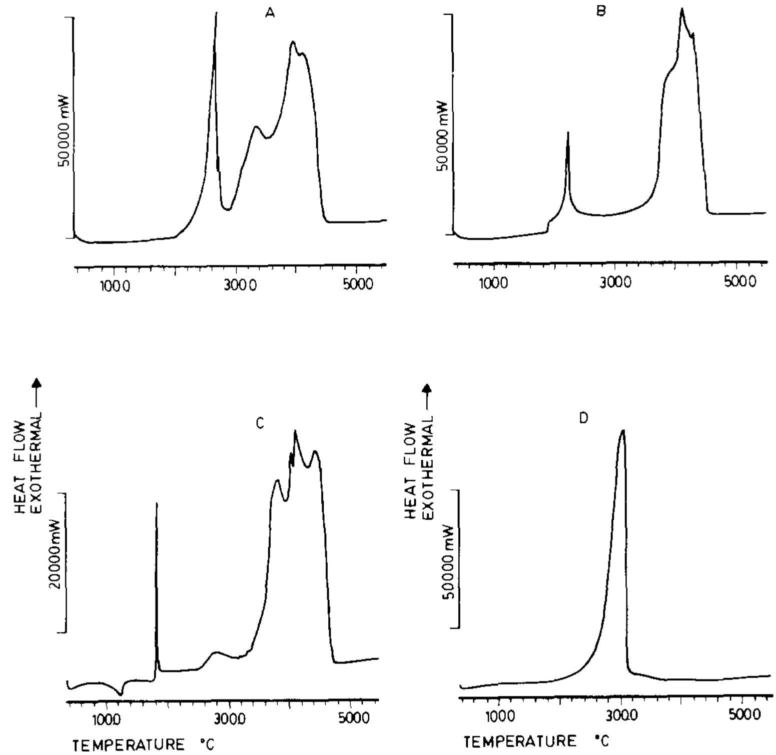

Fig. 3. DSC curves of **I** (A), **II** (B), **III** (C) and **IV** (D).

with the theoretical value for the elimination of one of the two free –COOH groups (7.42%). To prove this process, the IR spectrum of a sample of the complex heated at 200°C (end of strong weight loss effect), was recorded (Fig. 5). The presence of a broad band in the 2800–2200 cm^{-1} region can be

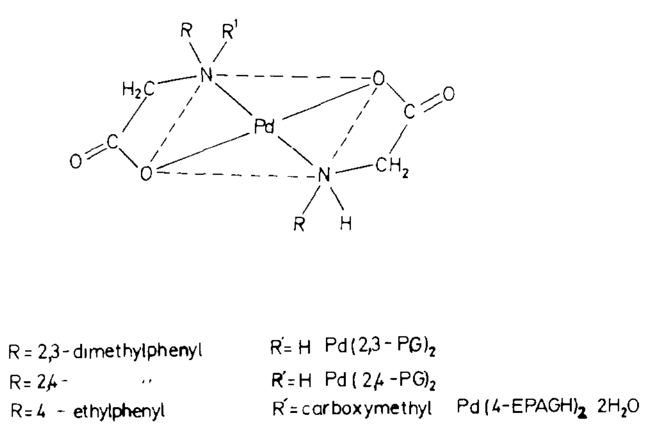

Fig. 4. Structures of Pd(2,3-PG)$_2$, Pd(2,4-PG)$_2$ and (4-EPAGH)$_2$·2H$_2$O.

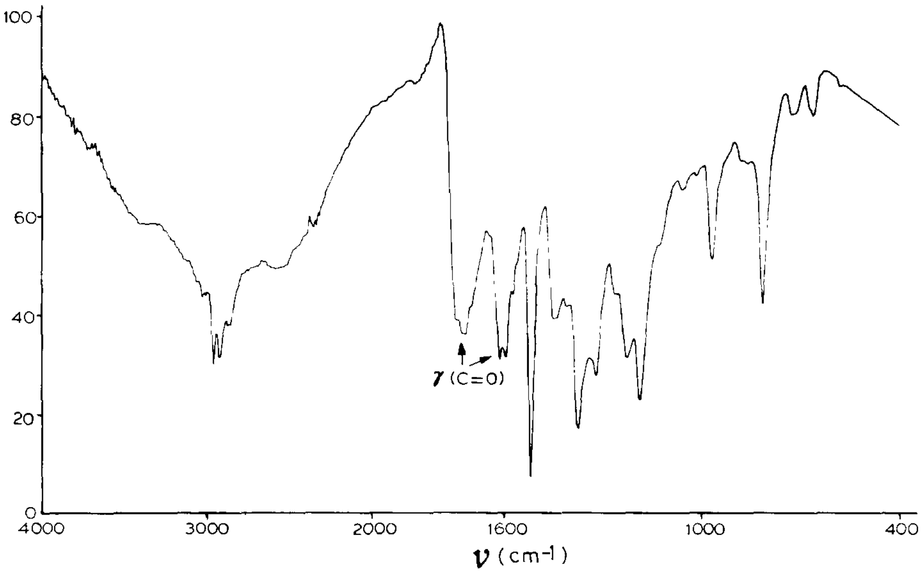

Fig. 5. IR spectra of Pd(4-EPAGH)$_2$·2H$_2$O heated at 200°C.

clearly observed in this IR spectrum corresponding to ν(OH) of the -COOH group, that is, intermolecular hydrogen bonds must exist between the -COOH group of two molecules of the glycine derivatives. Likewise, the band at 1720 cm^{-1} is assignable to ν(C=O) of a free -COOH group. The bands at 1615 and 1600 cm^{-1} correspond to the stretching vibration of the COO$^-$ groups coordinated to the Pd(II) ion. The foregoing results confirm the elimination of one of the free -COOH groups. This process appears in the DSC curve as an exothermic effect centered at 183°C. The decarboxylation enthalpy was 99.8 kJ mol^{-1}. At 280°C, in the DSC curve, there is another exothermic effect, which can be assigned to the elimination of the remaining -COOH group. The exothermic effects in the 320–480°C temperature range are probably due to the elimination of the carboxylato groups coordinated to the Pd(II) ion and pyrolysis of the organic matter. At the end of pyrolysis, the final residue was PdO (proven by IR spectroscopy), in agreement with the theoretical (19.92%) and experimental values (20.5%).

Pd(2,6-PAG)$_2$ (IV)

Finally, the DSC curve of Pd(2,6-PAG)$_2$ (whose structure is given in Fig. 6), presents only an exothermic effect at 290°C, which corresponds to the decarboxylation and pyrolysis of this complex, thus, indicating that the two COO$^-$ groups are equivalent and coordinated to the Pd(II) ion. The decarboxylation temperature is in agreement with that found for the analogous complexes M(2,6-PAG)$_2$ (where M = Cu(II) and Ba(II)) [9]. Likewise, the

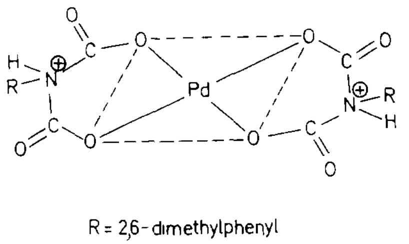

Fig. 6. Structure of $Pd(2,6\text{-}PAG)_2$.

TG curve confirms that the decomposition takes place in one step, since it shows only one weight loss effect in the 150–300°C temperature range. At this temperature, the residue obtained (21.7% of the original weight) corresponds to PdO.

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