

SYNTHESIS AND CHARACTERIZATION OF TWO DERIVATIVES OF ETHYL- α -KETOCYCLOPENTYLCARBOXYLATE WITH MERCURY(II)

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ABSTRACT

The compounds $\text{HgC}_8\text{H}_{12}\text{Cl}_2\text{O}_3$ and $\text{HgC}_{16}\text{H}_{22}\text{O}_6$ obtained by reaction between ethyl- α -ketocyclopentylcarboxylate and mercury(II) chloride and mercury(II) acetate, respectively, were prepared and studied. Both compounds were characterized by means of IR spectroscopy, differential thermal analysis and thermogravimetric analysis.

INTRODUCTION

In recent years, interest in the study of organomercuric compounds has grown owing, among other reasons, to their use in the synthesis of important organic functional groups, the ease with which they generate transmethylation reactions to form organometallic compounds useful in synthesis, and their antimicrobial, antifungal properties, etc. [1,2]. The present work reports on the synthesis, characterization and thermal study of two organomercuric compounds obtained by reacting ethyl- α -ketocyclopentylcarboxylate with mercury(II) chloride and acetate.

EXPERIMENTAL

The procedure employed to obtain the compounds was similar in both cases: with constant stirring, a freshly prepared ethanolic solution of the enolic form of ethyl- α -ketocyclopentylcarboxylate in the required proportions [3] was added dropwise to 30 ml of an ethanolic solution of mercury(II) chloride (0.015 mol) or to 100 ml of an aqueous solution of mercury(II) acetate (0.015 mol). The yield was approximately 50% in both cases. The reactions occurring are shown in Scheme 1.

The compounds were obtained in the form of a very fine powder; these were filtered, washed with water and dried in a desiccator over calcium

chloride. The compounds are insoluble in non-polar solvents and fairly or very insoluble in polar solvents, except DMSO and pyridine.

Metal contents were determined with EDTA using magnesium-EDTA complex for the replacement reaction and Erio T indicator powder [4]. Halogen content was determined by the Mohr method and chemical analysis of C and H was carried out by conventional methods at the Institute of Bio-Organic Chemistry of the CSIC (Barcelona, Spain). Analytical results were Hg, 46.7%; C, 18.2%; H, 2.3%; Cl, 16.8%. $\text{HgC}_8\text{H}_{12}\text{Cl}_2\text{O}_3$ calculated is: Hg, 46.9%; H, 2.8%; Cl, 16.6%, m.p., 114°C (dec.). And: Hg, 40.2%; C, 36.7%; H, 3.9%. $\text{HgC}_{16}\text{H}_{22}\text{O}_6$ calculated is: Hg, 39.3%; C, 37.6%; H, 4.3%; m.p., 129°C (dec.).

Thermogravimetric (TG) curves were obtained in flowing air ($45\text{ cm}^3\text{ min}^{-1}$) using a Perkin-Elmer model 3600 instrument coupled to a data station; the heating rate was $10^\circ\text{C min}^{-1}$.

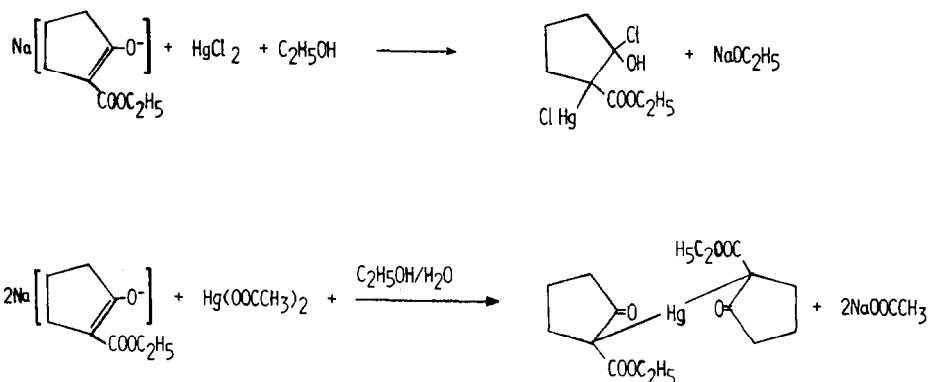
Differential thermal analysis (DTA) was performed using a Perkin-Elmer model 3600 instrument, using alumina to dilute the samples, with a heating rate of $10^\circ\text{C min}^{-1}$ in flowing argon, air and oxygen ($45\text{ cm}^3\text{ min}^{-1}$).

The FTIR spectra of the compounds and the successive decomposition residues at increasing temperatures were recorded using a Perkin-Elmer M1700 provided with a data station, using KBr pellets. The UV spectra were obtained on a Varian-Techtron apparatus model 635.

Thermal decomposition to obtain the residues was carried out in both flowing oxygen and argon, in order to achieve experimental conditions as close as possible to those used in TG and DTA, in a Heraeus RDK 3160 tubular furnace.

Magnetic susceptibilities were determined at room temperature using a Stanton MC-5 Gouy-type balance.

Finally, the powder diffractograms were recorded on a Siemens Kristalloflex 810 instrument, using Ni-filtered $\text{Cu K}\alpha$ radiation and standard conditions.



Scheme 1

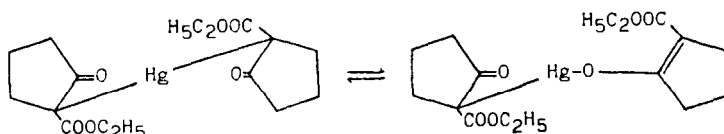
RESULTS AND DISCUSSION

Both compounds are diamagnetic and exhibit a single absorption band in the UV spectrum at 250 nm, coinciding with the charge transference band present in the enolic form of the ligand.

In the study of the IR spectra of the compounds and of the free ligand, the following findings are of interest (Fig. 1).

(1) The presence of an intense band at 3462 and 3461 cm^{-1} in the compounds due to the OH (str) vibration mode and to the possible formation of hydrogen bonds [5].

(2) The disappearance of bands from the ligand at 1757, 1724, 1659 and 1621 cm^{-1} corresponding to the C=O (ester), C=O (ketone), C=O (conjugated chelate) and C=C (str) vibrations to give a very intense and rather wide band at 1686 cm^{-1} in the compound $\text{HgC}_8\text{H}_{12}\text{Cl}_2\text{O}_3$ (**I**), and two bands, one at 1685 cm^{-1} similar to the previous one, and the other at 1624 cm^{-1} , in the compound $\text{HgC}_{16}\text{H}_{22}\text{O}_6$ (**II**). The bands at 1686 and 1685 cm^{-1} are attributed to the presence of the enol in the compounds and to the vibration of the C=O (ester) displaced towards lower frequencies owing to the formation of hydrogen bonds [6], whereas the band at 1624 cm^{-1} can be attributed to the vibration of the C=C (str) [3]. Accordingly, in compound **II**, there must be at least the following tautomeric forms analogous to those of similar compounds [7]



(3) In compound **I**, we attribute the presence of a band at 757 cm^{-1} , absent in both the ligand and compound **II**, to a C-Cl (str) vibration. A band at 519 cm^{-1} in compound **I** and another at 522 cm^{-1} in compound **II**,

TABLE 1
DTA data of mercury(II) compounds

Compound	Atmosphere	Heating rate ^a	Peaks ($^{\circ}\text{C}$) ^b
$\text{HgC}_8\text{H}_{12}\text{Cl}_2\text{O}_3$	O_2	10	165 exo, 310 exo, 430 exo
	Air	10	161 exo, 333 exo, 403 exo
	Ar	10	164 exo, 302 endo, 420 exo
$\text{HgC}_{16}\text{H}_{22}\text{O}_6$	O_2	10	142 exo, 311 exo, 433 exo
	Air	10	178 exo, 353 exo, 412 exo, 479 exo
	Ar	10	167 exo, 255 endo, 395 exo

^a $^{\circ}\text{C min}^{-1}$.

^b endo, exo = endothermal or exothermal peak.

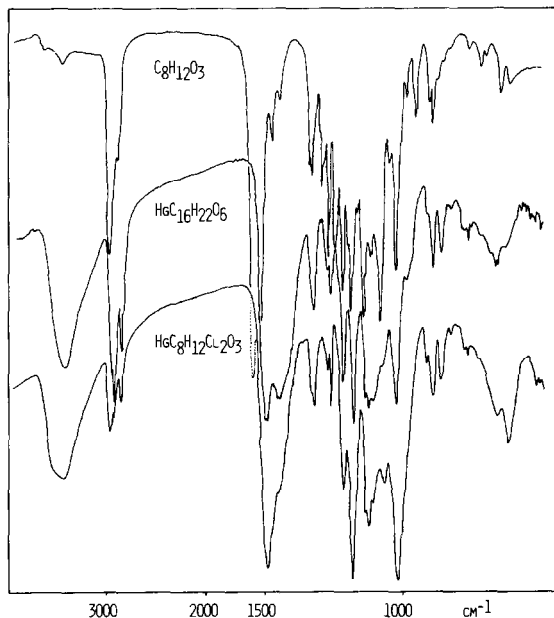


Fig. 1. IR spectra of mercury(II) compounds and of the free ligand.

not present in the ligand, are due to the C–Hg (str) vibration in both compounds. Finally, the band exhibited at 326 cm^{-1} in compound I may be attributed to the vibration of the Hg–Cl (str) [7–10].

The TG curves (Fig. 2) show similar behaviour for both compounds. Compound I begins to lose weight at around 125°C and a sharp loss in weight is seen at 166°C . We attribute this to pyrolysis of the ethyl carboxylate present in the compound, in accordance with the behaviour of the ligand and similar molecules and the behaviour of compounds with a

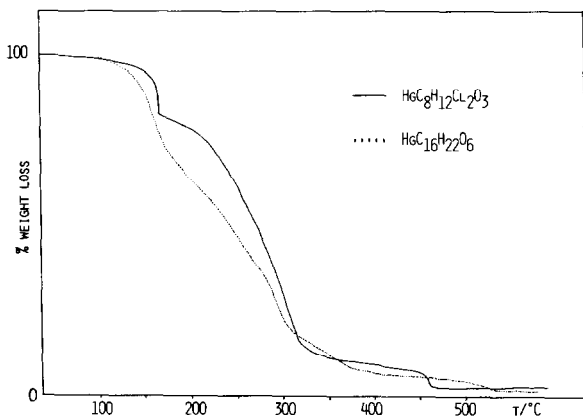


Fig. 2. TG curves of mercury(II) compounds in an air atmosphere.

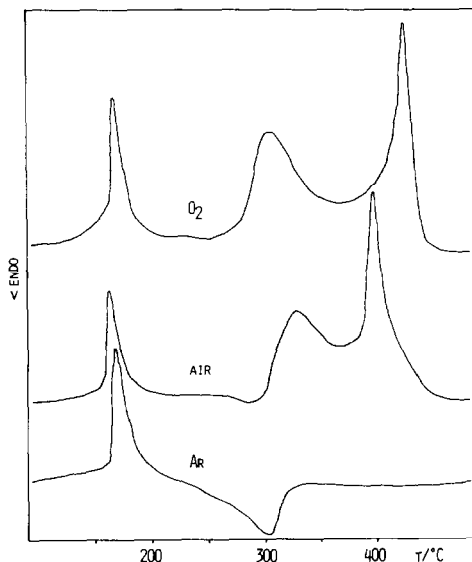


Fig. 3. DTA curves of $\text{HgC}_8\text{H}_{12}\text{Cl}_2\text{O}_3$.

similar formula [10,11], to the concordance between the theoretical and experimentally observed percentage weight loss and to the IR study carried out on the residue obtained at 200°C , in which the band corresponding to the carbonyl group of the ester was not observed. The weight loss continues progressively until a plateau is reached (370°C), at which temperature there is a carbon residue which does not contain mercury and which continues its oxidation process from around 455°C .

Compound **II** begins to lose weight from 110°C but not as sharply as compound **I**. For similar reasons to those suggested for the previous case, we attribute this weight loss to pyrolysis of the ethyl carboxylate groups present in the compound. This kind of thermal behaviour, which differs from that of the free ligand or of compound **I**, or from the behaviour of compounds with a structure similar to that of compound **I** [11], supports the proposed tautomeric forms for compound **II**, having a stoichiometry and structure different from those of compound **I** and similar compounds. Weight loss continues until a poorly defined plateau is reached at around 410°C , at which temperature all the mercury has been lost and after which progressive combustion of the carbon residue occurs.

The DTA curves of compounds **I** and **II** are consistent with their respective thermogravimetric curves (Figs. 3 and 4); the results are shown in Table 1. The first exothermic peak of compound **I** is at around $160\text{--}165^\circ\text{C}$ in all the atmospheres used. We attribute these to pyrolysis of the ethyl carboxylate, as we have shown for the TG curves. The liberation of CO_2 was detected by passing the released gases through a trap containing a solution of barium hydroxide. In an argon atmosphere, we observed an endothermic

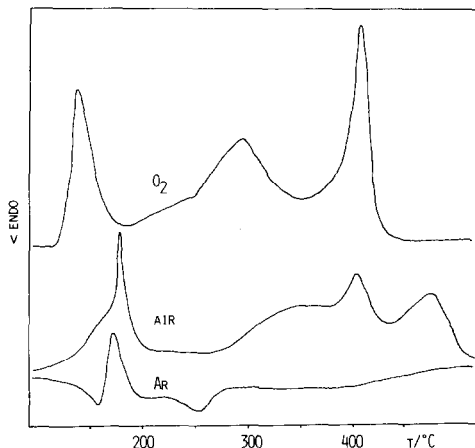


Fig. 4. DTA curves of $\text{HgC}_{16}\text{H}_{22}\text{O}_6$.

peak at 302°C that might have been due to the formation of mercury(II) chloride and its sublimation, and from 420°C onwards, the residue present is carbonized. In both oxygen and air, the behaviour is analogous, with an exothermic peak at 310°C (oxygen) and at 333°C (air), similar to that observed in the thermal decomposition of the ligand, with a final exothermic peak at 430 and 403°C , respectively, which we attribute to the combustion of the carbon residues produced.

In the residues obtained at 200 and 300°C with the three atmospheres, we detected metallic mercury and mercury(I) oxide chloride ($\text{Hg}_4\text{Cl}_2\text{O}$), which were identified by X-ray diffraction.

In an argon atmosphere, compound **II** exhibits an initial exothermic peak at 167°C which we attribute to pyrolysis of the ethyl carboxylate, as in the previous case; an endothermic peak at 255°C , which appears during the thermal decomposition of the free ligand in this atmosphere above 200°C and, from 395°C onwards, successive carbonizations of the final carbon residue. For the same reasons, the DTA curves of this compound under oxygen are similar to those obtained with compound **I**. In an air atmosphere, the peaks are obtained at higher temperatures; a striking feature is a peak at 353°C , possibly due to the sublimation of metallic mercury formed in the decomposition of the compound. Another peak appears at 497°C due to the combustion of the carbon residue. In the residues of this compound obtained at 200 and 300°C , it was only possible to identify metallic mercury.

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