Journal of Thermal Analysis, Vol. 30 (1985) 377–382

THERMAL STUDIES ON METAL COMPLEXES OF 5-NITROSO-PYRIMIDINE DERIVATIVES

III. Thermal behaviour of Hg(II) complexes of 6-amino-5-nitrosouracil derivatives

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(Received September 13, 1984)

Four Hg(II) complexes, containing as ligands 6-amino-5-nitrosouracil (AH), 6-amino-3-methyl-5-nitrosouracil (BH) or 6-amino-1-methyl-5-nitrosouracil (CH), have been synthesized and their thermal behaviour studied by TG and DSC techniques: $Hg_3Cl_6(AH)_4$, $HgCl_2(BH)_2 \cdot 2\ H_2O$, $HgCl_2(BH)_2 \cdot H_2O$ and $HgC_2 \cdot 2\ H_2O$.

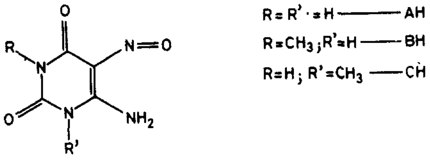
The dehydration processes take place in only one step, with enthalpies in the range 40.2–60.0 kJ · $mole^{-1}$ H_2O.

Pyrolytic processes start between 200 and 250°, in all cases the thermal stability of the corresponding pyrimidine derivative being lower than that of the free ligand. These processes finish between 600 and 750°, with no residue.

It is well known that metal complexes of pyrimidine derivatives and their nucleotides play an important role in many biological systems [1, 2]. Consequently, during recent years a large number of these complexes have been synthesized and studied from both inorganic chemical [3–8] and biological [9–12] aspects.

However, practically all the work found in the available literature concerned the structural study of these complexes using spectral and X-ray techniques, but not their thermal behaviour.

For this reason, and as a continuation of our research involving thermal studies on diverse metal-pyrimidine complexes [13–16], in this paper we report the thermal behaviour of Hg(II) complexes of 6-amino-5-nitrosouracil (AH), 6-amino-3-methyl-5-nitrosouracil (BH) and 6-amino-1-methyl-5-nitrosouracil (CH).



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Experimental

The pyrimidine derivatives were prepared by methods previously reported [17]. All the chemicals used in this work were of analytical reagent grade.

Preparation of the complexes

10 ml of an aqueous solution of mercury(II) chloride (8 mmole) was added slowly, with stirring, to a hot aqueous solution (200 ml) of the corresponding ligand (2 mmole):

Hg(II)/AH system: A brown powder precipitate immediately.

Table 1 Chemical analysis of isolated complexes

Complex	Colour	C%	H%	N%	Hg%
$Hg_3Cl_6(AH)_4$	Brown	13.81 (13.34)	1.50 (1.11)	16.11 (15.57)	41.04 (41.83)
$HgCl_2(BH)_2 \cdot 2\,H_2O$	Rose	19.22 (18.53)	2.34 (2.47)	18.12 (17.29)	30.50 (30.98)
$HgCl_2(BH)_2 \cdot H_2O$	Rose pale	19.43 (19.05)	1.85 (2.22)	16.98 (17.79)	31.50 (31.86)
$HgC_2 \cdot 2\,H_2O$	Red	21.30 (20.88)	2.15 (2.44)	18.67 (19.49)	34.16 (34.91)

In parenthesis, calculated values.

Hg(II)/BH system: After a few days, a pale-rose powder was obtained and, from the filtrated solution by evaporation at room temperature, rose needle-shaped crystals were isolated.

Hg(II)/CH system: When the solution was left to stand at room temperature, a red powder was obtained after some days.

The isolated compounds were washed consecutively with water and ethanol, and dried with diethyl ether. Their chemical analyses are given in Table 1.

Apparatus

Microanalysis of C, H and N was performed in the Department of Bio-organic Chemistry of C. S. I. C. (Barcelona). Hg was determined by atomic absorption spectrophotometry, with a Perkin—Elmer-290 apparatus.

TG curves were obtained under a dynamic atmosphere of nitrogen (100 ml $\cdot$ $\cdot$ min^{-1}), in a Mettler TG-50 thermobalance, at a heating rate of 10 deg min^{-1}. DSC curves were recorded in a Mettler DSC-20 differential scanning calorimeter, in the temperature range 35—300° at a heating rate of 5 deg min^{-1}. Thermal reactions were performed with samples varying in weight from 3.71 to 9.83 mg.

Results and discussion

In previous work on these complexes [18], carried out using spectral methods (IR and ^{1}H-NMR), we have shown that in the complexes $Hg_3Cl_6(AH)_4$, $HgCl_2(BH)_2 \cdot 2\,H_2O$ and $HgCl_2(BH)_2 \cdot H_2O$ the pyrimidine derivative acts as a monodentate ligand, some of the carbonyl oxygen atoms being the most probable binding site.

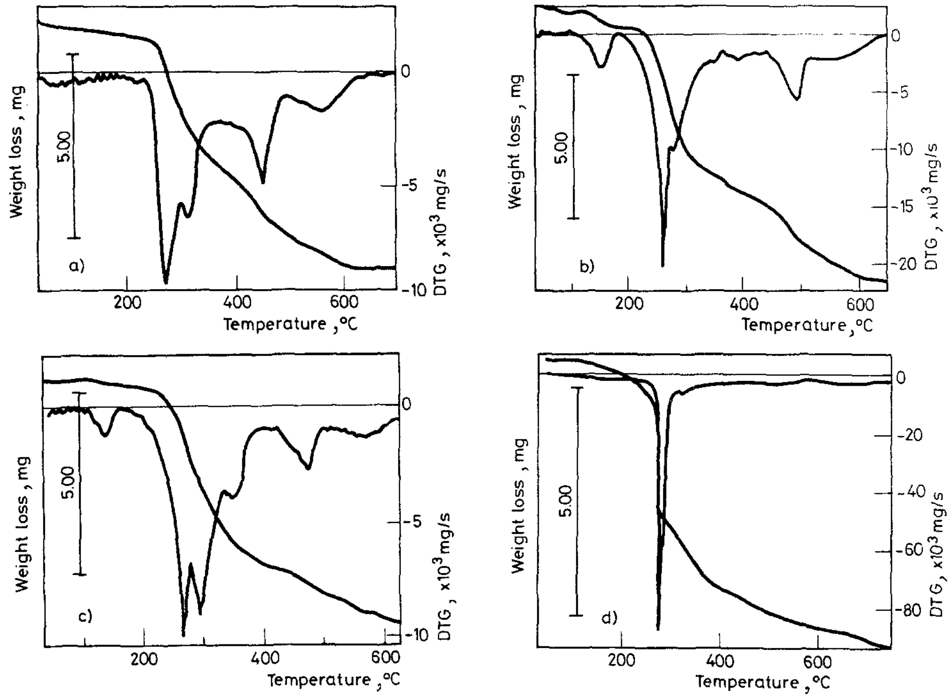

Fig. 1 TG and DTG plots for isolated complexes: (a) $Hg_3Cl_6(AH)_4$, (b) $HgCl_2(BH)_2 \cdot 2\,H_2O$, (c) $HgCl_2(BH)_2 \cdot H_2O$ and (d) $HgC_2 \cdot 2\,H_2O$

For the first compound, the spectral data do not permit the proposal of any structure; however, its composition is analogous to that reported by Battistuzzi and Peyronel in recent work [19], in which complexes of Hg(II) with 4,6-dimethylpyrimidine-2(1H)-one are described. Likewise for BH complexes the data suggest a distorted tetrahedral structure, in which the water molecules are linked by hydrogen-bonds to suitable atoms of the ligands.

On the other hand, the experimental results obtained for $HgC_2 \cdot 2\,H_2O$ show that in this compound the coordination of 6-amino-1-methyl-5-nitrosouracil to the Hg(II) ion takes place in deprotonated nitrosophenolic form, through the nitrogen and oxygen atoms of the 5-nitroso and 6-oxide groups, respectively. For this compound too we have suggested a distorted tetrahedral structure, in which the water molecules are bound in a similar way as in the BH complexes.

TG plots for the isolated complexes are given in Fig. 1, and DSC curves in Fig. 2.

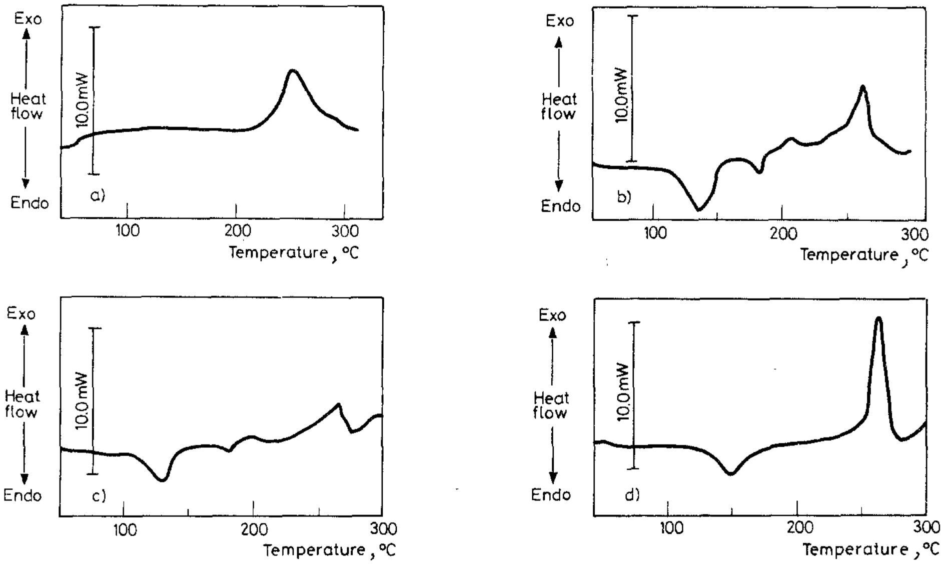

Fig. 2 DSC plots: (a) $Hg_3Cl_6(AH)_4$ (b) $HgCl_2(BH)_2 \cdot 2\,H_2O$, (c) $HgCl_2(BH)_2 \cdot H_2O$ and (d) $HgC_2 \cdot 2\,H_2O$

Dehydration processes

The data on calculated and observed weight losses, DSC peak temperatures and the corresponding dehydration enthalpy values are listed in Table 2.

From Figs 1b, c and d, we can observe that all dehydration processes take place in one step, which suggests that in $HgCl_2(BH)_2 \cdot 2\,H_2O$ and $HgC_2 \cdot 2\,H_2O$ the two water molecules occupy equivalent positions in the crystal structure. Likewise, the expected endothermic behaviour due to the dehydration has been observed from the DSC plots (Figs 2b, c and d) in the same temperature ranges as in the TG curves.

The enthalpies of dehydration, calculated from the areas of the corresponding endothermic peaks, are given in Table 2. They are in agreement with the bonding of each water molecule in the corresponding complex by a hydrogen-bond, and indicate

Table 2 TG and DSC data for dehydration processes

Process	Weight loss, %		Peak temperature DSC, °C	Dehydration enthalpy, kJ · $mole^{-1}$ H_2O
	calcd.	obsd.		
$HgCl_2(BH)_2 \cdot 2\,H_2O \rightarrow HgCl_2(BH)_2 + 2\,H_2O$	5.56	5.5	133	59.9
$HgCl_2(BH)_2 \cdot H_2O \rightarrow HgCl_2(BH)_2 + H_2O$	2.86	3.0	127	60.0
$HgC_2 \cdot 2\,H_2O \rightarrow HgC_2 + 2\,H_2O$	6.27	6.2	146	40.2

that in $HgCl_2(BH)_2 \cdot 2\,H_2O$ and $HgCl_2(BH)_2 \cdot H_2O$ they are linked in practically the same manner, since their elimination takes place at the same temperature and the two complexes need approximately equal energies per mole of water for their dehydration.

These values are similar to those found for other complexes of Ag(I) [14], Zn(II) [15] and Cd(II) ions [16] with the same uracil derivatives.

Pyrolytic processes

After dehydration, the isolated mercury complexes undergo pyrolytic decomposition. The TG and DSC data for these processes are given in Table 3.

The DSC plots of the anhydrous complexes show (Fig. 2) several exothermic effects which must be attributed to the combustion of organic matter. In all cases, the thermal decomposition of the complexes starts at lower temperature than that of the free ligand [18], which indicates that the thermal stability of the latter decreases when it bound to the Hg(II) ion.

It is remarkable that, after pyrolytic decomposition, the DSC plots of the $HgCl_2(BH)_2 \cdot 2\,H_2O$ and $HgCl_2(BH)_2 \cdot H_2O$ compounds (Figs 2b and c) show an endothermic effect centred at about 180°, which is not accompanied by any weight loss in the corresponding TG plots (Figs 1b and c). From the area of the peaks, we have calculated the energy necessary for these processes (11.1 and 6.0 $kJ \cdot mole^{-1}$, respectively). These values are in accordance with those found in the available literature for several structural changes [20–22].

Table 3 Thermoanalytical data for pyrolytic processes

Reaction	Final temperature TG, °C	DSC peak temperature, °C
$Hg_3Cl_6(AH)_4 \rightarrow$ a	600	252 (exo)
$HgCl_2(BH)_2 \rightarrow$ a	625	180 (endo), 205 (exo), 262 (exo)
$HgCl_2(BH)_2 \rightarrow$ a	625	182 (endo), 200 (exo), 265 (exo)
$HgC_2 \rightarrow$ a	750	262 (exo)

a Total elimination.

On the other hand, it can be observed from Figs 2b and 2c that these two complexes show practically the same DSC plot, which indicates that the two have similar structures. This conclusion is consistent with that suggested by spectral studies [18].

Finally, the pyrolytic decomposition of these four complexes finishes between 600 and 750° (Fig. 1) without any residue, due to the elimination of mercury either as mercury chloride or as metallic mercury [23].

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Zusammenfassung — Vier 6-Amino-5-nitrosouracil (AH), 6-Amino-3-methyl-nitrosouracil (BH) oder 6-Amino-1-methyl-5-nitrosouracil (CH) als Liganden enthaltende Hg(II)-Komplexe wurden synthetisiert: $Hg_3Cl_6(AH)_4$, $HgCl_2(BH)_2 \cdot 2\,H_2O$, $HgCl_2(BH)_2 \cdot H_2O$ und $HgC_2 \cdot 2\,H_2O$. Die Dehydratisierungsprozesse verlaufen in nur einem Schritt mit Enthalpien im Bereich von 40.2–60.0 kJ pro mol H_2O. Pyrolitische Prozesse setzen zwischen 200 und 250° ein. In allen Fällen ist die thermische Stabilität der entsprechenden Pyrimidin-Derivate geringer als die der freien Liganden. Diese Prozesse sind zwischen 600 und 750° beendet, wobei kein Rückstand zurückbleibt.

Резюме — Методами ТГ и ДСК изучено термическое поведение синтезированных комплексов двухвалентной ртути состава $Hg_3Cl_6(AH)_4$, $HgCl_2(BH)_2 \cdot 2\,H_2O$, $HgCl_2(BH)_2 \cdot H_2O$, и $HgC_2 \cdot 2\,H_2O$, где АН — 6-амино-5-нитрозоурацил, ВН — 6-амино-3-метилнитрозоурацил и СН — депротонированный 6-амино-метил-5-нитрозоурацил. Процессы дегидратации протекают в одну стадию с энтальпией, находящейся в области значений 40.2–60.0 кДж · моль$^{-1}$ H_2O. Пиролитические процессы начинаются между 200 и 250° и заканчиваются в интервале температур 600–750° без образования какого-либо остатка. Во всех случаях термическая устойчивость соответствующего комплекса была ниже, чем свободного лиганда.