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THERMAL BEHAVIOUR OF URANIUM(VI) COMPLEXES. URANYL ACETATE DIHYDRATE -*N*,*N*′-DIPHENYLTHIOUREA SYSTEM: SYNTHESIS AND DECOMPOSITION

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ABSTRACT

The solid-state syntheses of adducts of uranyl acetate and *N*,*N*′-diphenylthiourea have been performed in both a DSC calorimeter and a thermoanalyser.

The results suggest that a solid–solid interaction occurs and a 1:1 adduct is formed. A mass effect in the solid state has been observed and the reaction even seems incomplete with a large excess of ligand, in agreement with IR measurements.

INTRODUCTION

The complexes of uranyl salts with compounds having oxygen or nitrogen as donor atoms have been widely studied [1–7].

The solid-state syntheses between salts of the "hard" uranyl ion and O- or N-donor ligands have been previously performed; the results suggested that in these cases the uranyl ion is able to coordinate with more than one ligand molecule [8–13].

Also, the possibility of obtaining adducts of uranyl ion with more than one molecule of S-donor ligands has been successively investigated by solid–solid interactions, but the attempts were unsuccessful: the solid-state syntheses between uranyl acetate dihydrate and S-donor ligands (thiourea, *N*-phenylthiourea) were performed, but the results indicated that the 1:1 adducts are products of the reactions [14,15]. In particular, the presence of a mass effect in the solid state, which influences the degree of conversion of the reactions, was observed for the uranyl acetate dihydrate–*N*-phenylthiourea system [15].

In this paper we report on the solid–solid interactions between uranyl acetate dihydrate ($UO_2Ac_2 \cdot 2H_2O$) and *N*,*N*′-diphenylthiourea (DPhT). The syntheses were attempted according to the following scheme

$$UO_2Ac_2 \cdot 2H_2O + n\text{DPhT} \rightarrow UO_2Ac_2 \cdot (\text{DPhT})_n + 2H_2O \ (n = 1\text{–}6)$$

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The uranyl acetate dihydrate was used because of the inability of the anhydrous salt to react.

EXPERIMENTAL

Materials

Uranyl acetate dihydrate (J.T. Baker) and *N,N'*-diphenylthiourea (C. Erba RPE) were used without any further purification.

Syntheses of the compounds

The compounds used for the thermal decompositions and IR measurements were prepared as follows: finely powdered stoichiometric molar amounts of uranyl acetate dihydrate and *N,N'*-diphenylthiourea (from 1:1 to 1:6) were well mixed and then heated in an oven at 100°C for a few minutes. The products obtained were used without purification.

DSC measurements

The DSC measurements were performed in a Mettler 20 DSC calorimeter, in a dynamic nitrogen atmosphere (5 $\mathrm{l\ h^{-1}}$) and in covered aluminium pans. The reference was an empty closed aluminium pan. The heating rate was 4°C $\mathrm{min^{-1}}$.

The syntheses were performed by introducing finely powdered stoichiometric mixtures of uranyl acetate dihydrate and *N,N'*-diphenylthiourea into the DSC pan and heating successively. The weight of the reactant system was about 4–6 mg. The ΔH values associated with the thermal effects were evaluated using ΔH_{melt} of indium as a standard (6.79 cal $\mathrm{g^{-1}}$).

TG and DTG measurements

The thermogravimetric curves were obtained using a Mettler TA model 50 thermoanalyser, in a dynamic nitrogen atmosphere (3.6 $\mathrm{l\ h^{-1}}$). Open alumina crucibles and a heating rate of 10°C $\mathrm{min^{-1}}$ were used, the sample weight being about 5–15 mg.

The solid–solid interactions were performed analogously to the DSC measurements; for the thermal decompositions we utilized the products obtained in an oven as reported above.

IR measurements

The IR spectra were performed as KBr pellets, using a Perkin-Elmer model 457 spectrophotometer (4000–250 $\mathrm{cm^{-1}}$).

RESULTS AND DISCUSSION

The solid-state syntheses were performed in DSC apparatus and the curves obtained compared with that of uranyl acetate dihydrate previously reported [14] and that of DPhT.

The DSC curve of *N,N'*-diphenylthiourea shows a sharp endothermic effect at 145–155°C due to melting immediately followed, before the peak is complete, by another large endothermic effect in the temperature range 155–215°C, due to decomposition of the product (Fig. 1).

The DSC curves corresponding to the thermal syntheses show three endothermic effects for all stoichiometric mixtures used. The first peak appears at 90–130°C, while the other two occur at 145–155 and 155–215°C, respectively. These last two peaks are unresolvable, along with those observed in the DSC curve of DPhT. At higher temperatures only the anhydrous uranyl acetate decomposition (T_{max} = 360°C) is observed. The shape of the curves of the 1:1, 1:2, 1:3 and 1:4 stoichiometric mixtures (Fig. 2) is very similar to that of DPhT and different from that of other mixtures investigated (Fig. 3).

The presence of all characteristic thermal effects of both reactants in the DSC curves associated with the syntheses could indicate that between $UO_2Ac_2 \cdot 2H_2O$ and DPhT no interaction occurs in the solid state.

By contrast, the quantitative DSC data indicate a different behaviour of the several mixtures investigated, according to the different shape of the DSC curves. The enthalpic values of stoichiometric mixtures from 1:1 to 1:4 (Table 1), associated with the peaks at 90–130 and 145–215°C are close to the ΔH values associated with the dehydration of the uranyl salt (thermal effect at 90–130°C) and with the melting and decomposition of DPhT

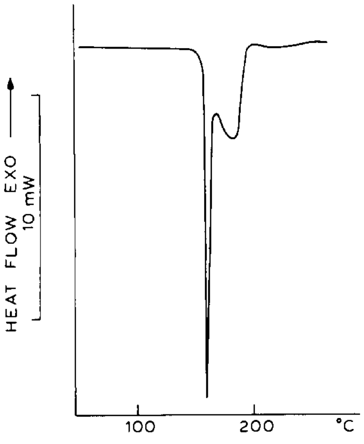

Fig. 1. DSC curve of *N,N'*-diphenylthiourea.

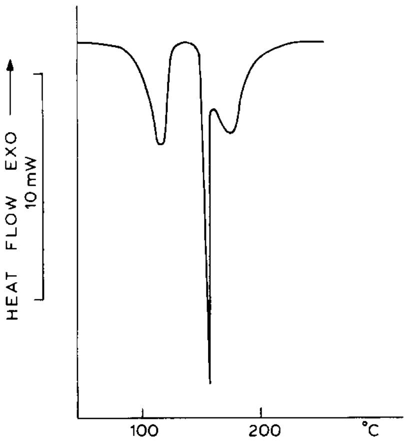

Fig. 2. DSC curve of the $UO_2Ac_2 \cdot H_2O$–*N*,*N*′-diphenylthiourea mixture in the 1:2 stoichiometric ratio.

(thermal effect at 145–215°C), respectively, thus indicating that no reaction occurs. A different behaviour is observed for the other mixtures investigated. The ΔH values obtained (Table 1) suggest that: (i) uranyl acetate dihydrate and DPhT react in the solid state in the temperature range 90–130°C, simultaneously with uranyl salt dehydration; (ii) the adducts formed successively decompose to form anhydrous uranyl acetate and DPhT, and DPhT melts and decomposes (thermal effects at 145–215°C).

The ΔH values obtained allow no decisive conclusions to be made on the stoichiometry of the adducts formed, but their trend, very similar to that observed for the uranyl acetate–*N*-phenylthiourea syntheses, and the same

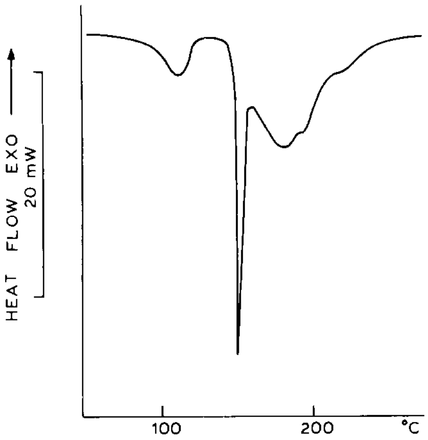

Fig. 3. DSC curve of the $UO_2Ac_2 \cdot 2H_2O$–*N*,*N*′-diphenylthiourea mixture in the 1:6 stoichiometric ratio.

TABLE 1

Temperatures (°C) and ΔH values (kJ mol^{-1}) associated with the DSC peaks. ΔH_d = enthalpic effect of the dehydration of uranyl acetate dihydrate; ΔH_{T_1} = total enthalpic effect of the thermal processes at temperature T_1; $\Delta H_{(m+d)}$ = enthalpic effect of the melting and decomposition of DPhT; ΔH_{T_2} = total enthalpic effect of the thermal processes at temperature T_2. The ΔH_d and ΔH_{T_1} values refer to 1 mole of uranyl acetate dihydrate; the $\Delta H_{(m+d)}$ and ΔH_{T_2} values refer to 1 mole of DPhT

System	T_1	ΔH_d	ΔH_{T_1}	T_2	$\Delta H_{(m+d)}$	ΔH_{T_2}
N,*N*′-Diphenylthiourea				145–215	137.9	
$UO_2Ac_2 \cdot 2H_2O$	90–130	121.7				
$UO_2Ac_2 \cdot 2H_2O$ + 1 DPhT	90–130		120.4	145–215		135.2
$UO_2Ac_2 \cdot 2H_2O$ + 2 DPhT	90–130		122.6	145–215		139.6
$UO_2Ac_2 \cdot 2H_2O$ + 3 DPhT	90–130		120.3	145–215		138.5
$UO_2Ac_2 \cdot 2H_2O$ + 4 DPhT	90–130		121.2	145–215		135.9
$UO_2Ac_2 \cdot 2H_2O$ + 5 DPhT	90–130		145.0	145–215		101.6
$UO_2Ac_2 \cdot 2H_2O$ + 6 DPhT	90–130		182.3	145–215		97.4

"soft" nature of the S-donor ligands, suggest that also in this case the 1:1 adduct is formed and the degree of conversion of the reaction is influenced by the excess of ligand. Nevertheless, in this case the solid–solid interaction seems to be incomplete even in the presence of a large excess of ligand.

TABLE 2

Temperatures (°C) of the thermal processes and experimental and theoretical weight losses. The theoretical weight losses are calculated by considering that the thermal process at 80–130°C is due to the dehydration of uranyl salt, and those at 140–200 and 140–260°C are due to decomposition of all the DPhT present in the mixtures

System	T (°C)	Exp. weight loss (%)	Theor. weight loss (%)
$UO_2Ac_2 \cdot 2H_2O$ + 1DPhT	80–130	5.81	5.52
	140–200	34.5	34.9
$UO_2Ac_2 \cdot 2H_2O$ + 2DPhT	80–130	4.32	4.09
	140–200	50.4	51.8
$UO_2Ac_2 \cdot 2H_2O$ + 3DPhT	80–130	3.55	3.25
	140–200	60.3	61.7
$UO_2Ac_2 \cdot 2H_2O$ + 4DPhT	80–130	2.77	2.69
	140–200	67.5	68.2
$UO_2Ac_2 \cdot 2H_2O$ + 5DPhT	80–130	2.40	2.30
	140–200	71.8	72.9
	200–260		
$UO_2Ac_2 \cdot 2H_2O$ + 6DPhT	80–130	2.00	2.01
	140–200	76.0	76.3
	200–260		

This last hypothesis is also supported by the spectroscopic measurements performed. The IR spectra of the products obtained in an oven from the 1:1, 1:2, 1:3 and 1:4 stoichiometric mixtures show no shift of the ν_3 antisymmetric stretching frequency (942 cm^{-1}) of the uranyl group, thus confirming that no reaction occurs. On the contrary, in the IR spectra of the products obtained from other investigated mixtures, the band at 942 cm^{-1} of the unlinked uranyl group is present together with a band at 909 cm^{-1} due to the linked uranyl group, confirming the formation of adducts and the simultaneous presence of unreacted uranyl acetate.

TG and DTG curves were also recorded on heating in a thermobalance, both of the reactant stoichiometric mixtures and the products obtained in an oven as described in the Experimental section, but no difference was observed, apart from the dehydration step of the uranyl salt. The shape of the curves was in agreement with the DSC results. For the 1:1, 1:2, 1:3 and 1:4 mixtures, two single steps (80–130 and 140–200°C) were observed (Fig. 4). The TG and DTG curves of other investigated mixtures (Fig. 5) show a different behaviour: after the step at 80–130°C, analogous to the mixtures having a smaller donor ligand excess, a double step at 140–200 and 200–260°C was observed, thus indicating the existence of two thermal processes; the last DTG peak increases on increasing the excess of DPhT. In

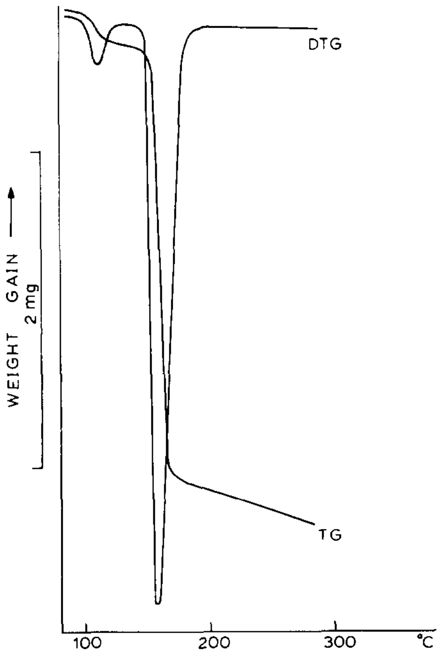

Fig. 4. TG and DTG curves of the $UO_2Ac_2 \cdot 2H_2O$–*N*,*N*′-diphenylthiourea mixture in the 1:2 stoichiometric ratio.

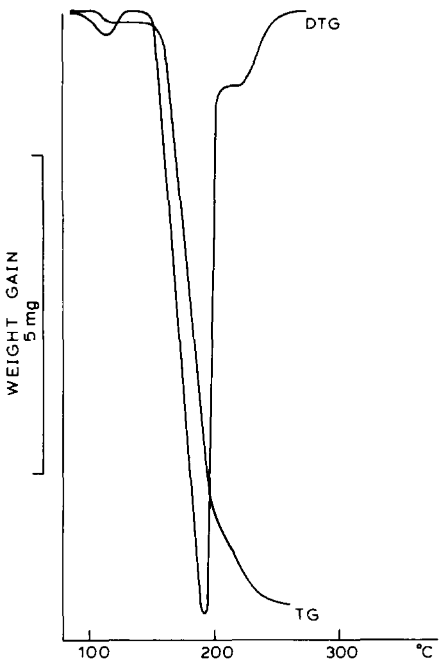

Fig. 5. TG and DTG curves of the $UO_2Ac_2 \cdot 2H_2O$–*N*,*N'*-diphenylthiourea mixture in the 1:6 stoichiometric ratio.

every case the anhydrous uranyl acetate decomposition occurs at a higher temperature.

The experimental weight losses of 1:1, 1:2, 1:3 and 1:4 mixtures clearly indicate that the two steps observed are due to uranyl salt dehydration (thermal process at 80–130°C) and DPhT decomposition (thermal process at 140–200°C), no reaction occurring.

The thermal behaviour observed for all other mixtures shows that, also for these, uranyl salt dehydration occurs at 80–130°C. The two successive thermal processes are not quite resolvable from the DTG curves. It is worth noting that: (i) the temperature of the first peak coincides with the decomposition temperature of DPhT; (ii) the last DTG peak, smaller than the first, increases on increasing excess of DPhT; (iii) the experimental total weight losses associated with the processes at 140–200 and 200–260°C are in agreement with the theoretical weight losses calculated as due to the decomposition of all the DPhT present in the mixtures (Table 2). Considering these results, we think that the two steps are due, respectively, to the decomposition of unlinked DPhT, and that of the DPhT obtained from the adduct formed by linkage of the coordinative bond. These data confirm that the solid–solid interaction is also incomplete in the presence of a large excess of ligand.

CONCLUSIONS

The measurements performed seem to indicate that the uranyl acetate dihydrate and *N,N'*-diphenylthiourea react in the solid state only in the presence of a large excess of DPhT. The comparison with results previously obtained for similar systems [14,15] suggests that the 1:1 adduct is formed, which decomposes at a higher temperature according to the following scheme

$$UO_2Ac_2 \cdot 2H_2O + n\mathrm{DPhT} \xrightarrow{80-130^\circ C} UO_2Ac_2 \cdot \mathrm{DPhT}$$

$$+ (n-1)\mathrm{DPhT} + 2H_2O \ (n = 5{,}6)$$

$$UO_2Ac_2 \cdot \mathrm{DPhT} \xrightarrow{145-215^\circ C} UO_2Ac_2 + \mathrm{DPhT}$$

$$\mathrm{DPhT} + (n-1)\mathrm{DPhT} \xrightarrow{145-215^\circ C} \text{melt and decomposition}$$

$$UO_2Ac_2 \xrightarrow{360^\circ C} \text{decomposition}$$

Small temperature differences between DSC and TG measurements are due to the different experimental conditions.

A mass effect in the solid state is also observed for the uranyl acetate-*N*-phenylthiourea system, but in this case the reaction even seems incomplete in the presence of a large excess of ligand according to the lesser donor properties of DPhT compared to *N*-phenylthiourea.

Nevertheless, the enthalpic values do not allow the enthalpic values associated with the formation and decomposition of the adduct to be evaluated.

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