THERMAL BEHAVIOUR OF URANIUM(VI) COMPLEXES
Uranyl acetate dihydrate·-N-phenylthiourea system: synthesis and decomposition

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The solid-state syntheses of complexes of uranyl acetate dihydrate and N-phenylthiourea have been attempted by heating various stoichiometric mixtures of the reactants directly in a DSC and in a TA apparatus. Both the DSC and the TG results indicate that only the 1:1 adduct is formed, independently of the molar ratios of the reactants. It appears that the reaction is complete only with a large excess of N-phenylthiourea, in agreement with IR data.

The ability of uranyl ion in solution or in the solid state to coordinate more than one ligand molecule having oxygen or nitrogen donor atoms has been reported [1–7]. In contrast, similar behaviour in the case of sulphur donor ligands still remains controversial [2, 6].

In a recent work [8], we used uranyl acetate dihydrate ($UO_2Ac_2 \cdot 2 H_2O$) and thiourea in an attempt to prepare solid-state adducts of the uranyl ion with more than one molecule of S-donor ligand. The results, however, indicated that the product of the reaction is the complex ($UO_2Ac_2 \cdot$ thiourea), independently of the stoichiometric ratio of the reactants.

In this paper we report on studies of the solid-state interactions between uranyl acetate dihydrate and N-phenylthiourea (PhT), made to investigate whether the presence of the phenyl group in the thiourea molecule can influence the donor properties of the ligand. The syntheses were attempted according to the following scheme:

$$UO_2Ac_2 \cdot 2 H_2O + n \, PhT \rightarrow UO_2Ac_2 \cdot (PhT)_n + 2 H_2O \quad (n = 1-6)$$

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-phenylthiourea (J. T. Baker) were used without any further purification.

DSC measurements: The DSC measurements were made in closed aluminium pans in a dynamic nitrogen atmosphere (5 $l \cdot h^{-1}$), using a Mettler 20 DSC calorimeter. The heating rate was 4 degree $\cdot$ min^{-1}. The reference was a closed aluminium pan. Reactions were performed by introducing into the pan finely-powdered stoichiometric mixtures of the reactants, the total weight being 4–6 mg, and heating. The ΔH values associated with the thermal effects were calculated using the ΔH_{melt} of indium (6.79 cal $\cdot$ g^{-1}) as standard.

TG and DTG measurements: The thermogravimetric curves were obtained with a Mettler TA 50 thermoanalyzer, in a dynamic nitrogen atmosphere (3.6 $l \cdot h^{-1}$). Open alumina crucibles and a heating rate of 10 degree $\cdot$ min^{-1} were used. The sample weights were about 3–5 mg. The solid–solid interactions were oerformed analogously to the DSC measurements.

IR measurements: The IR spectra were obtained from KBr pellets, using a Perkin–Elmer 457 spectrophotometer (4000–250 cm^{-1}).

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

Results and discussion

DSC measurements

The DSC curve of uranyl acetate dihydrate has been reported previously [8].

The DSC curve of N-phenylthiourea (Fig. 1) shows an endothermic effect at 130° due to the $\alpha \rightarrow \beta$ transition ($\Delta H_{\alpha \rightarrow \beta} = 3.5$ kJ $\cdot$ $mole^{-1}$). Above this temperature, two consecutive and unresolvable endothermic effects are evident: (i) the melting process (*m*) at 145–155°, and (ii) the decomposition process (*d*) at 155–200°. The total $\Delta H_{(m+d)}$ value is reported in Table 1.

The DSC curves (Fig. 2) corresponding to the synthetic processes show three endothermic effects for all stoichiometric mixtures: the first occurs in the temperature range 90–130°; the remaining two are not separable and occur in the temperature ranges 145–155° and 155–200°, respectively. Upwards of this temperature, only a decomposition process is observed ($T_{max} = 360°$).

Because of the presence of all the characteristic thermal effects of both reactants, the DSC curves corresponding to the syntheses could indicate that, on the heating of solid mixtures of uranyl acetate and N-phenylthiourea, no interaction occurs; in this case the thermal effect at 90–130° could be due to the contribution of the dehydration of uranyl salt and to the $\alpha \rightarrow \beta$ transition of PhT, while that at 145–200° could be related to the melting and decomposition of PhT present in the mixtures.
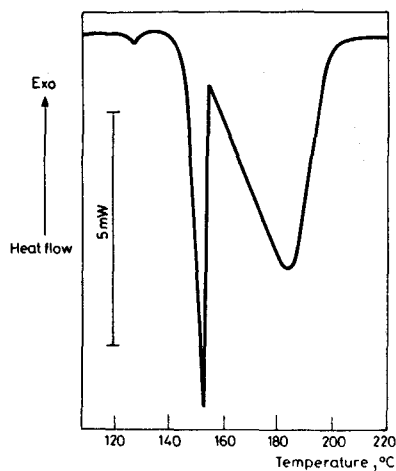
Fig. 1 DSC curve of *N*-phenylthiourea

Moreover, the ΔH values associated with the peaks at 90–130° and 145–200° were calculated (Table 1); the values obtained are different from the ΔH values associated with uranyl acetate dehydration and the $\alpha \to \beta$ transition of PhT (thermal effect at 90–130°) and with the melting and decomposition of PhT (thermal effects at 145–155° and 155–200°), respectively.

These results suggest that: (i) $UO_2Ac_2 \cdot 2 H_2O$ and PhT react in the temperature range 90–130°, simultaneously with the dehydration of the uranyl salt; (ii) in the temperature range 145–200° the adducts formed decompose with loss of PhT, and simultaneously the PhT melts and decomposes. The obtained ΔH values exclude the formation of 1:n adducts with the same composition as the reactant mixtures. Remembering that the solid–solid interaction of uranyl acetate and thiourea (Th) yields only the complex $UO_2Ac_2 \cdot Th$, independently of the stoichiometric ratio of the reactants [8], we can suppose that: (i) only the 1:1 adduct is formed between $UO_2Ac_2 \cdot 2 H_2O$ and PhT, and uranyl acetate dihydrate and *N*-phenylthiourea react in the solid state; (ii) the 1:1 adduct gives rise to anhydrous uranyl acetate and PhT, the latter melting and decomposing together with the uncomplexed *N*-phenylthiourea excess present in the mixture (endothermic processes at 145–200°). The overall thermal process occurs according to the following mechanism:
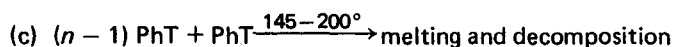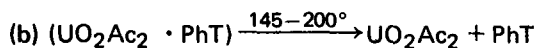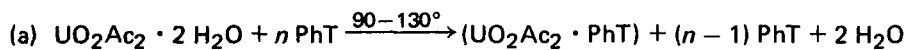
(a) $UO_2Ac_2 \cdot 2 H_2O + n\ PhT \xrightarrow{\ 90-130°\ } (UO_2Ac_2 \cdot PhT) + (n-1)\ PhT + 2 H_2O$

(b) $(UO_2Ac_2 \cdot PhT) \xrightarrow{\ 145-200°\ } UO_2Ac_2 + PhT$

(c) $(n-1)\ PhT + PhT \xrightarrow{\ 145-200°\ } $ melting and decomposition

Table 1 Temperatures (°C) and ΔH values (kJ · mole^{-1}) associated with the DSC peaks

System	T_1	ΔH_d	ΔH_{T_1}	T_2	$\Delta H_{(m+d)}$	ΔH_{T_2}	ΔH_{dec}	ΔH^*_{dec}
N-phenylthiourea								
$UO_2Ac_2 \cdot 2\,H_2O$	90–130	121.7		145–200	81.2			
$UO_2Ac_2 \cdot 2\,H_2O + 1\,PhT$	90–130		117.5	145–200		28.3	−52.9	−218.4
$UO_2Ac_2 \cdot 2\,H_2O + 2\,PhT$	90–130		120.4	145–200		42.5	−38.7	−159.8
$UO_2Ac_2 \cdot 2\,H_2O + 3\,PhT$	90–130		119.8	145–200		58.2	−23.0	−94.9
$UO_2Ac_2 \cdot 2\,H_2O + 4\,PhT$	90–130		116.3	145–200		65.1	−16.1	−66.5
$UO_2Ac_2 \cdot 2\,H_2O + 5\,PhT$	90–130		114.1	145–200		64.8	−16.4	−67.7
$UO_2Ac_2 \cdot 2\,H_2O + 6\,PhT$	90–130		129.3	145–200		65.0	−16.2	−66.9

* 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 PhT; ΔH_{T_2} = total enthalpic effect of the thermal processes at temperature T_2; $\Delta H_{dec} = \Delta H_{T_2} - \Delta H_{(m+d)}$. The ΔH_d and ΔH_{T_1} values refer to 1 mole of uranyl acetate dihydrate; $\Delta H_{(m+d)}$, ΔH_{T_2} and ΔH_{dec} refer to 1 mole of N-phenylthiourea; the ΔH^*_{dec} value is obtained from the ΔH_{dec} value and refers to 1 mole of 1:1 adduct.
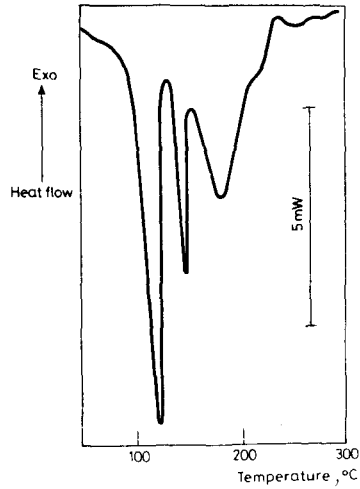
Fig. 2 DSC curve of the mixture $UO_2Ac_2 \cdot 2\, H_2O$ and N-phenylthiourea in 1:2 stoichiometric ratio

The ΔH_{T_2} values associated with the peaks at 145–200° were calculated to obtain the ΔH_{dec} value associated with reaction (b), via the equation:

$$\Delta H_{dec} = \Delta H_{T_2} - \Delta H_{(m+d)}$$

($\Delta H_{(m+d)}$ = comprehensive enthalpic effect associated with the melting and decomposition of PhT).

In Table 1 the ΔH_{T_2}, $\Delta H_{(m+d)}$ and ΔH_{dec} values are reported; it is worth noting that the experimental ΔH_{T_2} values are less endothermic than the $\Delta H_{(m+d)}$ value for N-phenylthiourea, indicating that the decomposition of the adduct is an exothermic process; furthermore, the exothermic ΔH_{dec} value so calculated is not constant, but the more n increases, the more ΔH_{dec} decreases, reaching a constant value only for $n = 4, 5$ and 6. In our opinion, this result suggests that a solid–solid interaction occurs, but is complete only in the presence of a large N-phenylthiourea excess. Therefore, two hypotheses are possible: (a) $|\Delta H_{dec}| > |\Delta H_{(m+d)}|$: in this case the ΔH_{T_2} value should become gradually less endothermic as the degree of conversion increases, and should be exothermic when the reaction is complete; (b) $|\Delta H_{dec}| < |\Delta H_{(m+d)}|$: in this case the ΔH_{T_2} value should be exothermic and should decrease on increase of the percentage of adduct formed. The experimental data agree with hypothesis (b), and we presume that the ΔH_{dec} value calculated from the 1:4, 1:5 and 1:6 systems is the correct enthalpic effect associated with the decomposition of the 1:1 adduct.

No useful information was obtained from the endothermic peaks at 90–130°; the associated ΔH_{T_1} values could not be rationalized and the reaction ΔH_r associated with the formation of the 1:1 adduct was not evaluable. This fact can probably be

explained by the very different c_p values of the mixtures before and after the de-hydration process and by the slight decomposition of the PhT before the complete dehydration of the uranyl salt (see TG measurements).

TG and DTG measurements

Thermal decomposition of the reactants

The thermal behaviour of uranyl acetate dihydrate has been reported previously [8].

The decomposition of PhT occurs in two steps (130—160° and 160—200°), the total weight loss being 89.2% (Fig. 3). A comparison of this result with that from the DSC experiment indicates that the PhT partially decomposes on melting.
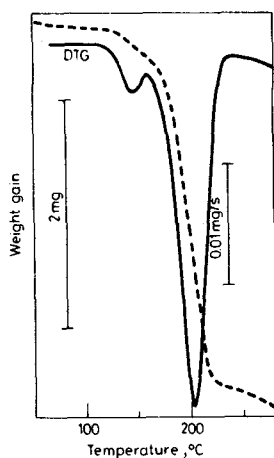

Fig. 3 Thermal decomposition of *N*-phenylthiourea

Thermogravimetric analysis of the mixtures

The TG and DTG curves of the stoichiometric mixtures were compared with those of the products obtained in the oven as reported in the experimental section; apart the dehydration step, no difference was observed.

For all investigated mixtures the TG and DTG curves (Fig. 4) provide evidence of two processes: dehydration of the uranyl salt and decomposition of melting *N*-phenyl-thiourea, with partial overlap in the temperature range 80—160°. Above this tempera-ture, the TG curves show two processes, the first at 160—240° and the second at 240—300°; these are more clearly seen in the DTG curves. It is worth noting that the area of the second DTG peak relative to the first one decreases as the PhT excess in-creases (Fig. 5). This suggests that the unreacted PhT excess decomposes at 160—240°, whereas the bound PhT decomposes only at 240—300°. To confirm this hypothesis,
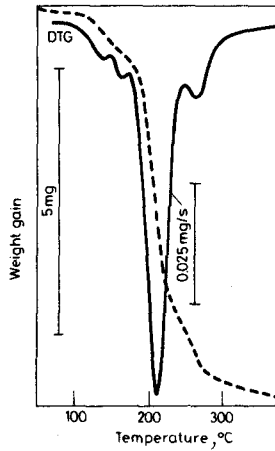
Fig. 4 Thermal decomposition of the mixture $UO_2Ac_2 \cdot 2\,H_2O$ and N-phenylthiourea in 1:3 stoichiometric ratio
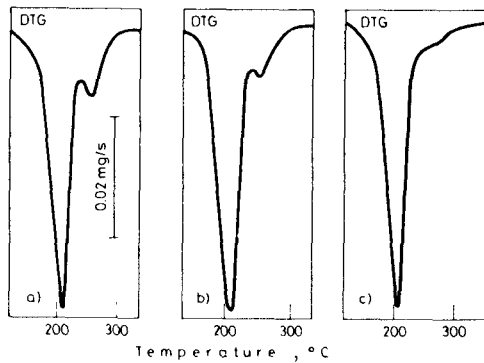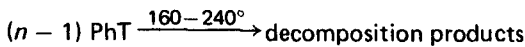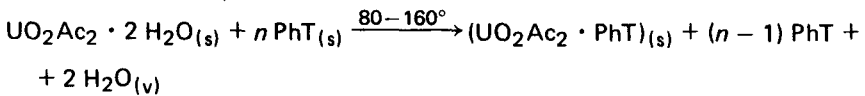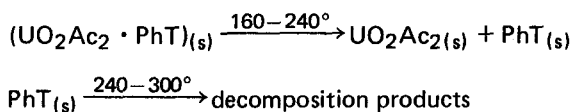

Fig. 5 DTG curves of the mixture $UO_2Ac_2 \cdot 2\,H_2O$ and N-phenylthiourea in (a) 1:2 molar ratio, (b) 1:3 molar ratio, (c) 1:5 molar ratio

the experimental weight losses of the stoichiometric mixtures in the temperature ranges 80–160°, 160–240° and 240–300° were evaluated and compared with the corresponding losses calculated on the assumption that only the 1:1 adduct is formed (Table 2). The results clearly indicate that only the adduct $UO_2Ac_2 \cdot PhT$ is formed, and that its formation is complete only in the presence of a large excess of N-phenyl-thiourea.

Therefore, the thermal processes are:

$$UO_2Ac_2 \cdot 2\,H_2O_{(s)} + n\,PhT_{(s)} \xrightarrow{80-160°} (UO_2Ac_2 \cdot PhT)_{(s)} + (n-1)\,PhT +$$

$$+ 2\,H_2O_{(v)}$$

$$(n-1)\,PhT \xrightarrow{160-240°} \text{decomposition products}$$

$$(UO_2Ac_2 \cdot PhT)_{(s)} \xrightarrow{160-240°} UO_2Ac_{2(s)} + PhT_{(s)}$$

$$PhT_{(s)} \xrightarrow{240-300°} \text{decomposition products}$$

Above 300° only the decomposition of uranyl acetate was observed (330—480°).

Small differences between the experimental and theoretical values for the thermal processes can be explained by considering that the unreacted PhT partially decomposes at 130°.

Table 2 Temperatures (°C) of the thermal processes, and experimental and theoretical weight losses

System	T, °C	Exp. weight loss, %	Theor. weight loss, %
$UO_2Ac_2 \cdot 2H_2O + 1\,PhT$	80—160	8.2	6.6
	160—240	19.2	—
	240—300	12.8	22.6
$UO_2Ac_2 \cdot 2H_2O + 2\,PhT$	80—160	7.5	5.3
	160—240	33.1	18.5
	240—300	11.6	18.5
$UO_2Ac_2 \cdot 2H_2O + 3\,PhT$	80—160	5.9	4.5
	160—240	43.5	36.1
	240—300	10.3	15.6
$UO_2Ac_2 \cdot 2H_2O + 4\,PhT$	80—160	6.1	3.9
	160—240	45.7	40.5
	240—300	12.9	13.5
$UO_2Ac_2 \cdot 2H_2O + 5\,PhT$	80—160	5.7	3.4
	160—240	47.8	47.6
	240—300	11.7	11.9
$UO_2Ac_2 \cdot 2H_2O + 6\,PhT$	80—160	5.6	3.1
	160—240	51.1	53.1
	240—300	10.5	10.6

*The theoretical weight losses are calculated by considering that the thermal process at 80—160° is due to dehydration of the uranyl salt, that at 160—240° is due to decomposition of unbound PhT, and that at 240—300° is due to decomposition of bound PhT.

IR spectra

IR spectroscopic measurements were made on the stoichiometric mixtures and on the products obtained in the oven as reported in the experimental section. The IR spectra were compared with one another and the spectral assignments were made on the basis of the values reported in the literature [9]. In the IR spectra of the mixtures, only the bands of uranyl acetate dihydrate and N-phenylthiourea are present. In the spectra of the products obtained in the oven, two cases are observed: the products prepared from the 1:4, 1:5 and 1:6 stoichiometric mixtures show a sharp red shift

of the ν_3 antisymmetric stretching frequency of the uranyl group from 942 to 915 cm^{-1}, confirming the complete reaction of $UO_2Ac_2 \cdot 2 H_2O$ and N-phenylthiourea, whereas the products obtained from the 1:1, 1:2 and 1:3 stoichiometric mixtures show bands at both 942 and 915 cm^{-1}, indicating the presence of unreacted $UO_2Ac_2 \cdot 2 H_2O$.

Useful information was also derived from the bands of the N-phenylthiourea groups, though in the products obtained in the oven a large unreacted N-phenylthiourea excess is present.

For the bands at 1610 cm^{-1} (ν_{NH_2}), 1516 cm^{-1} ($\nu_{asy\ NCS}$), 1445 cm^{-1} (ν_{NCN}), 1060 cm^{-1} ($\nu_{sym\ NCS}$) and 750 cm^{-1} ($\nu_{CS} + \nu_{CN}$), no shift was observed.

The bands at 610 cm^{-1} and 590 cm^{-1}, due to the CS group of unbound and bound N-phenylthiourea, respectively, were both observed, suggesting the formation of S—U bond, in accordance with the literature.

Conclusions

The experimental results of the DSC, TG, DTG and IR measurements mutually agree and suggest that only the 1:1 adduct is formed when solid mixtures of uranyl acetate and N-phenylthiourea are heated.

As for the uranyl acetate—thiourea system, no evidence of the existence of 1:n adducts with $n > 1$ was obtained, though the formation of a 1:2 adduct, prepared from petroleum ether solution, is reported in the literature [9]. Nevertheless, the most important conclusion from this study is the presence of a mass effect in the solid state, that influences the degree of conversion of the solid—solid reaction. This behaviour, compared with that of the corresponding thiourea system, can be explained by considering the weaker donor behaviour of PhT than that of thiourea.

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Zusammenfassung — Es wurde versucht, Komplexe von Uranylacetat und N-phenylthioharnstoff in fester Phase durch Erhitzen verschiedener stöchiometrischer Gemische der Reaktanten direkt in einer DSC- und einer TA-Apparatur herzustellen. Sowohl die DSC- als auch die TG-Ergebnisse deuten darauf hin, dass nur das 1:1-Addukt gebildet wird, und zwar unabhängig von den molaren Mischungsverhältnissen der Reaktanten. Übereinstimmend mit IR-Daten scheint die Reaktion nur bei einem grossen Überschuss an N-Phenylthioharnstoff vollständig zu verlaufen.

Резюме — Предприняты попытки твердотельных синтезов комплексов уранилацетата с N-фенилтиомочевиной нагреванием их непосредственно в приборах ДСК и ТА. Установлено, что независимо от молярного соотношения взятых реагентов, всегда получали аддукт состава 1:1. Согласно данным ИК спектроскопии, реакция протекает полностью только в присутствии значительного избытка N-фенилтиомочевины.