The Chemistry of Uranium.
Part 38. The Interaction of UI_4 with Sulphoxide Ligands and the Use of Dimethyl Sulphoxide as Oxidizing Agent in the Preparation of UO_2I_2 Complexes

JAN G. H. DU PREEZ and BEN ZEELIE
Uranium Chemistry Research Unit, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth 6000 (South Africa)

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Abstract

The reactions of UI_4 with a number of sulphoxide donor ligands have been studied in non-aqueous media and compared to the behaviour of UCl_4 and UBr_4 in the presence of these ligands. UI_4 is readily oxidized by dmso (dimethyl sulphoxide) and dibso (di-isobutyl sulphoxide) at room temperature and the only stable complexes isolated were $UI_4(dmso)_8$ and $UI_4(dibso)_6$. The large tbso (di-tertiarybutyl sulphoxide) gives stable, bis-complexes, UX_4L_2 for all three halides. The oxidation of UI_4 by dmso in ethyl acetate provides a relatively easy and reliable method for the preparation of uranyl iodide complexes, e.g. $UO_2I_4A_2$ ($A = Ph_4P^+$, Ph_4As^+, etc.), $UO_2I_2L_2$ (L = triphenylarsine oxide (tpao), tris-(dimethylamino)phosphine oxide (tdpo), *N,N'*-dimethylpropylene urea (dmpu), *N,N,N',N'*-tetramethylurea (tmu) and *N,N'*-dimethylethylene urea (dmeu) and $UO_2I_2L_4$ where L = tdpo and tpao.

Introduction

A reinvestigation of the thorium, uranium and plutonium tetrachloride dmso systems, together with the first results on the analogous protactinium and neptunium complexes has shown that three series of complexes are formed [1]. These are $MCl_4(dmso)_3$ (M = Th–Pu inclusive), $MCl_4(dmso)_5$ (M = Th–Np inclusive) and $MCl_4(dmso)_7$ (M = U–Pu inclusive). Infrared results indicate that in the 1:7 complexes, two of the dmso molecules are very weakly held in the lattice. The $UCl_4(dmso)_3$ complex is well known and the solid has been shown to exist in the form $[UCl_2(dmso)_6][UCl_6]$ [2]. UBr_4 gives the complexes $UBr_4(dmso)_6$ [3] and $UBr_4(dmso)_8$ [4]. The former complex is expected to have the eight-coordinated $[UBr_2(dmso)_6]Br_2$ structure whereas infrared results suggest the latter complex to be similar to the $UCl_4(dmso)_7$ complex in that some dmso molecules are either very weakly coordinated or held in the lattice [4]. Numerous attempts to prepare an auto-ionized $UBr_4(dmso)_x$ complex were unsuccessful and it has been found that the $UBr_4(dmso)_6$ complex starts to precipitate from acetone solutions at a UBr_4:L mole ratio of only 1:2.8 [5].

$UI_4(dmso)_8$ [6] has been prepared previously, but it was of interest to determine whether any significant uranium–iodide interaction exists in this complex and to establish whether other complexes, containing fewer dmso molecules could be prepared. In view of the absence of significant auto-ionization in the UBr_4–dmso system, it was also of interest to determine whether any auto-ionization occurs with UI_4 in the presence of dmso. The effect of ligand size and the nature of the complexes formed between the uranium tetrahalides (UCl_4, UBr_4 and UI_4) and sulphoxide ligands (dmso, dibso and tbso) were also investigated.

Experimental

The preparation and manipulation of hygroscopic complexes was done under dry nitrogen, either in Schlenk tubes or in glove boxes. Dmso (Hopkin and Williams) was dried over 3 Å molecular sieves before use. Tbso was prepared by the oxidation of di-tertiary sulphide with H_2O_2 in acetone and dibso by the oxidation of di-isobutyl sulphide by H_2O_2 in glacial acetic acid. Uranium tetrachloride [7], $UBr_4(mecn)_4$ [8] and $UI_4(mecn)_4$ [9] were prepared as described previously (mecn = methyl cyanide). Drying of solvents, spectroscopic measurements, thermogravimetric analysis and analysis of complexes were carried out as described previously [10].

Preparations

(a) $UCl_4(tbso)_2$, $UBr_4(tbso)_2$, $UCl_4(dibso)_2$, $UBr_4(dibso)_4$ [5] and $UBr_4(dmso)_6$ [3]

Were prepared as described previously.

(b) $UBr_4(dibso)_2$

1.0 g of $UBr_4(mecn)_4$ (1.39 mmol) was dissolved in 30 ml ethyl acetate and two equivalents of dibso

(2.78 mmol, 0.458 g) dissolved in 15 ml of ethyl acetate were added. To this mixture *c.* 10 ml petroleum ether was added and subsequently cooled to −18 ℃, upon which light green crystals of the product were formed. The solid was washed with petroleum ether and dried *in vacuo.*

(c) $UI_4(tbso)_2$

1.2 g of $UI_4(mecn)_4$ (1.32 mmol) were dissolved in 40 ml of a 9:1 mixture of mecn and ethyl acetate and two equivalents of tbso (2.64 mmol, 0.438 g) in mecn were added. The mixture was cooled to −18 ℃ upon which a light, yellow–green solid precipitated. The solid was washed with ethyl acetate, followed by petroleum ether and dried *in vacuo.*

(d) $UI_4(dmso)_8$

1.2 g of $UI_4(mecn)_4$ (1.32 mmol) were dissolved in 30 ml ethyl acetate and 8 equivalents of dmso (10.56 mmol, 0.82 g) dissolved in ethyl acetate were added with vigorous stirring. Light green $UI_4(dmso)_8$ precipitated immediately. This was washed with ethyl acetate followed by petroleum ether and dried *in vacuo.*

(e) $UI_4(dibso)_6$

1.2 g of $UI_4(mecn)_4$ (1.32 mmol) were dissolved in 30 ml of a 9:1 mixture of mecn and ethyl acetate. Six equivalents of dibso (7.92 mmol, 1.3 g), dissolved in a minimum of mecn, were added with stirring. Yellow–green $UI_4(dibso)_6$ started to precipitate almost immediately. The solid was washed with ethyl acetate followed by petroleum ether and dried *in vacuo.*

(f) $(PPh_4)_2UO_2I_4$

Two equivalents of dmso (3.3 mmol, 0.26 g) were added to 1.5 g of $UI_4(mecn)_4$ (1.65 mmol) dissolved in 50 ml of ethyl acetate. The mixture was then refluxed for 10 min. Two equivalents of Et_4NI (3.3 mmol, 0.85 g) were added, the mixture refluxed for a further 10 min and then cooled to −18 ℃ upon which solid Et_4NI_3 precipitated as black crystalline plates. The Et_4NI_3 was filtered off under N_2 and two equivalents of PPh_4I dissolved in a minimum of mecn were added. A dark red solid precipitated on cooling to −18 ℃. The solid was washed with ethyl acetate followed by petroleum ether and dried *in vacuo.*

Analytical and some physical data of the complexes are summarized in Table 1.

Results and Discussion

The UI_4–dmso System

No solid complexes of UI_4 with dmso could be isolated from the reaction of $UI_4(mecn)_4$ (in a mixture of mecn and ethyl acetate) with two to six equivalents of dmso (per uranium) at room temperature. These reaction mixtures, in contrast to similar mixtures of $UI_4(mecn)_4$ with P=O or C=O donor ligands which are yellow–green, are very dark in colour. At the same time, a very strong smell of dimethyl sulphide (dms) could be detected in a stream of $N_2(g)$ passed over the reaction mixture which would appear to suggest either oxidation of UI_4 by dmso, viz.

$$UI_4 + 2\text{dmso} \longrightarrow UO_2I_2 + I_2 + \text{dms}$$

or oxygen abstraction from dmso by UI_4.

Addition of a further two equivalents of ligand (e.g. tdpo, tpao, dmpu or tmu) to a mixture of $UI_4(mecn)_4$ and two equivalents of dmso which were stirred for *c.* 30 min, resulted in the precipitation of small amounts of the compounds $UO_2I_2L_2$ (orange),

TABLE 1. Analytical and physical data of the complexes

Compound	Analytical data (%)				IR data (cm^{-1})	
	U	X	C	H	ν(L=O)	νUO_2^{2+}
$UCl_4(tbso)_2$	33.5(33.79)	20.1(20.13)	27.3(27.28)	5.2(5.15)	925	
$UBr_4(tbso)_2$	26.8(26.98)	36.1(36.23)	21.6(21.78)	4.0(4.11)	911	
$UI_4(tbso)_2$	22.0(22.24)	47.0(47.43)	17.8(17.96)	3.3(3.39)	898	
$UCl_4(dibso)_2$	33.4(33.79)	20.1(20.13)	27.1(27.28)	5.2(5.15)	935	
$UBr_4(dibso)_2$	26.7(26.98)	36.2(36.23)	21.6(21.78)	4.0(4.11)	896	
$UI_4(dibso)_6$	13.5(13.84)	29.1(29.52)	33.6(33.53)	6.1(6.33)		
$UI_4(dmso)_8$	17.1(17.37)	36.9(37.03)	14.3(14.02)	3.7(3.53)	988	
$(PPh_4)_2UO_2I_4$	16.1(16.30)	34.1(34.76)	39.2(39.48)	2.6(2.76)		916
$UO_2I_2(tdpo)_2$	26.7(26.98)	28.4(28.77)	16.1(16.34)	4.1(4.11)	1081	926
$UO_2I_2(dmeu)_2$	31.4(31.65)	33.4(33.74)	12.5(12.78)	2.6(2.68)	[a]	920
$UO_2I_2(tmu)_2$	31.2(31.48)	33.3(33.57)	12.5(12.71)	3.2(3.20)	[a]	914

[a] Overlap of ν(C=O) and ν(N–C–N) result in broad combination bands in the region 1550–1600 cm^{-1}.

$UO_2(I_3)_2L_4$ (black) or a mixture of the two. The isolation of these complexes confirms that the process is oxidation and not oxygen abstraction as was observed for the reactions of $MoCl_5$ [11] and UCl_5 [12] with tpao to give $MoOCl_3$ and $UOCl_3$, respectively. When $UI_4(mecn)_4$ is reacted, however, with an excess of dmso (8–10 mol of dmso per mole of uranium) in a mixture of mecn and ethyl acetate, light green solutions, from which the light green solid $UI_4(dmso)_8$ precipitates, result. No dimethyl sulphide could be detected in a stream of nitrogen passed over such reaction mixtures.

Reaction of $UI_4(mecn)_4$ with dmso at low temperatures (−18 °C) resulted in the formation of two different complexes, stable at these low temperatures, but rapidly decomposing above 0 °C. (In view of the absence of proper analytical data for these complexes, they are not included in the preparative section.) When $UI_4(mecn)_4$ is reacted with three equivalents of dmso at −18 °C in CH_2Cl_2 a deep red solid is found to precipitate. Although stable at this low temperature (when in contact with the mother liquor) it rapidly decomposes upon drying even at 0 °C, resulting in the formation of a black residue. Neither the red solid nor its black residue after decomposition were analysed. The red solid does, however, dissolve in aqueous acetone solutions to give a bright green solution which is indicative of the presence of uranium(IV). The red colour of the complex, which is very similar to that of the auto-ionized α-$UI_4(tpao)_2$ [13], could be indicative of an auto-ionized species; the red colour can be ascribed to the presence of the UI_6^{2-} entity.

The reaction of $UI_4(mecn)_4$ with six equivalents of dmso in a mecn/ethyl acetate mixture at −18 °C results in the precipitation of a light yellow–green solid which appears to be stable at 0 °C but decomposes rapidly if the temperature is increased to room temperature. Uranium and iodide analysis of this compound, dried at 0 °C, indicate it to be $UI_4(dmso)_6$. No solid reflectance spectrum (room temperature) could be obtained for this compound, but it is expected to be similar to the $UBr_4(dmso)_6$ compound reported previously [3].

The solid reflectance electronic spectrum of $UI_4(dmso)_8$ (Fig. 1) is typical of spectra recorded for uranium(IV) complexes having a coordination number >6. It is of interest to note that the origin of the charge transfer bands is very low (~350 nm) suggesting no direct U–I interaction. (The origin of the charge transfer bands in compounds having direct U–I interaction, e.g. UI_4L_2 and $UI_2L_4^{2+}$, usually start at ~450–500 nm.) At the same time, the IR spectrum of the solid complex in nujol shows only a single, relatively broad S=O stretching frequency at *c.* 940 cm^{-1} and no features due to free ligand are present. The above observations thus strongly suggest the existence of $UI_4(dmso)_8$ as $[U(dmso)_8]I_4$.

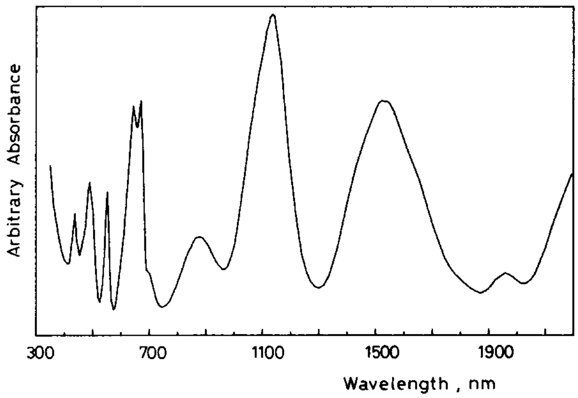

Fig. 1. Solid reflectance electronic spectrum of $UI_4(dmso)_8$.

The UI_4–dibso System

In view of the above results, it was of interest to establish whether stable UI_4 complexes with sulphoxide donor ligands, having direct U–I interaction, could be isolated. Previous spectroscopic studies in acetone solutions [5] indicated that dibso differs significantly from dmso in its behaviour towards UCl_4 and UBr_4. The most important differences observed were the increased importance of the six-coordinated $UX_4 \cdot L_2$ species compared to the smaller role of auto-ionized and ionized species and the weaker tendency towards coordination expansion after the $UX_4(dibso)_2$ species has been formed. With UCl_4, dibso gives the solid $UCl_4(dibso)_2$, whereas with UBr_4 both $UBr_4(dibso)_2$ and $UBr_4(dibso)_4$ can be obtained in the solid state. The bis-complexes are both six-coordinated, as is indicated by their solid reflectance electronic spectra, while the solid reflectance spectrum of $UBr_4(dibso)_4$ is typical of spectra of uranium(IV) complexes having coordination number >6.

The behaviour of UI_4 in the presence of dibso is quite different to those of UCl_4 and UBr_4 and is similar to that of the behaviour of UI_4 with dmso. No solid complex could be obtained by the reaction of $UI_4(mecn)_4$ with two equivalents of dibso in ethyl acetate, either at room temperature or at −18 °C. The resulting solutions are very similar to those obtained for the UI_4–dmso system and if these solutions are allowed to stir for 2–3 h at room temperature and two equivalents of tdpo added, orange $UO_2I_2(tdpo)_2$ is found to precipitate. This is mostly followed by a dark precipitate of some $UO_2(I_3)_2tdpo_4$. The reaction of UI_4 with two or three equivalents of dibso at −18 °C does not, however, lead to the oxidation of UI_4 (as addition of more ligand results in the formation of a yellow–green solution) and no evidence for the presence of auto-ionization could be found.

Reaction of $UI_4(mecn)_4$ with four equivalents of dibso in a mecn/ethyl acetate mixture at −18 °C results in the precipitation of a yellow–green solid.

This dry solid is again stable below 0 °C, but rapidly decomposes if the temperature is allowed to rise above 0 °C. Uranium and iodide analyses of the compound dried at 0 °C are indicative of $UI_4(dibso)_4$. The room temperature stable $UI_4(dibso)_6$ can readily be prepared as described. Its solid reflectance electronic spectrum is very similar to that recorded for $UBr_4(dmso)_6$ except for the red shift in the origin of the charge transfer bands to ~450 nm which suggests the presence of U–I bonding. The stability of this dibso complex as compared to the instability of the $UI_4(dmso)_6$ analogue indicates an effective stabilization by the more stereochemically crowded dibso.

The UI_4–tbso System

Of the three ligands studied, tbso is the most stereochemically crowded and should therefore be a slightly weaker donor towards uranium(IV). The levelling effect observed in the behaviour of UCl_4 and UBr_4 towards dibso in comparison with their behaviour towards the smaller dmso, i.e. the increased importance of six-coordinated species compared to higher coordinated species and the weaker tendency towards coordination expansion after the UX_4L_2 species has been formed, should become even more important for tbso even in its behaviour towards UI_4. This is clearly illustrated by the formation of very insoluble bis-complexes, $UX_4(tbso)_2$, for all three halides. No other solids having higher coordination numbers could be isolated for any of the three halides. The $UI_4(tbso)_2$ complex also appears to be indefinitely stable at room temperature and no evidence for the oxidation of UI_4 by tbso could be found at room temperature, either in solution or in the solid state.

The solid reflectance electronic spectra of the six-coordinated $UX_4(tbso)_2$ complexes are given in Fig. 2. The maxima of the characteristic low energy bands are given in Table 2 together with those of a selection of other bulky neutral ligands. When these values are compared vertically for each of the complexes, respectively, it can be seen that the peaks shift to lower wavelengths for increasing donor strength of the neutral ligand. When the values of the UX_4L_2 are compared horizontally for each of the different neutral ligand complexes, it becomes clear that the differences in the values for Cl^-, Br^- and I^- become smaller as the donor strength of the neutral ligand increases. (See the values in the fifth column where the differences in maxima for the bromo and iodo complexes are displayed.) In terms of the above arguments it appears that tbso has a donor strength between the bulky C=O amide and P=O ligands.

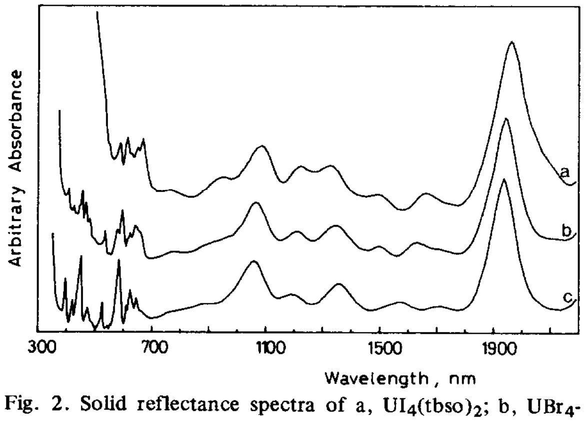

Fig. 2. Solid reflectance spectra of a, $UI_4(tbso)_2$; b, $UBr_4(tbso)_2$; c, $UCl_4(tbso)_2$.

TABLE 2. Wavelength (mμ) of low energy peaks of some UX_4L_2 complexes (L = bulky neutral ligands)

Compound[a]	Cl^-	Br^-	I^-	$\Delta I^- - Br^-$ [b]
$UX_4(ddu)_2$ [c]	1955	1970	2005	35
$UX_4(dmeu)_2$ [c]	1920	1945	1970	25
$UX_4(tbso)_2$	1935	1948	1965	17
$UX_4(tdpo)_2$ [d]	1910	1012	1910	2
$UX_4(tpao)_2$ [e]	1855	1840	1840	0

[a]ddu = *N,N'*-dimethyl-*N,N'*-diphenyl urea, dmeu = *N,N'*-dimethylethylene urea. [b]$\Delta I^- - Br^-$ = differences between values in columns three and four. [c]Taken from ref. 10. [d]Taken from ref. 14. [e]Taken from ref. 15.

The increase in shift of the S=O stretch frequency in going from the Cl^-, Br^- to I^- complex (Table 1) is to be expected although the presence of the two very bulky tertiary butyl groups on each S=O must restrict the U–O interaction very significantly.

Thermal Decomposition Studies

The thermal degradation curves for the $UX_4(tbso)_2$ complexes are given in Fig. 3. These clearly illustrate the stabilizing effect of tbso as compared to the other sulphoxide ligands. The $UX_4(tbso)_2$ complexes only start to decompose at ~155 (chloride), 150 (bromide) and 123 (iodide) °C. The corresponding values for the dibso complexes are ~120 (chloride), 75 (bromide) °C whereas UI_4 is oxidized by two equivalents of dibso, at room temperature, in solution.

UO_2I_2 Complexes

The existence of pure, anhydrous uranyl iodide is still uncertain [16]. The preparations of UO_2Cl_2 and UO_2Br_2 by oxidation of the respective tetrahalides in an oxygen atmosphere at elevated temperatures have been reported [17, 18]. Attempts to prepare UO_2I_2 by the oxidation of solid $UI_4(mecn)_4$ in dry oxygen atmospheres were unsuccessful due to a highly exothermic reaction of $UI_4(mecn)_4$ with oxygen at *c.* 40–60 °C which results in the formation of black uranium oxides. Complexes of uranyl iodide are usually prepared by metathesis from $UO_2(NO_3)_2$ or UO_2SO_4 using BaI_2 [19] or from UO_2Cl_2 using NaI in

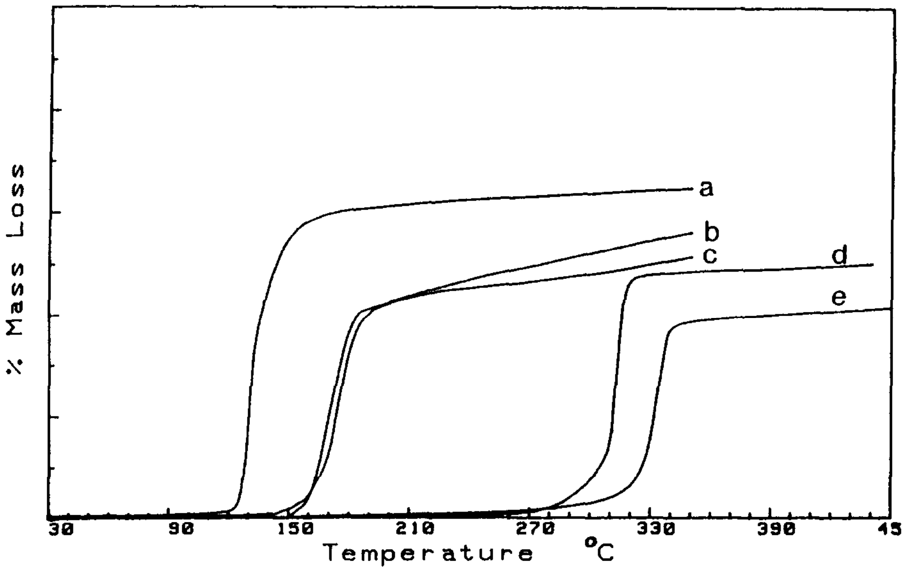

Fig. 3. Thermal degradation curves of a, $UI_4(tbso)_2$; b, $UBr_4(tbso)_2$; c, $UCl_4(tbso)_2$; d, $UO_2I_2(tdpo)_2$; e, $UO_2Cl_2(tdpo)_2$.

ether solution [20]. Solutions of UI_4 complexes are readily oxidized by air to give uranyl complexes. In such cases, the formation of free iodine proved to be problematic in view of the formation of tri-iodide species such as $UO_2(tdpo)_4(I_3)_2$ [21].

The oxidation of UI_4 by dmso in non-aqueous media (in the absence of O_2) provides a relatively easy and reliable method for the preparation of anhydrous solutions of UO_2I_2. Such solutions were found to be convenient starting materials for the preparation of a variety of UO_2I_2 complexes such as $(PPh_4)_2UO_2I_4$, $(AsPh_4)_2UO_2I_4$, $UO_2I_2L_2$ (L = tdpo. tpao, dmeu and tmu) and $UO_2I_2L_4$ (L = tdpo and tpao). (The method generally used for the preparation of UO_2I_2 solutions is outlined in 'Experimental' under the preparation of $(PPh_4)_2UO_2I_4$.) Although the oxidation of UI_4 by dmso in a dry nitrogen atmosphere proceeds spontaneously at room temperature in mecn or mecn/ethyl acetate solutions, it was found that oxidation proceeds much faster in boiling ethyl acetate. The iodine formed during the oxidation process can effectively be removed as Et_4NI_3 by the addition of a stoichiometric amount of Et_4NI. The resultant ethyl acetate solutions of UO_2I_2 appear to be stable at room temperature when stored in a nitrogen atmosphere. No attempts were made to isolate solid UO_2I_2 or solid ethyl acetate adducts of UO_2I_2 from these solutions.

The IR spectra of the UO_2I_2 complexes are typical of uranyl complexes. The uranium–oxygen stretching frequency (ν_3) for $(PPh_4)_2UO_2I_4$ is observed at 916 cm^{-1}. In complexes of the type UOX_2L_2, the uranium–oxygen stretching frequency shifts to higher energy on going from $X = Cl^-$ to $X = I^-$, e.g. from 912 cm^{-1} for $UO_2Cl_2(tdpo)_2$ to 926 cm^{-1} for $UO_2I_2(tdpo)_2$. This shift is accompanied by an increased shift in the P=O stretching frequency, i.e. from 1087 cm^{-1} for $UO_2Cl_2(tdpo)_2$ ($\Delta\nu(P{=}O) = 121$ cm^{-1}) to 1071 cm^{-1} for $UO_2I_2(tdpo)_2$ ($\Delta\nu(P{=}O) = 137$ cm^{-1}). No relationship could, however, be observed between the position of the uranium–oxygen stretching frequency and the donor strength of the neutral donor ligand (e.g. ν_3 for $UO_2I_2(dmeu)_2$ is observed at 920 cm^{-1} and for $UO_2I_2(tmu)_2$ ν_3 is observed at 914 cm^{-1}). This is in agreement with earlier reports [22].

Uranyl iodide complexes were reported to be generally much less stable than their chloro and bromo analogues [16]. This observation appears to hold for the halogeno complexes, e.g. $(PPh_4)_2UO_2I_4$ slowly decomposes at room temperature in a dry nitrogen atmosphere whereas similar chloro and bromo complexes are indefinitely stable. The $UO_2I_2L_2$ complexes prepared during this study do, however, appear to be very similar to their chloro analogues if moisture is excluded. Thermal decomposition studies of the $UO_2X_2(tdpo)_2$ complexes ($X = Cl^-$ and I^-) in a non-static nitrogen atmosphere show that both complexes decompose at approximately 300 °C (see Fig. 3). As in the case of the UI_4L_2 complexes, these complexes appear to be considerably more sensitive to moisture.

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