Inorganica Chimica Acta, 134 (1987) 303–308

The Chemistry of Uranium.
Part 36. Synthesis and Characterization of some Novel Triphenylarsine Oxide Complexes of UI_4

JAN G. H. DU PREEZ* and BEN ZEELIE

Uranium Chemistry Research Unit, University of Port Elizabeth, P.O. Box 16000 Port Elizabeth 6000, South Africa

(Received March 24, 1987)

Abstract

The reaction between UI_4 and triphenylarsine oxide (tpao) has been studied in non-aqueous solution. A number of solid complexes have been isolated, *viz.* α-UI_4tpao_2, β-UI_4tpao_2, UI_4tpao_4 and UI_4tpao_6. The room temperature stable UI_4tpao_2 (α form) proved not to be the *trans*-octahedral species as commonly found for UCl_4 and UBr_4, but an autoionized solid, *viz.* $[UI_2tpao_4][UI_6]$. The properties of these species are discussed and compared to their chloro- and bromo-analogues.

Introduction

Arsine oxide ligands are very strong neutral donor ligands [1] which are suitable for the stabilization of Lewis acids of A-type metals, as recently indicated by the relative stability of $CeCl_4tpao_2$ (tpao = triphenylarsine oxide) [2]. The interaction of some Lewis acids like $MoCl_5$ [3] and UCl_5 [4], however, is so strong that oxygen atom abstraction occurs; e.g. $MoOCl_3$ and $UOCl_3$ are formed. In the case of strongly reducing Lewis acids, oxidation of the metal species is also possible.

Arsine oxide ligands, however, form very stable UX_4 complexes [5] of the type UX_4L_2 (X = Cl and Br) which are only slightly soluble in commonly used polar non-aqueous solvents like acetone, methyl cyanide and nitromethane. Structural determinations indicated that U–O bond shortening and U–Cl bond lengthening occur in complexes of the type UCl_4L_2 (where L = teao) if the arsine oxide complex is compared with similar phosphine oxide and amide complexes [6]. In addition, the same effect is found on going from UCl_4teao_2 to UBr_4tpao_2, in which case the U–O bonds were found to be 2.16 Å [7] and 2.128 Å [8], respectively, (teao = triethylarsine oxide). The latter distance must be regarded as a particularly short U–O bond distance for a neutral oxygen donor ligand towards U(IV) if the U–O bond distance of 2.11 Å found in the U(V) complex UCl_5-tppo (tppo = triphenylphosphine oxide) [9], is considered. It was, therefore, of interest to study the interaction between UI_4 and an arsine oxide ligand like tpao, not only in a U:ligand ratio of 1:2, but also using excess ligand. Earlier work indicated [5] that a species UBr_4tpao_4 and a chloro-complex of similar approximate composition could be prepared.

A fundamental study of the reaction between UI_4 and tpao has been undertaken. Some solid complexes were isolated, characterized and their properties correllated with their behaviour in solution. These properties were then also compared to those of their chloro- and bromo-analogues. We now report the result of this study and some of the very uncommon aspects of this coordination chemistry.

Experimental

Materials

Triphenylarsine oxide (tpao) (Riedel de Haën) was dissolved in CH_2Cl_2 (or mecn) and dried over activated 3 Å molecular sieves before use. $AgClO_4$ (BDH) was dried over $Mg(ClO_4)_2$ in a desiccator for 48 h before use. UCl_4 and UBr_4mecn_4 [10], UI_4mecn_4 and a UI_4 stock solution [11] were prepared as described previously. All solvents used were dried over activated molecular sieves and distilled in a nitrogen atmosphere before use.

Preparations

UCl_4tpao_2, UBr_4tpao_2 and UBr_4tpao_4 were prepared as described previously [5].

UCl_4tpao_4

UCl_4 (1 g) was dissolved in a minimum amount of acetone and added to an excess (~5 equivalents) of tpao (from a ~0.4 M stock solution). The mixture was stirred for ~5 min and diethyl ether was added until a faint turbidity just persisted in the solution. The mixture was cooled to −18 °C, upon which a light green solid precipitated. The solid was washed with ethyl acetate (2X) followed by isopentane and dried *in vacuo*.

---

*Author to whom correspondence should be addressed.

0020-1693/87/$3.50

$UCl_2tpao_4(ClO_4)_2$

To 10 cm^3 of a 0.3 M UCl_4 stock solution was added two equivalents of $AgClO_4$ (in acetone) and the mixture was stirred for ~10 min. The solid AgCl was removed from the reaction mixture by centrifuging in a sealed tube. To this $UCl_2(ClO_4)_2$ solution was added four equivalents of tpao (from the stock solution). Diethyl ether was added to the reaction mixture until a faint turbidity just persisted in the solution. Cooling to –18 °C resulted in the precipitation of a light green solid which was washed with ethyl acetate (2X) followed by isopentane and dried *in vacuo.*

$UBr_2tpao_4(ClO_4)_2$

This compound was prepared similarly to UCl_2-$tpao_4(ClO_4)_2$, but starting from a UBr_4mecn_4 stock solution in acetone.

α-UI_4tpao_2

To ~0.8 g of UI_4mecn_4 dissolved in 10 cm^3 of ethyl acetate was added ~2 equivalents of Bu_4NI in a minimum of mecn (~5 cm^3), followed by two equivalents of tpao (from the stock solution in CH_2Cl_2). A bright orange–red solid precipitated immediately, wich was washed with isopentane (1 X 5 cm^3) and dried *in vacuo.*

β-UI_4tpao_2

Five cm^3 of the UI_4 stock solution (containing ~1.8 mmol of uranium) in a ~9:1 mixture of mecn and ethyl acetate was cooled to –10 °C. Two equivalents of tpao from the stock solution in mecn (also at –10 °C) were added and the mixture was stirred briefly. Yellow–green crystals started to form after ~5 min. The mixture was kept at –18 °C for ~2 h to allow complete precipitation of the complex. The yellow–green solid was washed with cold (–10 °C) ethyl acetate (2X) followed by cold isopentane and dried *in vacuo* at room temperature.

UI_4tpao_4

To 3 cm^3 of the UI_4 stock solution (~1.1 mmol of uranium), diluted to 10 cm^3 with mecn, were added four equivalents of tpao (from the stock solution). Isopentane was added to the mixture until the faint turbidity that formed just disappeared. The mixture was cooled to –18 °C, upon which a yellowish–green solid formed. The solid was washed with ethyl acetate, followed by isopentane and dried *in vacuo.*

UI_4tpao_6

To ~0.5 g of UI_4tpao_4 in CH_2Cl_2 were added an additional four equivalents of tpao and the mixture was stirred until no more solid could be detected in the reaction mixture. Isopentane was added until a faint turbidity just persisted in the solution. Cooling to –18 °C resulted in the formation of a light green solid which was washed with isopentane and dried *in vacuo.*

Instrumentation

Infrared studies

Infrared spectra of the solids were recorded on a Beckman 4250 (4000–200 cm^{-1}) instrument, as Nujol mulls mounted between CsI cells. Solution spectra were recorded in CH_2Cl_2 using KBr liquid cells.

Electronic spectra

Electronic spectra of the solids were recorded at room temperature with samples mounted as mulls, in fluorinated carbon, between glass plates, on a Beckman DK2A spectrophotometer. Spectra of solutions were recorded in CH_2Cl_2 on a Perkin-Elmer 330 UV–Vis spectrophotometer.

Thermogravimetric analysis

A Perkin-Elmer TGS-2 thermobalance was used as described previously [12]. Nitrogen was used as carrier gas and a constant heating rate of 5 °C per min was used.

Conductivity measurements

Conductivities of 0.003 M solutions (in acetone) of the metal complexes were recorded using a Phillips PW9505 conductivity meter and a Phillips PW 9510 conductivity cell. Solutions of hygroscopic complexes were prepared in a nitrogen atmosphere dry box using freshly distilled solvents.

Analysis

Uranium was precipitated as the hydrous oxide from aqueous acetone solutions by aqueous NH_3 and determined as U_3O_8 after ignition at 750 °C. Halide was determined by potentiometric titration after removal of the uranium by precipitation.

Results and Discussions

UX_4tpao_4 Complexes (X = Cl, Br and I)

The formation of solids having approximate compositions UCl_4tpao_4 and UBr_4tpao_4 have been mentioned previously [5]. We now have prepared UI_4tpao_4 as well as the latter two complexes. The infrared spectra of these complexes in Nujol mulls do not show the presence of any uncoordinated tpao. The solid reflectance spectra of these complexes are very similar to spectra normally obtained from six-coordinated uranium(IV) complexes, which suggests

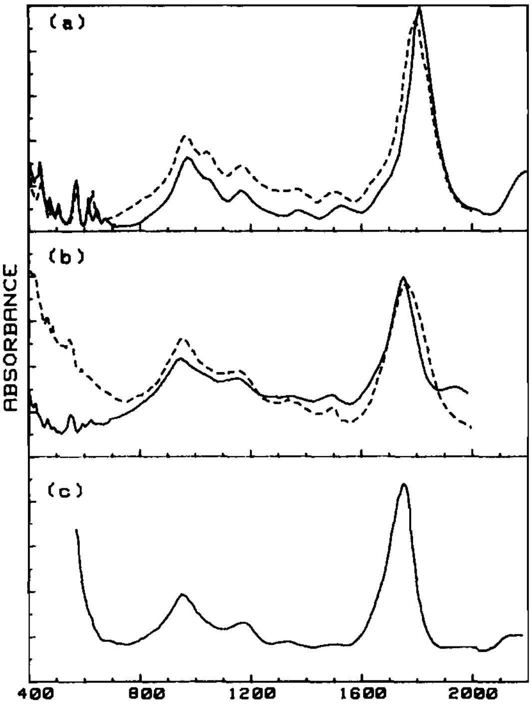

Fig. 1. Solid reflectance electronic spectra of: (a) UCl_4tpao_4 and $UCl_2tpao_4(ClO_4)_2$ (dotted line); (b) UBr_4tpao_4 and $UBr_2tpao_4(ClO_4)_2$ (dotted line); (c) UI_4tpao_4.

six-coordination in these complexes. In the light of the above, the logical structure for these complexes seemed to be $UX_2tpao_4^{2+}$ $2X^-$.

In order to obtain more supportive evidence for this supposition, $UX_2tpao_4(ClO_4)_2$ complexes (for $X = Cl^-$ and Br^-) were isolated. Their solid reflectance electronic spectra were found to be almost identical to the spectra of the corresponding UX_4L_4 complexes with respect to the positions and number of absorptions (see Fig. 1). The positions of the bonded As=O stretching frequencies are also very similar in the infrared spectra of UCl_4tpao_4 and $UCl_2tpao_4(ClO_4)_2$. This applies equally well to their bromo-analogues (see Table I). The non-coordinating nature of the perchlorate ion is confirmed by the presence of the very strong absorption at ~1100 cm^{-1}, which is ascribed to ionic perchlorate [13]. No complex of the type $UI_2tpao_4(ClO_4)_2$ could thus far be isolated. The close similarity between the solid reflectance electronic and mull infrared spectra of UI_4tpao_4 and the complexes UX_4tpao_4 and $UX_2tpao_4(ClO_4)_2$ ($X = Cl^-$ and Br^-), as well as the fact that the molar conductivities of all these complexes fall in the narrow range 175–205 S cm^2 mol^{-1}, suggest the presence of the hexa-coordinated unit $UX_2L_4^{2+}$ in all of these complexes.

The electronic spectra of UCl_4tpao_4 and UBr_4tpao_4 recorded in CH_2Cl_2 solution are somewhat different from the solid reflectance spectra in that an additional band appears in the spectrum at ~1900 nm (compare Fig. 1). The appearance of this additional band in the electronic spectra of the solution is accompanied by the presence of small amounts of uncoordinated tpao, as shown by the infrared spectra of these complexes recorded in CH_2Cl_2 (feature appearing at 880 cm^{-1}). It would thus appear that some coordination of the free halide ions in the solid complexes occurs upon dissolution, leading to the formation of a small amount of the UX_4L_2 species and free ligand. The UX_4tpao_2 ($X = Cl^-$ and Br^-) complexes do indeed show strong absorptions at

TABLE I. Analytical and Physical Data of the Complexes

Compound	Analytical data Found (Calc.) (%)				Infrared data (cm^{-1})		Conductivity Λ_{500} (S cm^2 mol^{-1})
	U	X	C	H	$\nu_{(As=O)}$	$\Delta\nu_{(As=O)}$	
tpao					880		
UCl_4tpao_2	23.0(23.24)	13.7(13.84)			838	42	
$UBr_4(tpao)_2$	19.7(19.80)	26.4(26.59)			824	56	
α-$UI_4(tpao)_2$	16.9(17.12)	36.3(36.52)	31.7(31.10)	2.31(2.18)	821	59	
β-$UI_4(tpao)_2$	16.9(17.12)	36.1(36.52)	30.8(31.10)	2.4(2.18)	805	75	
UCl_4tpao_4	14.1(14.26)	8.4(8.50)			840	40	176
UBr_4tpao_4	12.8(12.89)	17.1(17.31)			833	47	187
UI_4tpao_4	11.5(11.70)	24.6(24.95)	42.8(42.50)	3.14(2.97)	820	60	179
UI_4tpao_6	8.8(8.88)	18.7(18.95)	48.0(48.42)	3.7(3.39)	850–825		
			ClO_4^-				
$UCl_2tpao_4(ClO_4)_2$	13.0(13.25)	3.7(3.95)	10.7(11.07)		843	37	183
$UBr_2tpao_4(ClO_4)_2$	12.4(12.62)	8.3(8.48)	10.2(10.55)		835	45	196

1900 nm in CH_2Cl_2 solution. Small amounts of species like $UX_3tpao_3^+$ X^-, however, cannot totally be ruled out. It is further of interest to note that the indications for the formation of UBr_4tpao_2 from UBr_4tpao_4 in CH_2Cl_2 is not as prominent as for the formation of UCl_4tpao_2 from UCl_4tpao_4 in CH_2Cl_2. This is in agreement with the relatively stronger U–Cl interaction compared to U–Br interaction, as is also indicated by the infrared data (Table I) of the UX_4L_4 complexes. A larger As=O shift is found for UBr_4tpao_4 than for UCl_4tpao_4.

No indications for the formation of a UI_4tpao_2 complex from UI_4tpao_4 in CH_2Cl_2 could be obtained in the electronic or the infrared spectrum of the latter complex in CH_2Cl_2. Although the tendency for such a reaction would be much smaller than for the UBr_4tpao_4 complex, this observation must also be seen in the light of the low stability of the β-UI_4tpao_2 complex which is discussed below.

UI_4tpao_2 Complexes

The reaction of UI_4 with two equivalents of tpao is quite remarkable in that two types of UI_4tpao_2 complexes can be isolated. When UI_4 is reacted with two equivalents of tpao in a mecn/ethyl acetate mixture at room temperature, a deep red solution results. These red solutions were first interpreted in terms of oxidation of UI_4 by tpao, in view of the reported oxidation of UI_4 by tppo [14] and the yellow–green solutions normally obtained when UI_4 is reacted with C=O or P=O donor ligands [11]. Small amounts of red solid can usually be obtained from these red solutions and this proved to have UI_4tpao_2 stoichiometry by uranium, iodide, C and H analysis. The red solid α-UI_4tpao_2 can, however, be prepared in much larger yields by the reaction of UI_4mecn_4 with tpao in ethyl acetate solution (see experimental section).

When the reaction between UI_4 and two equivalents of tpao in a mecn/ethyl acetate solvent mixture is performed at –10 °C, however, the yellow–green β-UI_4tpao_2 precipitates (see experimental section). This solid is extremely hygroscopic and when kept in an inert nitrogen atmosphere at room temperature, its colour changes from yellow–green via yellow and red to black in a period of 7–14 days. Infrared spectra recorded of this complex over this time show the appearance of a band at ~920 cm^{-1} due to the formation of UO_2^{2+}.. The above observation is in agreement with the thermal decomposition studies performed on this complex in a dry N_2 atmosphere, which showed it to start degrading at ~110 °C. The solid reflectance spectrum of the β-UI_4tpao_2 complex is similar to the spectrum recorded for the six-coordinated UBr_4tpao_2 (see Fig. 2). U–I interaction does, however, cause the ultraviolet cut-off to occur at a considerably higher wavelength for the iodo complex, compared to the bromo-complex, as a result of the red shift of the charge-transfer bands. The infrared data recorded in the table for the UX_4L_2 complexes show a significant shift in the position of the As=O stretching frequency in going from UCl_4tpao_2 to β-UI_4tpao_2.

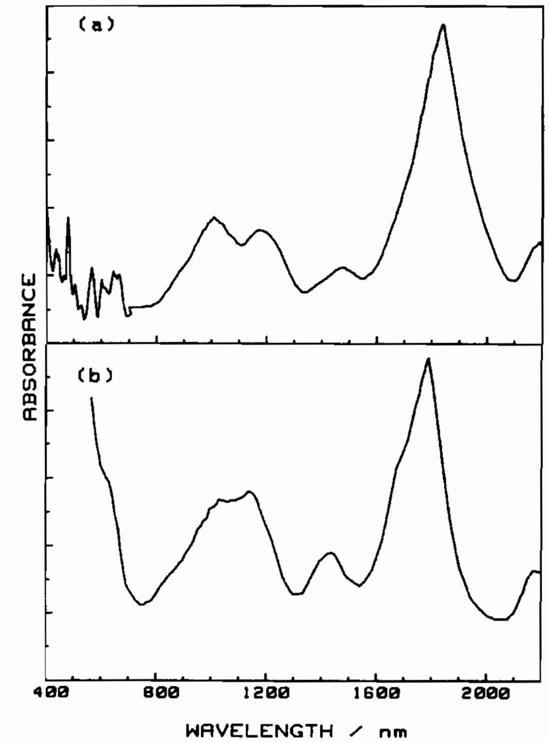

Fig. 2. Solid reflectance electronic spectra of: (a) UBr_4tpao_2 and (b) β-UI_4tpao_2.

The solid reflectance spectrum of the α-UI_4tpao_2 complex differs substantially from that recorded for the β-form in that an additional band at 2170 nm is present. The position of the As=O stretching frequency in the infrared spectrum of the α-form occurs some 15 cm^{-1} higher than for the β-form. Strong absorptions (relative to the rest of the electronic spectrum) in the 1800–2200 nm region are normally indicative of the presence of six-coordinated uranium(IV). The absorption occurring at ~2170 nm in the spectrum of α-$UI_4(tpao)_2$ corresponds with the analogous absorption found in the spectrum of UI_6^{2-} (Fig. 3). The absorption occurring at 1750 nm, on the other hand, corresponds to the analogous absorption found in the spectrum of UI_4tpao_4 (Fig. 3). The above observations thus suggest α-UI_4tpao_2 to be diiodotetrakis(triphenylarsine oxide)hexaiodouranate(IV), *i.e.* $[UI_2tpao_4][UI_6]$. The red colour of α-UI_4tpao_2 is in agreement with the above assignment, as the red colour could be ascribed to the typical red colour of the UI_6^{2-} entity present. The infrared spectra of α-UI_4tpao_2 and UI_4tpao_4 are shown in Fig. 4 and the positions of the As=O stretching

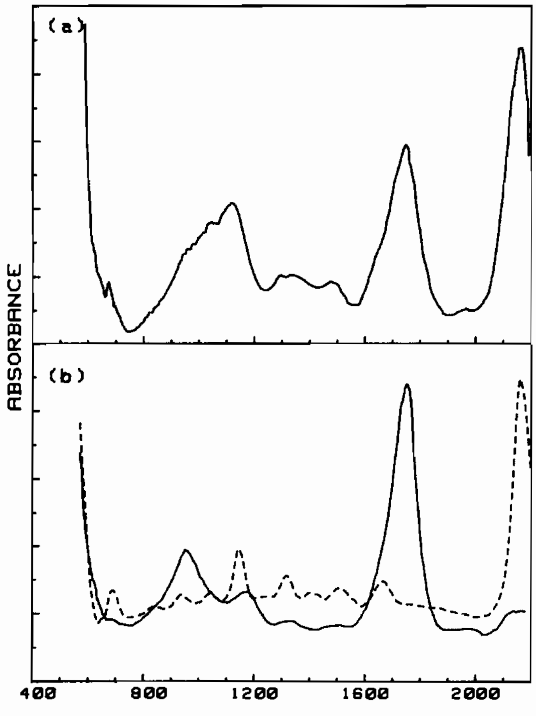

Fig. 3. Solid reflectance electronic spectra of: (a) α-UI_4tpao_2, and (b) UI_4tpao_4 and $(Ph_4P)_2UI_6$ (dotted line).

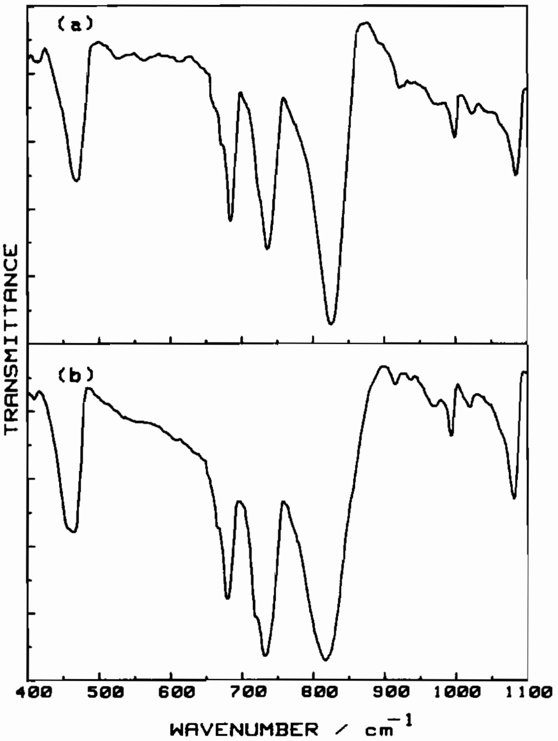

Fig. 4. Infrared spectra of (a) UI_4tpao_4 and (b) α-UI_4tpao_2.

frequencies are recorded in Table I. It can be seen that the spectra of these two complexes are virtually identical, especially with reference to the position of the As=O stretching frequency.

Although auto-ionization is not uncommon for uranium(IV), it is rather surprising in this case. Auto-ionization of Lewis acids of the type MX_n (M = metal, X = anion and $n = 2-6$) are normally expected for cases where the anionic ligands and competing neutral donor ligand is of comparable donor strength [15]. In all the examples of auto-ionization known for UX_4 species, the above postulation seems to hold; examples being $UCl_4(dmso)_3$, *i.e.* $[UCl_2(dmso)_6][UCl_6]$ [16]; and $UCl_4(depa)_{2.5}$, *i.e.* $[UCl_3(depa)_4][UCl_5depa]$ (depa = N,N-diethylpropionamide) [17]. The crystal structure of UBr_4tpao_2 has recently been published [8] and it was concluded that the U–O bond length (found to be 2.12 Å) must be close to the critical distance for the existence of uranium(IV). The infrared data recorded for the UX_4L_2 complexes ($X = Cl^-$ and Br^-) and for β-UI_4tpao_2 (Table I) show a significant shift in the position of the As=O stretching frequency in going from Cl^- to I^-. This shift is indicative of a general U–O bond shortening in the direction of $UCl_4tpao_2 \rightarrow$ β-UI_4tpao_2 and it can thus be stated, with a certain amount of confidence, that the U–O bond length in β-UI_4tpao_2 will be significantly shorter than in UBr_4tpao_2. It must, however, also be kept in mind that U–O bond shortening is usually accompanied by a general U–X bond lengthening [6], so that the relative U–I bond strength would also play a significant role in the stability of a *trans*-octahedral uranium(IV) complex such as UI_4tpao_2.

The relative stabilities of β-UI_4tpao_2, α-UI_4tpao_2 and UI_4tpao_4 are clearly illustrated by their thermal degradation curves in Fig. 5. Decomposition of these complexes starts at ~110 °C, ~200 °C and ~180 °C, respectively. Thermal decomposition of $(As\phi_4)_2UI_6$ was reported to start above 200 °C [4]. The stability of the large UI_6^{2-} ion is strongly dependent on cation size [4]. The cation in α-UI_4tpao_2, *viz.* $[UI_2tpao_4]^{2+}$

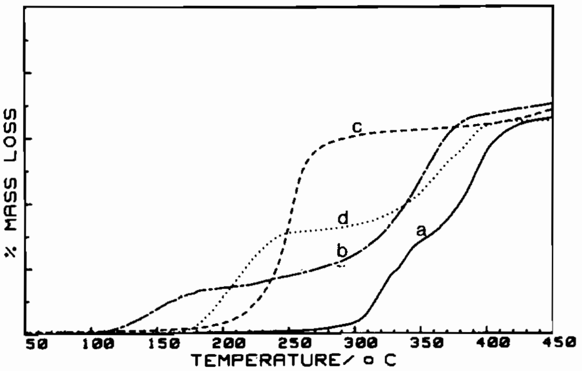

Fig. 5. Thermal degradation curves of: (a) UBr_4tpao_2; (b) β-UI_4tpao_2; (c) α-UI_4tpao_2, and (d) UI_4tpao_4.

is very large and thus very suitable as a counter ion for UI_6^{2-}. Furthermore, the replacement of two iodide ions in the *trans*-octahedral UI_4tpao_2 species by two additional arsine oxide ligands results in a more stable species. The ion-pairing between the two large matching ions provides further stabilization. This occurs to such an extent that $[UI_2tpao_4][UI_6]$ appears to be considerably less hygroscopic than the $(Ph_4P)_2UI_6$ salt. The former is also only very slightly soluble in commonly used non-aqueous solvents like acetone and methyl cyanide.

The relative instability of the *trans*-octahedral complex can partly be explained by the stability of the auto-ionized species mentioned above, but partly by the very significant U–I bond weakening as a result of the very strong U–O interaction of the tpao in the former species.

UI_4tpao_6 Complex

Triphenylarsine oxide is apparently capable of totally replacing iodide from the coordination sphere of uranium(IV) through the formation of UI_4tpao_6 when excess ligand is used (ratio of U:tpao greater than 1:8 in solution). The solid reflectance electronic spectrum suggests it to be six-coordinated. The major typical peak is at 1710 nm, thus somewhat lower than that of UI_4tpao_4. The start of the charge-transfer peak (ultraviolet cut-off) is in the region of 400 nm. This is significantly shifted even from that of UI_4tpao_4 (~500 nm). The mull infrared spectrum has no indication of free ligand although the presence of free tpao is indicated in its CH_2Cl_2 solution.

Conclusions

In conclusion it can be stated that the very strong ligand tpao plays a very dominating role in its complexation with UI_4. This is clearly revealed in the large shifts in the solid reflectance electronic spectra experienced when its UI_4 complexes are compared with the corresponding spectrum of UI_6^{2-}.

In the case of the *trans*-octahedral species, the interaction is so strong that instead of the stabilization which normally occurs with UX_4tpao_2 species (X = Cl or Br), destabilization occurs and the auto-ionized species is formed somewhat unexpectedly.

Acknowledgements

The authors thank the South African Council for Scientific and Industrial Research, and the University of Port Elizabeth for financial assistance.

References

1 J. G. H. du Preez, B. J. Gellatly, M. L. Gibson, D. R. Groot and H. E. Rohwer, *J. S. Afr. Chem. Inst., 29,* 105 (1976).

2 J. Barry, J. G. H. du Preez, T. I. A. Gerber, A. Litthauer, H. E. Rohwer and B. J. A. M. van Brecht, *J. Chem. Soc., Dalton Trans.,* 1265 (1983).

3 S. M. Horner and S. Y. Tyree, *Inorg. Chem., 1,* 122 (1962).

4 K. W. Bagnall, D. Brown and J. G. H. du Preez, *J. Chem. Soc.,* 5217 (1965).

5 J. G. H. du Preez, B. J. Gellatly and M. L. Gibson, *J. Chem. Soc., Dalton Trans.,* 1062 (1977).

6 J. G. H. du Preez, B. J. Gellatly, G. Jackson, L. R. Nassimbeni and A. L. Rodgers, *Inorg. Chim. Acta, 27,* 181 (1978).

7 J. G. H. du Preez, B. J. Gellatly and M. Laing, *J. Inorg. Nucl. Chem., 38,* 1872 (1976).

8 J. F. de Wet and M. R. Caira, *J. Chem. Soc., Dalton Trans.,* 2043 (1986).

9 G. S. Smith, Q. Johnson and R. E. Elson, *Acta Crystallogr., 22,* 300 (1967).

10 J. G. H. du Preez, M. L. Gibson and C. P. J. van Vuuren, *J. S. Afr. Chem. Inst., 24,* 135 (1971).

11 J. G. H. du Preez and B. Zeelie, *Inorg. Chim. Acta, 118,* L25 (1986).

12 J. G. H. du Preez, A. Litthauer, C. P. J. van Vuuren, *Thermochim. Acta, 39,* 163 (1980).

13 (a) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.,* 3091 (1961); (b) M. Vidali, P. A. Vigato, U. Casellato, E. Tondello and O. Traverso, *J. Inorg. Nucl. Chem., 37,* 1715 (1975); (c) F. L. Wimmer and M. R. Snow, *Aust. J. Chem., 31,* 267 (1978).

14 N. Kumar and D. G. Tuck, *Inorg. Chim. Acta, 95,* 211 (1984).

15 V. Gutmann, 'Coordinatión Chemistry in Non-Aqueous Solutions', Springer-Verlag, Vienna/New York, 1968.

16 G. Bombieri and K. W. Bagnall, *J. Chem. Soc., Chem. Commun.,* 188 (1975).

17 K. W. Bagnall, R. L. Beddoes, O. S. Mills and Li Xing-fu, *J. Chem. Soc., Dalton Trans.,* 1361 (1982).