The Chemistry of Uranium.
Part X. Octahedral Pentahalouranate(IV) Complexes

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Spectrophotometric and conductometric evidence for the existence of the octahedral $(UX_5 \cdot L)^-$ species (X = Cl, Br and I and L = neutral monodentate ligand) has been obtained. The conditions for the formation of these and their UX_6^{2-} analogues in different non-aqueous solvents and in the presence of a variety of neutral ligands are reported. The following donor strength order was established using the data obtained: chloride $\geqq$ tmpo, hmpa > sulphoxides (dmso), C=O amides (dma, cl, etc.) > Br⁻ > acetone, acetonitrile > iodide (tmpo = trimethylphosphine oxide, hmpa = hexamethylphosphoramide, dmso = dimethyl sulphoxide, dma = N,N-dimethylacetamide, cl = ε-caprolactam). The positions of nitrate and thiocyanate are also discussed. The implications of this order on the positions of the different equilibria obtained in the practical chemistry of uranium(IV) in non-aqueous solution are discussed. Conductometric evidence obtained for $ThCl_4$ suggests that eight coordinated $(ThCl_5 \cdot 3L)^-$ and $ThCl_8^{4-}$ species exist in non-aqueous solution.

Introduction

Although a pentachloro solvated uranate(IV) species, *viz.* $(UCl_5 \cdot xacetone)^-$ was proposed in the literature[1] to explain the uncommon stoichiometry of the $UCl_4 \cdot 3acetone$ complex, more substantial evidence for the existence of such a species, specifically the value of x and the symmetry of the species, was not given.

During recent spectrophotometric studies on acetone solutions of UCl_4 in which the purpose was to study the relative donor strengths of anions and neutral oxygen donor ligands, we observed that the electronic spectrum of the UCl_4 acetone solvate changed from that of eight (or higher) coordinated uranium to that of a typical octahedral uranium(IV) species upon addition of one chloride ion per mole of UCl_4. This result, and a similar end-point obtained in a corresponding conductometric titration, left little doubt that the predominant species present in such a solution is

an octahedral pentachlorouranate(IV) solvate of acetone, *viz.* $(UCl_5 \cdot acetone)^-$.

The conditions under which this species, other similar species and the corresponding hexaanionic species can be obtained with chloride, bromide, iodide and thiocyanate in different non-aqueous solutions and in the presence of a variety of neutral oxygen donor ligands, were now studied. The ligands used were N,N-dimethylacetamide (dma), ε-caprolactam (cl), α,α-diphenyl-N,N-dimethylacetamide (ddma), N,N-dimethylbenzamide (dmba), trimethylphosphine oxide (tmpo), hexamethylphosphoramide (hmpa) and triphenylphosphine oxide (tppo). The results of this work were used to set up a donor strength order of the anions and neutral donors studied. The implications of these results upon the practical chemistry of uranium(IV) is discussed. Efforts were made to isolate M(UX₅·solvate) complexes (where M = large monovalent cation).

Experimental

Titrations

The reaction between a $0.004 M$ acetone solution of the uranium or thorium species and a $0.4 M$ solution of the titrant was followed spectrophotometrically (600–1200 nm region) and conductometrically. Measurements were made initially and after successive additions of 0.5 (spectrophotometric) and 0.1 (conductometric) molar equivalents up to a total of ten molar equivalents.

Materials

$UCl_4 \cdot 2.5ddma$, $UBr_4 \cdot 3dmba$, $UBr_4 \cdot 5dma$, $(Net_4)_2 UBr_6$, UCl_4 and $UBr_4 \cdot 4MeCN$ were prepared as previously described.[2,3]

Analysis

Thorium,[4] uranium and halide analysis were performed as previously described.[2]

Apparatus

Electronic spectra were determined by a Beckman DK2A spectrophotometer. Conductivity measurements were obtained using a Metrohm Konduktoskop.

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Attempts to Prepare M(UX$_5$L) (M = Large Monovalent Cation, X = Cl and Br and L = Strong Oxygen Donor Ligands)

[P(Ph)$_4$](UCl$_5$·dmso):

One mmol of each of UCl$_4$, P(Ph)$_4$Cl and dmso were dissolved in acetone and mixed. The solution was vacuum concentrated and cooled. A green product separated, which was washed with diethyl ether, vacuum dried and analysed. Found: U, 23.7%, Cl, 18.7%. Calculated for [P(Ph)$_4$](UCl$_5$·dmso): U, 28.59%; Cl, 21.31% and for [P(Ph)$_4$]$_2$UCl$_6$: U, 21.09%; Cl, 18.86%. The dma and tmpo analogues were tried similarly. These results also proved to be mixtures having Cl:U ratios bigger than five.

[P(Ph)$_4$](UBr$_5$·L)

When 1:1:1 ratios of [P(Ph)$_4$]Br, UBr$_4$ and L (L = dmso, dma and tmpo) were mixed in acetone and treated similarly to the chloro complexes, the analysis of the products indicated that they were mixtures. If a slight excess of neutral donor was used the neutral complex crystallized out. UBr$_4$·6dmso could be prepared by the following method. A methyl cyanide solution (5 ml) of dmso (0.3 g) was slowly added to a hot solution (20 ml) of (Net$_4$)$_2$UBr$_6$ in the same solvent. The green crystals which separated upon cooling, were washed once with ethyl acetate, twice with diethyl

ether, vacuum dried and analyzed. Found: U, 23.2; Br, 30.6%. Calc. for UBr$_4$·6dmso: U, 23.18; Br, 31.14%.

Results and Discussion

The various spectrophotometric titrations performed are listed in Table I. The uranium species (0.004 *M* acetone solutions unless otherwise stated) are given in the first column and the titrant species (0.4 *M* dissolved in the same solvent) are given in the second column.

(UX$_5$·acetone)$^-$ Species (X = Cl and Br)

When an acetone solution of UCl$_4$ is titrated with one equivalent of chloride ion (Nbut$_4$Cl) the electronic spectrum changes from that of eight coordinated uranium(IV) to a spectrum typical of octahedral uranium(IV) and similar to that of (Net$_4$)$_2$UCl$_6$ (see curves a and b in Figure 1). In the corresponding conductometric titration an end-point is obtained under similar conditions (see first end-point in curve a, Figure 2). It is now assumed that the uranium species at this end-point consists mainly of octahedral (UCl$_5$·acetone)$^-$. Addition of another equivalent of a chloride ion has only a small effect on the spectrum (curve c, Figure 1). The reduction in molar extinction

TABLE 1. Spectrophotometric Titrations.

		Solution Titrated[a]	Titrant
(a)	(i)	UCl$_4$ + 1 equivalent of chloride	1 equivalent of each of dma, dmso, cl, tmpo, tppo and hmpa, respectively.
(a)	(ii)	Each of UCl$_4$·2.5dma, UCl$_4$·3dmba, UCl$_4$·2.5ddma and UCl$_4$·4cl (the latter was also titrated in a methylene dichloride solution)	chloride ions[b]
(a)	(iii)	(Net$_4$)$_2$UCl$_6$ in each of methyl cyanide and nitro methane	dma, dmso, cl and tmpo
(a)	(iv)	Tetraphenyl phosphonium hexachlorouranate(IV) in CH$_2$Cl$_2$ solution	cl
(a)	(v)	Each of UBr$_4$·6cl, UBr$_4$·2.5ddma, UBr$_4$·3dmba and UBr$_4$·5dma (UBr$_4$·6cl was also titrated in methylene dichloride solutions)	bromide ions
(a)	(vi)	(Net$_4$)$_2$UBr$_6$ in methyl cyanide solution	each of dma, dmso, cl and tmpo
(b)	(i)	UCl$_4$	each of bromide, iodide and thiocyanate
(b)	(ii)	UBr$_4$	each of iodide and thiocyanate
(b)	(iii)	UCl$_4$ + 1 mole dma	one equivalent of each of chloride, bromide, thiocyanate and iodide

[a] Acetone was used as solvent in all cases except otherwise stated.

[b] Chloride, bromide and iodide were used in the form of their tetrabutylammonium salts and thiocyanate as the tetraethylammonium salt.
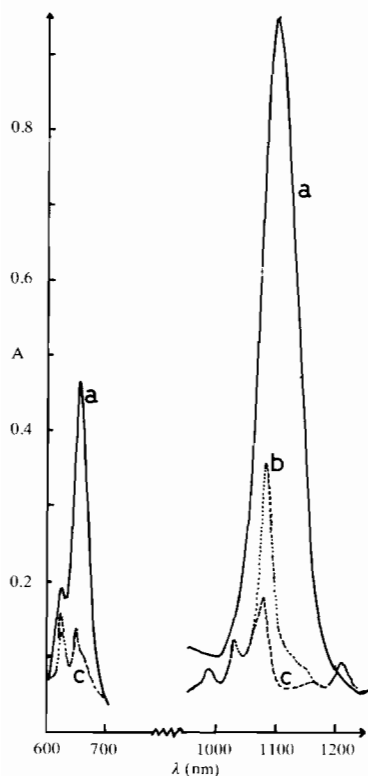
Figure 1. Electronic spectra of 0.004 M UCl_4 species in acetone solutions. Curve a, UCl_4 alone; curve b, UCl_4 + 1 equivalent of chloride (Tetrabutylammonium salts were used for both chloride and bromide in all the titrations); curve c, UCl_4 + 2 equivalents of chloride and UCl_4 + 1 equivalent of each of chloride and dma.

Figure 2. Conductometric titrations of 0.004 M acetone solutions of MX_4 species (M = U and Th, X = Cl and Br). Curve a, UCl_4 titrated with chloride; curve b, UBr_4 titrated with bromide; curve c, $UCl_4 \cdot 2.5$dma titrated with chloride; curve d, UBr_4 plus 2.5 mol equivalents of dma titrated with bromide; curve e, $ThCl_4 \cdot 4$dma titrated with chloride. Numerical divisions above abcissa refer only to $ThCl_4 \cdot 4$dma titration.

and very slight increase in the energy of the peak, from 1080 to 1075 nm, can be interpreted in terms of the formation of the more stable and centrosymmetric UCl_6^{2-} species. The end-point after two chloride equivalents have been added in the conductometric titration supports this (curve a, Figure 2).

Similar reactions take place in the reaction of bromide with UBr_4 in acetone solution. The "weaker" end-points in the corresponding conductometric titration (curve b, Figure 2) and the slightly larger "eight coordinated" shoulder in the spectrum after the addition of the equivalent of one bromide ion, as well as the slightly larger excess of bromide ions necessary to produce a constant spectrum (Figure 3, curves a, b and c) suggests smaller formation constants for the bromo species. This is to be expected in the light of the weaker donor strength of bromide as compared to chloride.

The above equilibria can be represented by equations 1 and 2:
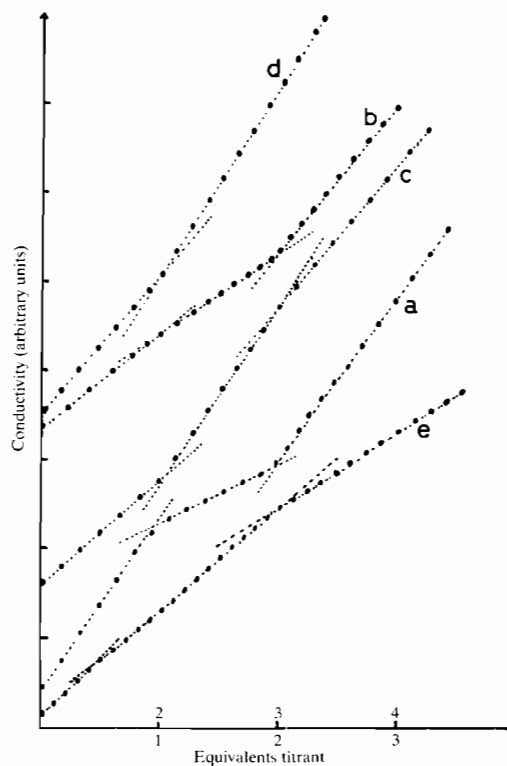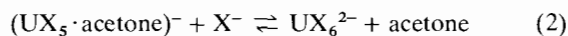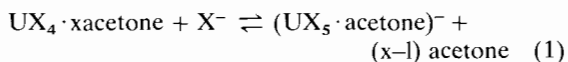
$$UX_4 \cdot x\text{acetone} + X^- \rightleftharpoons (UX_5 \cdot \text{acetone})^- + (x-1)\text{ acetone} \quad (1)$$

$$(UX_5 \cdot \text{acetone})^- + X^- \rightleftharpoons UX_6^{2-} + \text{acetone} \quad (2)$$
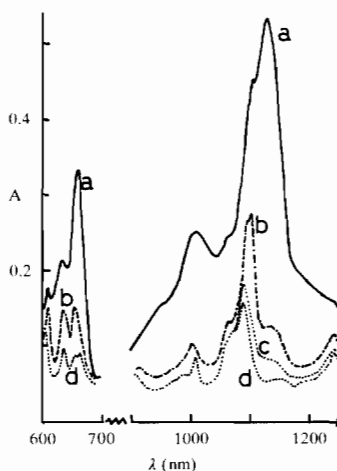

Figure 3. Electronic spectra of 0.004 M UBr_4 species in acetone. Curve a, UBr_4 alone; curve b, UBr_4 + 1 equivalent of bromide; curve c, UBr_4 + 2 equivalents of bromide; curve d, UBr_4 + 3 equivalents of bromide (spectra of UBr_4 + 1 equivalent of bromide + 1 equivalent of dmso is very similar to curve d).
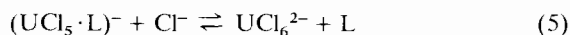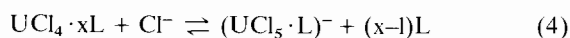
(UX₅·ligand)⁻ Species (X = Cl and Br)

The different types of titrations (see Table I a(i)–(vi)) were performed to determine under which conditions the above species are formed for each of dma, cl, dmso, tmpo, tppo and hmpa. A purely octahedral species is formed upon addition of one mol equivalent of ligand to the mixtures of 1 mol equivalent UCl_4 and one equivalent tetrabutylammonium chloride for each of these ligands (see Figure 1, curve c for dma as ligand). This not only indicates that these ligands are much stronger than acetone as a ligand for uranium(IV) but also exclude the possiblity that a dimeric centro-symmetric $U_2Cl_{10}^{2-}$ species forms under these conditions, since the concentration of such a species should be higher in the presence of the weaker donor solvent molecules (acetone) alone. Such a species would have "explained" the relatively low molar extinction values of the octahedral species formed. The above reactions can therefore be represented by eq. 3.

$$(UCl_5 \cdot acetone)^- + ligand \rightleftarrows (UCl_5 \cdot ligand)^- + acetone \quad (3)$$
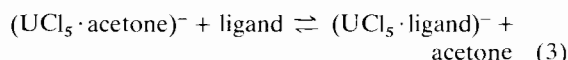
It is, however, possible that some disproportionation of $(UCl_5 \cdot L)^-$ takes place to form the more symmetrical UCl_6^{2-} and $UCl_4 \cdot 2L$ species, especially in the case of phosphoryl donor ligands where stable *trans* octahedral species, *e.g.* $UCl_4 \cdot 2hmpa$, are known to exist.[5] Their almost identical spectra do not allow any determination of the relative concentrations of these different species. This "disproportionation" does not, however, take place with dma, cl and dmso since acetone solutions of UCl_4 containing two equivalents of each of these do not produce pure octahedral spectra, which strongly suggests that the main octahedral species under these conditions is $(UCl_5 \cdot ligand)^-$.

A number of UCl_4 complexes of neutral oxygen donor ligands which have eight coordinated spectra, *viz.* $UCl_4 \cdot 2.5dma$, $UCl_4 \cdot 3dmba$, $UCl_4 \cdot 2.5ddma$ and $UCl_4 \cdot 4cl$ were now titrated with chloride ions (Table I, a(ii)).

Addition of one equivalent of chloride ion produced the same octahedral spectrum as obtained by titration a(i) (Table I) in each of these cases. Addition of more chloride ion did not change the spectra significantly. In the corresponding conductometric titrations two end-points were obtained in these cases at one and two equivalents of chloride ion, respectively (a typical titration curve for $(UCl_4 \cdot 2.5dma)$ is represented by curve c, Figure 2). These end-points were slightly "weaker" than in the corresponding titrations of acetone solutions of pure UCl_4. The reactions which take place in these instances can be represented by eq. 4 and 5:

$$UCl_4 \cdot xL + Cl^- \rightleftarrows (UCl_5 \cdot L)^- + (x-1)L \quad (4)$$

$$(UCl_5 \cdot L)^- + Cl^- \rightleftarrows UCl_6^{2-} + L \quad (5)$$

The presence of free ligand (L) was indicated by infra-red studies in these reactions. Similar results to these were obtained[6] when this spectrophotometric method was also applied to the eight coordinated $UCl_4 \cdot 4pa$ complex (pa = N-isopropylacetamide) in a recent study of the influence of the structure of the neutral donor ligand on its UCl_4 complex.

In order to determine how excess donor ligand reacts with hexachlorouranate(IV) the titrations listed in Table I a(iii) were performed. Methyl cyanide and nitromethane solutions were used for each titration (acetone could not have been used in these instances because of the low solubility of $(Net_4)_2UCl_6$ in this solvent). The spectrum remained that of octahedral uranium(IV) even after addition of a large excess of each of dma, dmso and cl.

Although the actual concentrations of $(UCl_5 \cdot L)^-$ and UCl_6^{2-} cannot be determined by this spectrophotometric method, these results indicate that chloride is clearly a stronger donor to uranium(IV) than dmso, dma or cl. A solution of $(Net_4)_2UCl_6$ in *pure* dma still contains only octahedral uranium(IV), *i.e.* UCl_6^{2-} and $(UCl_5 \cdot dma)^-$. In the case of tmpo an eight coordinated component was gradually built into the spectrum after addition of three equivalents of the ligand. The results were the same in both solvents. Tmpo, therefore, appears to be similar to chloride in donor strength.

The bromo complexes were titrated similarly to their chloro analogues (Table I, a(v). The spectra of each of these only gradually obtained a greater octahedral component when titrated with tetrabutylammonium bromide (see the curves in Figure 4 for $UBr_4 \cdot 6cl$). A conductometric titration of $UBr_4 \cdot 2.5dma$ had only an end-point after one equivalent of bromide was added
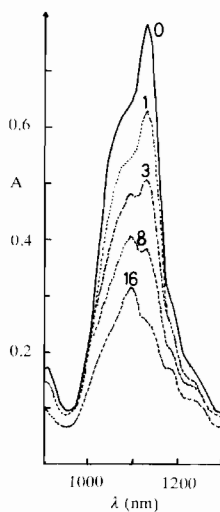

Figure 4. Electronic spectra of $0.0046M$ $UBr_4 \cdot 6$ cl species in acetone. The number of each curve corresponds with the number of equivalents $Nbut_4Br$ added per mole $UBr_4 \cdot 6cl$.

(Figure 2, curve d). Spectrophotometric titrations of $(Net_4)_2UBr_6$ with each of dma, dmso, cl and tmpo formed the octahedral $(UBr_5 \cdot L)^-$ species upon the addition of one mol equivalent. This corresponds with the slight reduction in ε_M value of the 1095 nm peak and its accompanying shift to about 1080 nm. The gradual increase of the eight coordinated component from as early as the second mol equivalent added, indicates how readily bromide is replaced by these neutral ligands (see the curves in Figure 5 for dmso).

Donor Strength Order of Ligands

The previous experiments suggest that the bromide ion is a stronger donor towards uranium(IV) than the weaker neutral donor ligands, *e.g.* acetone and methyl cyanide but weaker than the stronger ones, *e.g.* tmpo, dma, dmso, cl, *etc.* The chloride ion is stronger than all of these, but about equally as strong as the strongest phosphoryl ligands, *e.g.* hmpa and tmpo.

The experiments in Table I(b) were performed to extend this comparison to other anionic ligands. A considerable excess of iodide ions (5 equivalents) is necessary to react with UCl_4 in an acetone solution before a mainly octahedral species is formed, *e.g.* $(UCl_4 \cdot I \cdot acetone)^-$ and even the addition of twenty equivalents of iodide does not produce a completely octahedral species. Very similar results were obtained using UBr_4 instead of UCl_4. These data suggest that iodide is a weaker donor than even acetone.

The addition of one equivalent of thiocyanate to a UCl_4 solution in acetone produced a predominantly
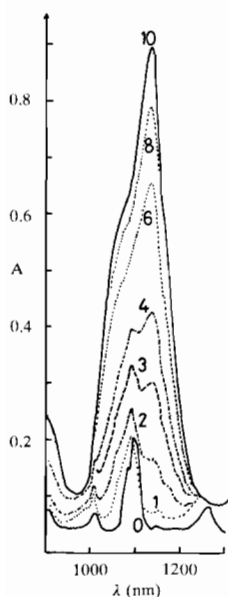

Figure 5. Electronic spectra of $0.005\,M$ $(Net_4)_2UBr_6$ species in methyl cyanide. The number of each curve corresponds with the number of equivalents of dmso added per equivalent of $(Net_4)_2UBr_6$.

octahedral species though with a bigger eight coordinated shoulder than that obtained in the corresponding titration of UBr_4 vs bromide. Since pure thiocyanato complexes of uranium(IV) are without exception eight coordinated,[7] the presence of a small amount of an eight coordinated species in this titration may possibly be due to the presence of a small amount of an eight coordinated uranium(IV) species containing U:NCS ratios of bigger than 1:1 already at this stage. This method cannot, therefore, be used effectively as a measure of its donor strength. The octahedral species present could, however, contain a large amount of the $(UCl_4 \cdot CNS \cdot acetone)^-$ species.

The following donor strength order is suggested by these data: chloride $\geqq$ hmpa, tmpo > sulphoxides (dmso), C=O amides (dma, cl, ddma, dmba) > bromide > acetone, acetonitrile > iodide.
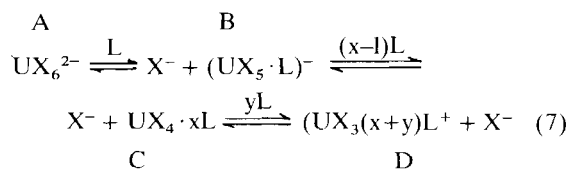
This spectrophotometric method can only be used effectively for neutral donors of which their uranium (IV) complexes have eight coordinated (or higher than six coordinated) structures in solution and anions which are known to form octahedral uranium(IV) complexes (UX_6^{2-}) in the solutions studied. Although it cannot, therefore, be used to determine the donor strength order of the nitrate ion or a donor strength order towards thorium ions, some information about these can be obtained from non-aqueous conductivity data. Conductometric titrations of dilute acetone solutions of $UX_4 \cdot 2hmpa$ (X = Cl, Br and NO_3) with excess hmpa now indicated that the order of replacement of these ligands is $Br^- > NO_3^- > Cl^-$, nitrate being closer to bromide than chloride. Hardly any increase of conductivity was obtained in the case of the chloride, indicating that it is not replaced under these conditions.

When a dilute acetone solution of $ThCl_4 \cdot 4dma$ is titrated with tetrabutylammonium chloride weak endpoints are obtained at one and four equivalents of the chloride (see Figure 2, curve e). Tetrabutylammonium bromide gave similar end-points. The end-point at four equivalents of chloride suggests that the $ThCl_8^{4-}$ species forms under these conditions. Solid complexes of this type have been claimed in the earlier literature.[8] It is also known that the anhydrous hexachlorothorate salts cannot be obtained pure from aqueous solutions as is the case with uranium.[9] Thorium tetrachloride adducts often have higher neutral donor to $ThCl_4$ ratios than those of UCl_4, *e.g.* $ThCl_4 \cdot 4dma$ but $UCl_4 \cdot 2.5dma$.[10] It is, therefore, likely that the weak end-point at one equivalent of chloride corresponds with the formation of an eight coordinated pentachlorothorate complex, *viz.* $(ThCl_5 \cdot 3dma)^-$. The reactions in the above conductometric titration can then be represented by the equilibria in eq. 6:

$$ThCl_4 \cdot 4dma + xCl^- \rightleftharpoons [ThCl_{(4+x)}(4-x)dma]^{x-}$$

$$(4 \geqq x \geqq 0)$$ (6)
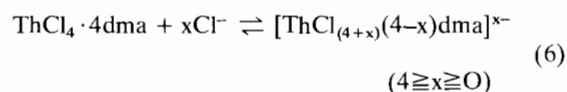
Applications of Donor Strength Order
The equilibria set out in eq. 7

$$\text{UX}_6^{2-} \underset{}{\overset{L}{\rightleftharpoons}} \overset{A}{X^-} + \overset{B}{(UX_5 \cdot L)^-} \overset{(x-1)L}{\rightleftharpoons}$$

$$X^- + \underset{C}{UX_4 \cdot xL} \overset{yL}{\rightleftharpoons} \underset{D}{(UX_3(x+y)L^+ + X^-} \quad (7)$$

can now be used to apply this order to the practical chemistry of uranium(IV). Solutions of M_2UCl_6 in strong donor solvents (dmso, dma), where the MCl species is also soluble in the solvent, give purely octahedral spectra and complexes of the type $UCl_4 \cdot xL$ cannot be prepared from these. If, however, MCl is insoluble in the system, chloride is removed from the equilibrium (eq. 7) and such complexes can be isolated, e.g. $UCl_4 \cdot 2.5$dma from Cs_2UCl_6 in acetone.[10] In spite of the fact that the $(UCl_5L)^-$ species is present in the equilibrium in acetone solutions of $(Net_4)_2 UCl_6$ in dma and dmso or even exists as the predominant species in an acetone solution containing UCl_4, Net_4Cl and dma or dmso in $1:1:1$ ratios, solid complexes of the type $M[UCl_5 \cdot L]$ could not be isolated (see Experimental). This must be ascribed to the low lattice energy of such species as compared to those of M_2UCl_6 and $UCl_4 \cdot xL$. The latter species (type C, eq. 7) are best prepared from JCl_4 itself and ionized species (type D) are seldom if ever obtained in non-aqueous media.

In the case of the weaker bromide the positions of all the equilibria are shifted to the right hand side in eq. 7 for the same ligand concentration as compared to those of chloride. $(UBr_5 \cdot L)^-$ species can, however, still be obtained in high concentrations in acetone solution at UBr_4:soluble bromide:ligand ratios of $1:1:1$. Solid complexes could not be obtained from such solutions for the reasons mentioned for chloride. Addition of a small excess of neutral donor increases the concentration of species C (eq. 7) to such an extent that such species can crystallize under these conditions in spite of the presence of soluble bromide (see preparation of $UBr_4 \cdot 6$dmso under Experimental). In the case of iodide it is very difficult to isolate a UI_6^{2-} species from a non-aqueous solution[11] and species of the type D is generally formed, e.g. $UI_4 \cdot 8cl$, $UI_4 \cdot 8$dmso.[1]

Autocomplex formation (eq. 8) is favoured when the donor properties of an anion and competing neutral ligand are similar:[12]

$$2MX_4 \overset{xL}{\rightleftharpoons} [MX_3(x-1)L]^+ + [UX_5 \cdot L]^- \quad (8)$$
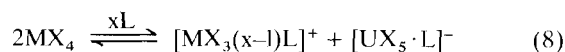
Strong evidence for autocomplex formation of MX_4 species (M = U and Th; and X = Cl, Br and NO_3) was recently obtained from the way in which their conductivities vary with the amount of neutral ligand added in conductometric titrations with dmso, dma and tmpo.[1,13] Although the anionic species in these solutions are of the $(UX_5 \cdot L)^-$ type and compounds like $UCl_4 \cdot 3$dmso, $UCl_4 \cdot 2.5$dma, $U(NO_3)_4 \cdot 2.5$dma and $Th(NO_3)_4 \cdot 2.5$dma are almost certainly also autoionized in the solid state, the nature of the anionic species in the solid state cannot merely be assumed to be the same and only full X-ray structure determinations will be conclusive.

Acknowledgement

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