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Complexes of Uranium(III) with Cyclic Polyethers and with Aromatic Diamines

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*The complexes $(UCl_3)_3$(benzo-15-crown-5)$_2$, UCl_3(cyclohexyl-15-crown-5), $(UCl_3)_3$(18-crown-6)$_2$, $(UCl_3)_5$(dibenzo-18-crown-6)$_3$, $(UCl_3)_5$(*cis-syn-cis*-dicyclohexyl-18-crown-6)$_3$, UCl_3(1,10-phenanthroline)$_2$, and UCl_3(2,2'-bipyridyl)$_2$ have been prepared by zinc amalgam reduction of acetonitrile or acetonitrile/propionic acid solutions of UCl_4 and the appropriate ligands. Reduction by sodium hydride was also used in one case. The complexes are brown, red, or purple solids which are oxidised in air and are insoluble in those common organic solvents with which they do not react. Electronic spectra were obtained by reflectance in the range 350–1500 nm, and magnetic susceptibilities of the crown ether complexes at 298 K are in the range 2.72–2.91 BM.*

Introduction

Moderately vigorous reduction of uranium(IV) will readily produce uranium(III) ($E_0 = -0.631$ v in 1 *M* $HClO_4$) [1]. However the simple reduced species is unstable in water and very unstable in air, and this has tended to hinder the study of the coordination chemistry of uranium(III). Also, a fairly strongly reducing metal ion may be expected to be incompatible with common oxygenated ligands such as NO_3^-, ClO_4^-, acac$^-$, $OPPh_3$, or $OSMe_2$. However, very considerable advances have been made recently. Thus Zn/Hg reduction in CH_3CN gives air-stable K_2UCl_5 [2, 3] or KU_2Cl_7 [3], from which diamide complexes, *e.g.* $[U(Me_2NCOCH_2CONMe_2)_4]^{3+}$, have been obtained [4]. An X-ray structure of air-stable $NH_4U(SO_4)_2(H_2O)_4$ has appeared [5], as have studies of complexes of U^{3+} with bidentate phosphonates [6].

Complexes formulated as UX_3(18-crown-6) (X = Cl or BH_4) were obtained [7] by NaH reduction of UCl_4 in thf followed by addition of the ligand (X = Cl) or by metathesis (X = BH_4). In neither case were the analytical results of these very air-sensitive compounds quite satisfactory, the average discrepancy being 1.60%. Preliminary X-ray results however indicated that derived crystalline material was $U_4(BH_4)_{12}$(18-crown-6)$_3$. By reaction of $NH_4UCl_4 \cdot 5H_2O$ [8] with the ligands in ethanol the following complexes were obtained [6]: UCl_3(18-crown-6), $U(PF_6)_3$(18-crown-6)$_2$, $UCl_2(BPh_4)$(dicyclohexyl-18-crown-6*), UCl_3(15-crown-5)$\cdot H_2O$ and $(UCl_3)_4$(dicyclohexyl-18-crown-6*)$_3$.

In view of our continuing interest in complexes of the lanthanides, particularly those of polydentate amines [9] and of crown ethers [10], and considering the similarity of ionic radius between U^{3+} (1.03 Å) and lanthanides (Ce^{3+}, 1.03 Å), we have investigated the reactions of U^{3+} with such ligands.

Experimental

Uranium tetrachloride was prepared by the action of hexachloropropene on uranium trioxide. The crown ethers were prepared by published methods and purified by one or more of the following as appropriate; treatment with P_4O_{10} to remove hydroxylic impurities, column chromatography, distillation, or crystallisation alone or as adducts with $Pb(ClO_4)_2$, $(H_3O)ClO_4$, or CH_3CN. Solvents were redistilled after drying over CaH_2 (acetonitrile) or Na/benzophenone (thf) and deoxygenated by freeze pumping or passage of nitrogen. Nitrogen was freed from traces of oxygen using a CrO column and from moisture by molecular sieve. While preparing the uranium(III) complexes, the reactions, filtrations, evaporations, transfers and other operations were carried out either under nitrogen or under vacuum as appropriate, using appropriate Schlenk-type apparatus.

Preparation of U_3Cl_9(benzo-15-crown-5)$_2$ (I)

A solution of UCl_4 (0.76 g, 2 mmol) and benzo-15-crown-5 (0.268 g, 1 mmol) in acetonitrile (50 cm^3) and propionic acid (1 cm^3) was freeze-degassed and shaken under nitrogen with excess zinc amalgam. A finely divided yellow-orange crystalline precipitate had formed after three hours but shaking was continued overnight to complete the reaction. The

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*It was not stated whether the *syn* or the *anti* form of the ligand was used, or a mixture.

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amalgam was separated and the product was then collected by filtration, washed thrice with acetonitrile, and dried at room temperature under vacuum. The yield was almost quantitative with respect to the crown ether. This yellow-orange product contained acetonitrile (strong, sharp infrared bands at 2266 and 2300 cm^{-1}) and analysis indicates U_3Cl_9(benzo-15-crown-5)$_2 \cdot 1.5CH_3CN$. *Anal.* Found: C, 22.5; H, 2.7; N, 1.4; Cl, 20.7%. $C_{28}H_{40}O_{10}Cl_9U_3 \cdot 1.5CH_3CN$ requires: C, 22.8; H, 2.75; N, 1.2; Cl, 19.6%. When heated at 110 °C under vacuum for 7 hours, the acetonitrile was removed (infrared) to leave the deep red unsolvated complex. *Anal.* Found: C, 21.0; H, 2.5; Cl, 20.9%. $C_{28}H_{40}O_{10}U_3Cl_9$ requires: C, 21.4; H, 2.6; Cl, 20.3%. The deep red complex immediately reacts with small traces of acetonitrile or water vapour to give yellow-orange solvated complexes (infrared).

Use of a different molar ratio (UCl_4: crown ether = 1:1.5) gave the same product as above, as shown by elemental analysis. Neither this complex nor those described below, gave solutions in non-reactive solvents.

Preparation of UCl_3(cyclohexyl-15-crown-5) (II)

UCl_4 (0.76 g, 2 mmol) and cyclohexyl-15-crown-5 (0.55 g, 2 mmol) were allowed to react with zinc amalgam under the conditions described above. The intensely red-purple product was isolated in a similar manner, and was dried under vacuum at 110 °C. *Anal.* Found: C, 26.6; H, 4.25; Cl, 16.9%. $C_{14}H_{26}O_5Cl_3U$ requires: C, 27.2; H, 4.2; Cl, 17.2%. This material readily combined with traces of moisture, as indicated by its infrared spectrum. The experiment was repeated using a different molar ratio (UCl_4: crown ether = 2:1) but the same product was obtained, as shown by elemental analysis.

Preparation of U_3Cl_9(18-crown-6)$_2$ (III)

Method a

UCl_4 (0.76 g, 2 mmol) and 18-crown-6 (0.28 g, 1 mmol) were allowed to react with zinc amalgam under the conditions described above. The red-brown crystalline product was collected, washed thrice with acetonitrile, and dried under reduced pressure at 110 °C. *Anal.* Found: C, 18.5; H, 2.95; Cl, 20.2%. $C_{24}H_{48}O_{12}U_3Cl_9$ requires: C, 18.45; H, 3.1; Cl, 20.4%. The same product was obtained using a ratio UCl_4: crown of 1:2.

Method b

UCl_4 (0.76 g, 2 mmol) in thf (50 cm^3) was treated with an excess of NaH (0.48 g). After 3 hours stirring, the mixture was pale purple. Stirring was continued for a further 17 hours, by which time the mixture was deep purple and was filtered from NaCl onto 18-crown-6 (0.28 g, 1 mmol). The solution immediately became red and a red-brown crystalline precipitate was deposited after a few minutes. After 5 hours, the solution was cooled overnight and the solid product was collected, washed with thf and dried under reduced pressure. The product (45% yield) was identical (UV and infrared) with that obtained by Method a.

Preparation of $(UCl_3)_5$(dibenzo-18-crown-6)$_3$ (IV)

UCl_4 (0.76 g, 2 mmol) and dibenzo-18-crown-6 (0.37 g, 1 mmol) were allowed to react with zinc amalgam under the conditions described above. The deep red product was collected, washed with acetonitrile, and dried under reduced pressure at 100 °C. *Anal.* Found: C, 25.9; H, 2.8; Cl, 19.6%. $C_{60}H_{72}O_{18}Cl_{15}U_5$ requires: C, 25.7; H, 2.6; Cl, 19.0%.

*Preparation of $(UCl_3)_5$(*cis-syn-cis-*dicyclohexyl-18-crown-6)$_3$ (V)*

UCl_4 (0.76 g, 2 mmol) and *cis-syn-cis*-dicyclohexyl-18-crown-6 (0.38 g, 1 mmol) were allowed to react with zinc amalgam under the previously described conditions. The red microcrystalline product was collected, washed with acetonitrile and dried under reduced pressure at 100 °C. *Anal.* Found: C, 25.5; H, 3.8; Cl, 18.5%. $C_{60}H_{108}O_{18}Cl_{15}U_5$ requires: C, 25.4; H, 3.8; Cl, 18.7%. The use of different molar ratios of reactants with UCl_4: crown = 1:1 or 1:1.5 gave identical products (analysis, UV and infrared).

Preparation of UCl_3(1,10-phenanthroline)$_2$ (VI)

UCl_4 (0.38 g, 1 mmol) and 1,10-phenanthroline (0.54 g, 3 mmol) were allowed to react with zinc amalgam under the conditions described above, with the difference that the propionic acid was omitted, as it was found to be inimical to reduction. The violet-purple microcrystalline product was collected, washed with acetonitrile, and dried at room temperature under reduced pressure. *Anal.* Found: C, 39.6; H, 2.2; N, 7.7; Cl, 16.3%. $C_{24}H_{16}N_4UCl_3$ requires: C, 40.9; H, 2.3; N, 7.95; Cl, 15.1%.

Preparation of UCl_3(2,2'-bipyridyl)$_2$ (VII)

UCl_4 (0.38 g, 1 mmol) and 2,2'-bipyridyl (0.48 g, 3 mmol) were allowed to react with zinc amalgam. Conditions were as described above for the phenanthroline complex, with the exception that the mixture was cooled in CO_2-acetone during the reaction. The deep purple product was collected, washed with acetonitrile and dried under reduced pressure. *Anal.* Found: C, 34.6; H, 2.4; N, 7.95; Cl, 18.1%. $C_{20}H_{16}N_4UCl_3$ requires: C, 36.6; H, 2.5; N, 8.5; Cl, 16.2%. The bipyridyl and the phenanthroline complexes were instantly decomposed by traces of air.

Magnetic susceptibilities were measured at 298 K by the Faraday method.

Complex	10^6 χ (cm^3 mol^{-1})	10^6 χ diamag (cm^3 mol^{-1})	μ eff (BM)
I	2972	−226	2.77
II	3237	−299	2.91
III	2847	−230	2.72
IV	2729	−245	2.67
V	2807	−268	2.72

Electronic spectra were obtained by reflectance measurements on powdered samples, using a Beckman DK2A spectrophotometer. Peak positions are shown in Table I, and in order to allow an appreciation of the general character of the spectra, the spectrum of (*III*) is shown as the Fig. 1. The *f–f* spectra of the amine complexes were obscured by broad strong absorption throughout the region 350–2000 nm, and those of the crown ether complexes were obscured to a lesser extent by similar absorption in the region 350–600 nm.

TABLE I. Electronic Spectra of Complexes *I* to *VII* (nm).

I (adduct)	*I*	*II*	*III*	*IV*	*V*	*VI*	*VII*
387			383	384	384		
			400	398	398		
			413				
			426	426	426		
			438	436	440		
439		447	458	469	464		
		459	470				
	473						
	493	493	487	489	487		
			498		502		
518	510	537	524	519	525		
	519	543	535	531	540		
				542	546		
582	579	557	565	569	578		
	587	588	576				
607	611	617	611	593	610		
				602			
641	636	636	627	623	630		
				639			
663	666	667					
713	720	719	696	693	701		
862	863	863	840	840	849		
985	984	988	966	974	979		
1040	1042	1043	1019	1025	1028		1037
				1094		1090	
1131			1118	1159	1180		
			1164				
1200	1202	1197	1204	1206	1221		
1354	1348	1374	1332	1332	1334	1346	1333

Discussion

The Crown Ether Complexes

One of the most interesting aspects of these compounds is the variation in stoichiometry between complexes of different crown ether ligands. Thus we have UCl_3L, where L = cyclohexyl-15-crown-5; $(UCl_3)_3L_2$, where L = 18-crown-6 or benzo-15-crown-5; and $(UCl_3)_5L_3$, where L = dibenzo-18-crown-6 or *cis-syn-cis*-dicyclohexyl-18-crown-6. In previous work, UCl_3(18-crown-6) has been claimed twice [6, 7] though as stated above, analyses were poor; while UCl_3(15-crown-5)·H_2O and a product "corresponding closely to" $(UCl_3)_4$(dicyclohexyl-18-crown-6)$_3$ were also obtained [6]. However, in our present work, alteration of the molar ratios of the reagents gave no different products. The analytical values given above for the crown ether complexes isolated in our work are satisfactory for the stoichiometries stated and did not vary significantly in a second preparation. It therefore appears certain that a ligand:metal ratio smaller than 1:1 does frequently occur in this type of complex. It is also relevant that in lanthanide (Ln) nitrate crown ether complexes a $\{Ln(NO_3)_3\}_4L_3$ stoichiometry was established [10, 11] and shown by X-ray [12] to correspond, for Ln = Nd, with the suggested [10] formulation $[Ln(NO_3)_2L]_3[Ln(NO_3)_6]$. An X-ray study of a uranium(IV) crown ether complex has been reported [13], namely the 9- and 6-coordinated $[UCl_3$(*cis,syn,cis*-dicyclohexyl-18-crown-6)$]_2$-$[UCl_6]$.

For our U(III) complex, it would be tempting to suggest structures $[UCl_3L]$ for the 1:1 complex, $[UCl_2L]_2(UCl_5)_{n/n}$ for the 3:2 complexes and $[UCl_2L]_3[U_2Cl_9]$ for the 5:3 complexes. With all the ether oxygen atoms coordinated, this could give 8-coordinated uranium in the cations and 6 or 7-coordinated uranium in the anions. This suggestion seems inadequate, however, because these coordination numbers seem rather low when compared with 9-coordinated uranium(IV) [13] in $[UCl_3$(*cis-syn-cis*-dicyclohexyl-18-crown-6)$]^+$, or with 9-coordinated uranium(III) in UCl_3. It is likely that the 3:2 and 5:3 complexes possess fairly complicated structures which involve chloride bridges. Thus the 3:2 structure

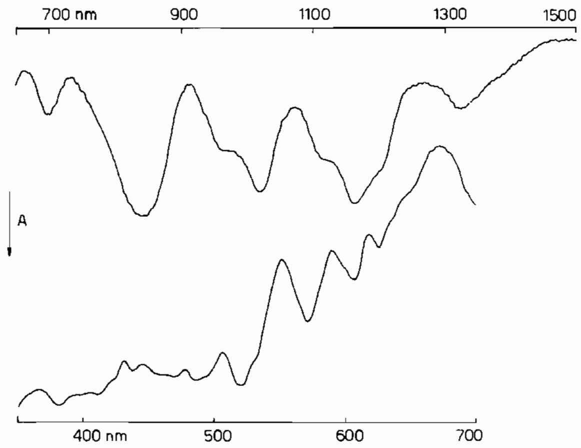

Fig. 1. The electronic spectrum of (*III*).

might be of the type (crown)U(μ-Cl)$_3$U(Cl$_3$)(μ-Cl)$_3$U-(crown).

While a structure of this general nature seems a possibility, in the absence of single crystal X-ray data any suggestions are of course speculative. Despite many attempts, no single crystals suitable for X-ray could be obtained.

The infrared spectra are consistent with the crown ligands being coordinated to the U(III) ion, and not uncoordinated as, for example, in Ln(NO$_3$)$_3$-(H$_2$O)$_3$·(18-crown-6) [10]. Thus all the ligands have a strong, broad, stretching mode of the –CH$_2$CH$_2$-OCH$_2$CH$_2$–system at about 1090–1130 cm^{-1}. In the spectra of the complexes, this band is shifted to lower wavenumber as follows: *I*, 1070; *II*, 1060; *III*, 1075; *IV*, uncertain, very broad with fine structure; *V*, 1070 cm^{-1} (all are broad bands showing fine structures; the approximate baricentre has been quoted). The bathochromic shifts of these bands upon complexation are similar to that in La(NO$_3$)$_3$-(18-crown-6) [10] and there is a general similarity between the crown ligand components of the spectra of *III* and La(NO$_3$)$_3$(18-crown-6).

The room temperature magnetic moments of the crown ether complexes lie in the range 2.67–2.91 BM. This is rather below the general range of the comparatively few values known for U(III) complexes, which range from 3.35 BM for KUCl$_4$·5H$_2$O [8] to 2.97 BM for [U{CH$_2$CONMe$_2$)$_2$}$_4$]-(BPh$_4$)$_3$ [4].

The reflectance electronic spectra of the solid samples in the range 350–2300 nm showed absorption of two types: (a) a strong broad featureless absorption in the range 350–600 nm, and (b) many peaks, throughout the entire range, of half-height width about 300 cm^{-1}.

While the type (a) absorption is doubtless due to $5f^3 \rightarrow 5f^2 6d^1$ transitions, the type (b) absorption is doubtless due to $5f^3 \rightarrow 5f^3$ transitions. Although extinction coefficients cannot of course be obtained from reflectance spectra, qualitative inspection of the spectra strongly indicates that the type (b) peaks are of much too low intensity to be allowed transitions, whether $5f \rightarrow 6d$ or any other type. Their relative sharpness would also be consistent with a $5f \rightarrow 5f$ origin. There is a very good correlation of these U(III) crown ether spectra, *e.g.* that of (UCl$_3$)$_3$-(18-crown-6)$_2$, with the published spectra of the U(III) ion in anhydrous HF/AsF$_5$ [14] and particularly in DClO$_4$ [15]. This fact is apparent not so much by comparison of tables of numerical wavelengths alone as by a careful comparison of all three spectral curves. This correlation would tend to confirm suggestions [16] that crystal field effects are fairly small in the case of tripositive actinide ions and hence the spectra are comparatively little altered by change of coordination number or ligand field strength. However, complexes of actinides in oxidation states of four or more, with their greater degree of covalency, tend to show in their spectra greater sensitivity to the environment of the metal ion.

In the present state of knowledge of the energy levels of the three-electron actinide ions it is very difficult and possibly unsound to attempt a correlation between theoretical energy level schemes such as Jørgensen's term scheme [17] based on intermediate coupling, and experimentally observed spectra, though such correlations have been attempted.

A peak-by-peak comparison of the spectra of (UCl$_3$)$_3$(18-crown-6)$_2$ and U^{3+} in DClO$_4$ [15] in the region 400–1400 nm shows that the crown complex spectrum is shifted to short wave length of the deuterated aquo complex. Of 13 peaks compared, the average shift Δ of the crown spectrum to higher energy was 512 cm^{-1} and the average value of Δ/(aquo complex peak wavenumber) was 0.038. This energy shift of approximately 4% is consistent with a smaller extent of electron donation in the crown complex, with chloride and ether ligands, than in the deuterated aquo complex. While the direct peak-for-peak comparison was uncertain in one or two cases, doubtless being complicated to some extent by the almost certain presence of two types of U(III) ion in this 3:2 complex, the average values of the shifts must quantitatively be approximately correct. The complexes are insoluble in common organic solvents. They are oxidised in air, as well as being hygroscopic. The degrees of reactivity towards the air and moisture differ drastically for the most and least stable complexes. The deep red (UCl$_3$)$_3$(benzo-15-crown-5)$_2$ which was obtained by heating a sample of the yellow-orange adduct complex, (UCl$_3$)$_3$(benzo-15-crown-5)$_2$·1.5CH$_3$CN, at 110 °C under reduced pressure for seven hours, is least stable and immediately changed to the hydrated yellow-orange species in contact with air (infrared). The hydrate was subsequently oxidized to pale green uranium(IV) within *ca.* 30 min in the air. On the other hand, the most stable complex, deep red $(UCl_3)_5$(dibenzo-18-crown-6)$_3$, is oxidized completely only during 15 h in the air. The other complexes are oxidized over a period of 2 to 10 h in the air. However, all the complexes are much more stable in dry air, and under dry nitrogen in a sealed tube they are stable indefinitely. Contact with solvents accentuates their oxidative instability.

The Amine Complexes

These very reactive complexes could not be obtained entirely pure, as shown by their analytical values, but they will be briefly discussed as a matter of record. Exposure to traces of air causes immediate decomposition, as shown by loss of their characteristic purple colour. The dark colour is associated in their reflectance spectra with broad intense absorption in the visible and near infrared, so that the $5f^3 \rightarrow 5f^3$ transitions are not clearly evident at shorter wavelengths than 1000 nm. The broad intense absorption is probably of both $5f^3 \rightarrow 5f^2 6d^1$ and $5f^3 \rightarrow 5f^2 l^1$ character, where l represents an unoccupied ligand orbital associated with the aromatic ring system. It is of interest that complexes of Ce^{3+} (yellow) [18, 19] and Eu^{2+} (deep blue) [20] with aromatic amines have intense visible absorption. The series Ce^{3+}, Eu^{2+} and U^{3+} is one of increasing ease of oxidation and all have an $f \rightarrow d$ transition in the near UV seemingly brought into the visible by complexation with conjugated amines. The energy of the acceptor orbital may well be altered by interaction with a d orbital so that the transition is not pure $f \rightarrow l$ or $f \rightarrow d$. In this connection, it is apparently incorrectly stated [16] that lanthanide and actinide bipyridyl and phenanthroline complexes do not show inverted electron-transfer bands at appreciably lower energies than the $f \rightarrow d$ bands in their halogeno-complexes. As stated just previously, such bands are in fact present, at least with easily oxidised metal ions.

These uranium(III) chloride-phenanthroline or bipyridyl complexes are of similar formulation to $LnCl_3L_2$ (L = 2,2′-bipyridyl or 1,10-phenanthroline, Ln = a lanthanide) [18, 19] whose structures were not determined by X-ray. The infrared evidence tends to indicate that the amine ligands in the uranium(III) complexes are, as would be expected, completely coordinated. Thus the phenanthroline CH bending mode (740 cm^{-1} in the free ligand) is entirely shifted to 724 cm^{-1} in the complex; while the bipyridyl ring stretching modes (1550 cm^{-1} and 1576 cm^{-1} in the free ligand) are entirely shifted to 1565, 1574 cm^{-1} and 1596, 1603 cm^{-1} in the complex, and the CH bending mode at 756 cm^{-1} in free bipyridyl becomes 765 cm^{-1} in the complex. However the precise structure of these diamine complexes, whether 7-coordinated monomers, or whether incorporating bridging chloride with a higher uranium coordination number, must remain uncertain.

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