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Formation of Lanthanide and Actinide Oxonium Ion Complexes with Crown Ethers from a Liquid Clathrate Medium[†]

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Reaction of $MCl_3\cdot nH_2O$ (M = La, Eu) with 18-crown-6 in HCl/toluene affords the crystalline oxonium complexes $(H_9O_4)[LaCl_2(H_2O)(\text{18-crown-6})]Cl_2$ (**1**) and $(H_3O)[EuCl(H_2O)_2(\text{18-crown-6})]Cl_2$ (**2**). In complex **1** the $H_9O_4^+$ cation is of the unusual linear chain type with O···O contacts of 2.560(9), 2.430(9), and 2.483(9) Å. The analogous reaction with $YbCl_3\cdot 6H_2O$ results in the isolation of the known species $(H_5O_2)[H_3O\cdot(\text{18-crown-6})]Cl_2$. Analogous reaction of $YbCl_3\cdot 6H_2O$ with 15-crown-5 gives $[Yb(H_2O)_8]Cl_3\cdot(\text{15-crown-5})$ (**5**). Reaction of uranyl acetate with 15-crown-5 within a toluene/HCl mixture results in the formation of a yellow liquid clathrate layer from which crystals of $(H_5O_2)[UO_2(H_2O)_2Cl_3]\cdot 2(\text{15-crown-5})$ (**6**) are deposited. The $H_5O_2^+$ ion in this material exhibits a particularly short O···O separation of 2.371(8) Å. On standing, loss of HCl results in the transformation of **6** into a species of empirical formula $[UO_2(H_2O)_3Cl_2]\cdot(\text{15-crown-5})$ (**7**) which has been shown by X-ray crystallography to contain 16 unique uranium complexes, arranged in infinite hydrogen-bonded chains in the solid state. Crystal data for **1**: monoclinic, $P2_1/c$, $a = 7.6950(2)$ Å, $b = 21.2160(16)$ Å, $c = 15.8650(10)$ Å, $\beta = 92.866(2)°$, $V = 2586.8(3)$ Å^3, $Z = 4$. **2**: orthorhombic, $Pbn2_1$, $a = 10.2267(6)$ Å, $b = 14.7231(9)$ Å, $c = 29.8565(18)$ Å, $V = 4495.5(5)$ Å^3, $Z = 4$. **5**: monoclinic, $P2_1/n$, $a = 9.1740(3)$ Å, $b = 17.1900(3)$ Å, $c = 15.2450(5)$ Å, $\beta = 92.643(2)°$, $V = 2401.60(12)$ Å^3, $Z = 4$. **6**: orthorhombic, $Pmcn$, $a = 12.1740(5)$ Å, $b = 14.7740(7)$ Å, $c = 18.4920(11)$ Å, $V = 3325.9(3)$ Å^3, $Z = 4$. **7**: trigonal, $P3_2$, $a = 35.3500(2)$ Å, $c = 21.3755(2)$ Å, $V = 23\,132.7(3)$ Å^3, $Z = 48$.

Introduction

The phenomenon of liquid clathrate formation arises from the separation of anions and cations of salts dissolved in nonpolar, aromatic media such as benzene, toluene, xylene, etc. Large anions such as $[Al_2Me_6N_3]^-$ form partially ordered, liquid layer structures in which cations are incorporated. The role of the aromatic solvent is to support the poorly packed layers and insulate the cations from one another.[1−3] Typically liquid clathrates spontaneously separate from a suspension of salt within the aromatic solvent. In some cases, as a consequence of the high lattice energy of the salt (e.g., NaH), liquid clathrates do not form, and this problem has been overcome through the use of crown ethers. The resulting increase in cation size reduces lattice energy and results in liquid clathrate behavior.[1] A particular system of interest has been that arising from the interaction of HCl gas with a toluene solution of 18-crown-6 in the presence of a little moisture, which gives rise to a liquid clathrate layer of composition $[H_3O\cdot(\text{18-crown-6})][HCl_2]\cdot 3.8C_6H_5Me$, eventually depositing crystals of $[H_3O\cdot(\text{18-crown-6})][HCl_2]$.[4] In the presence of additional water, the mixed oxonium ion complex $(H_5O_2)[H_3O\cdot(\text{18-crown-6})]Cl_2$ is formed.[5] Indeed, a variety of subsequent studies have established that 18-crown-6 is selective for H_3O^+.[6−11] Similarly, use of larger crown ethers has resulted in the incorporation of larger oxonium ions within the macrocyclic cavity such as $[H_5O_2\cdot(\text{21-crown-7})][WOCl_5]$,[12] while dibenzo-30-crown-10 is able to encapsulate two H_3O^+ ions.[13] Crown ethers smaller than 18-crown-6 are unable to encapsulate oxonium ions, and instead large aggregates such

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(1) Atwood, J. L. In *Inclusion compounds*; Atwood, J. L., Ed.; Academic Press: London, 1984; Vol. 1, pp 375−405.

(2) Atwood, J. L. In *Chemical Separations*; Atwood, J. L., Ed.; Litarvan: Denver, 1986; pp 335−354.

(3) Atwood, J. L. In *Separation Technology*; Atwood, J. L., Ed.; United Engineering Trustees: New York, 1988; pp 46−56.

(4) Atwood, J. L.; Bott, S. G.; Coleman, A. W.; Robinson, K. D.; Whetstone, S. B.; Means, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 8100−8101.

(5) Atwood, J. L.; Bott, S. G.; Robinson, K. D.; Bishop, E. J.; May, M. T. *J. Crystallogr. Spectrosc. Res.* **1991**, *21*, 459−462.

(6) Behr, J.-P.; Dumas, P.; Moras, D. *J. Am. Chem. Soc.* **1982**, *104*, 4540−4543.

(7) Buschmann, H.-J. *Inorg. Chim. Acta* **1987**, *118*, 77.

(8) Chenevert, R.; Chamberland, D.; Simard, M.; Brisse, F. *Can. J. Chem.* **1989**, *67*, 32.

(9) Atwood, J. L.; Bott, S. G.; Junk, P. C.; May, M. T. *J. Organomet. Chem.* **1995**, *487*, 7−15.

(10) Atwood, J. L.; Bott, S. G.; Junk, P. C.; May, M. T. *J. Coord. Chem.* **1996**, *37*, 89−105.

(11) Ming, W.; Boyi, W.; Peiju, Z.; Wenji, W.; Jie, L. *Acta Crystallogr., Sect. C* **1988**, *44*, 1913−1916.

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as $H_9O_4^+$ are observed within the crystalline lattice.[14] The isolation of these interesting species from the liquid clathrate phase is crucially dependent on the incorporation of bulky anions such as $[W(CO)_4Cl_3]^-$ and $[WOCl_5]^-$, which aid in crystallization of the large oxonium cations as well as providing hydrogen bond acceptor sites which stabilize the crystal lattice.[9,10,12−14]

Liquid clathrates are by no means unique in producing crystalline oxonium ion salts. Rogers et al. have isolated solid materials containing the $[H_3O\cdot(18\text{-crown-}6)]^+$ cation in the presence of the $[(UO_2(NO_3)_2)_2C_2O_4]^{2-}$ anion from aqueous nitric acid, while related reactions with benzo-15-crown-5 result in the isolation of $H_5O_2^+$ and a linear $H_9O_4^+$-containing species.[15] A neutron diffraction study on *o*-sulfobenzoic acid trihydrate has resulted in the characterization of an $H_7O_3^+$ ion, best formulated, $H_5O_2^+\cdot H_2O$,[16] in contrast to other, more symmetrical $H_7O_3^+$ species,[16,17] while Cotton et al. have reported an unusually short O···O distance of 2.336(14) Å in the $H_5O_2^+$ complex $[Et_4N]_3(H_5O_2)[Mo_2Cl_8H][MoCl_4O(H_2O)]$.[18] Crystallographic studies of even more extensively hydrated protons have been reported more recently, e.g., $(H_{13}O_6)[PtCl_5(H_4O_2)]\cdot 2(18\text{-crown-}6)$, while species up to $(H_2O)_{21}H^+$ and $(H_2O)_{28}H^+$ have been observed by mass spectrometry.[19]

One investigation which has yet to be attempted is the incorporation of lanthanide and actinide ions within the crown ether/liquid clathrate system, although a significant amount of work has been carried out in aqueous and other media.[15,20,21] This type of experiment is of interest for two important reasons. First, the presence of large lanthanide and actinide ions, with their high coordination numbers,[22] may well result in the isolation of ever more hydrated forms of the oxonium ion according to crystal-packing arguments.[1−3] This effect may be enhanced in a relatively lipophilic environment since the oxophilic lanthanide and actinide ions may compete more strongly with H_3O^+ for the crown ether cavity, resulting in formation of larger oxonium ions in the less restricted extracavity space. Second, in the absence of oxonium ion formation, unusual crystal-packing motifs may arise from the interaction of hydrogen bond acceptors, such as crown ethers, with hydrogen bond donors, such as hydrated metal ions. This is of particular interest when the species in question exhibit a symmetry mismatch, resulting in complex hydrogen-bonded arrays, taking account of the steric and symmetry properties of both donor and acceptor. Also, although not directly relevant to liquid clathrate chemistry, there is interest, especially in the chemistry of the actinides, in acidic media because of the wide variety of actinide separation processes which lead to high-level radioactive wastes in nitric and hydrochloric acid solutions.[15,23]

Scheme 1. Liquid Clathrate Forming Reactions

$$\mathrm{M + L + HCl_{(g)} + H_2O} \xrightarrow[\text{1 - 12 h}]{\text{toluene}} \text{two phase liquid clathrate / toluene mixture} \xrightarrow{\text{crystallisation}} \text{products}$$

Results and Discussion

Reactions with 18-Crown-6. A variety of reactions involving a macrocyclic ligand (L) and a metal salt (M) were investigated according to the general method shown in Scheme 1. The results are summarized in Table 1. Initially reactions of $MCl_3\cdot nH_2O$ (M = La, Eu, Yb; $n = 6-7$) with 18-crown-6 were attempted. Equimolar amounts of metal salt and crown were found to give disappointing results, with no liquid clathrate formation observed. Increasing the amount of crown ether (3:1 mole ratio) in the toluene phase, however, resulted in the formation of large liquid clathrate layers over a period of ca. 2−12 h for all three lanthanides, accompanied by complete dissolution of the metal salt. The mixture was allowed to stand for periods of 3−7 days, resulting in the deposition of colorless, rectangular crystals from the clathrate layer as well as a larger amount of feathery needles (M = La, Eu). In the case of the ytterbium complex, large colorless needles were deposited over a period of ca. 1 week. Upon isolation, the crystalline samples were found to be extremely deliquescent, dissolving completely in water absorbed from the atmosphere within a matter of minutes. ^1H NMR spectra of the crystalline samples in D_2O demonstrated the presence of 18-crown-6 (δ 3.65 ppm). In the europium case the ^1H NMR spectrum of the liquid clathrate layer showed the presence of toluene and 18-crown-6 in the ratio 2:1. Mass spectra were recorded in the FAB mode for all three samples. In the case of the La and Eu samples, molecular ion peaks were observed at *m/z* 544 and 559, respectively, with associated fragmentation peaks, corresponding to the formulations $[MCl_3(H_2O)_2(18\text{-crown-}6)]$ (M = La, Eu). The mass spectrum of the ytterbium sample showed peaks corresponding only to 18-crown-6.

All three sets of crystals were subjected to analysis by X-ray crystallography (Table 3), which demonstrated the formulations $(H_9O_4)[LaCl_2(H_2O)(18\text{-crown-}6)]Cl_2$ (**1**) and $(H_3O)[EuCl(H_2O)_2(18\text{-crown-}6)]Cl_2$ (**2**). In the case of the ytterbium complex the crystals proved to consist solely of the mixed oxonium ion complex $(H_5O_2)[H_3O\cdot(18\text{-crown-}6)]Cl_2$ previously prepared by Atwood et al.[5] The lanthanide-containing cations in complexes **1** and **2** in the absence of oxonium cations have been observed by Rogers et al. from the reaction of $MCl_3\cdot nH_2O$ (M = La, Eu) with 18-crown-6 in an acetonitrile/methanol mixture. These reactions gave the complexes $[LaCl_2(H_2O)(18\text{-crown-}6)]Cl$ (**3a**), $[LaCl_2(H_2O)(18\text{-crown-}6)]Cl\cdot 1.5H_2O$ (**3b**), and $[EuCl(H_2O)_2(18\text{-crown-}6)]Cl_2\cdot 2H_2O$ (**4**), and in general, the crystallographically determined lanthanide cation geometry is the same in the present work.[20]

The $H_9O_4^+$ cation in **1** is of the unusual linear chain type[15] with O···O contacts from O(1S)−O(2S)−O(3S)−O(4S) of 2.560(9), 2.430(9), and 2.483(9) Å, respectively, suggesting that it may be regarded as intermediate between a fully symmetrical $H_9O_4^+$ and $H_2O\cdot H_5O_2^+\cdot H_2O$ (typical O···O separations in $H_5O_2^+$ 2.40−2.45 Å,[5,12,15,16,19] compared to oxonium···H_2O distances of ca. 2.7 Å[16,24]). This contrasts to the complex $(H_9O_4)_2[Co(H_2O)(15\text{-crown-}5)]_2[Co(15\text{-crown-}5)][CoCl_4]_4$, in which the linear O···O separations are 2.573, 3.036, and 2.585 Å, suggesting a form more resembling two associated $H_5O_2^+$ ions, each coordinated to a Co^{2+} center![14] Separations between

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(12) Junk, P. C.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1995**, 1551−1552.

(13) Atwood, J. L.; Junk, P. C. Submitted for publication.

(14) Atwood, J. L.; Junk, P. C. *Angew. Chem., Int. Ed.*, submitted for publication.

(15) Rogers, R. D.; Bond, A. H.; Hipple, W. G.; Rollina, A. N.; Henry, R. F. *Inorg. Chem.* **1991**, *30*, 2671−2679.

(16) Attig, R.; Williams, J. M. *Inorg. Chem.* **1976**, *15*, 3057−3061.

(17) Ratcliffe, C. I.; Irish, D. E. In *The nature of the hydrated proton*; Franks, F., Ed.; Cambridge University Press: Cambridge, 1986; pp 149−214.

(18) Bino, A.; Cotton, F. A. *J. Am. Chem. Soc.* **1979**, *101*, 4150−4154.

(19) Ratcliffe, C. I.; Irish, D. E. In *The nature of the hydrated proton*; Franks, F., Ed.; Cambridge University Press: Cambridge, 1988; pp 1−78.

(20) Rogers, R. D.; Rollins, A. N.; Etzenhouser, R. D.; Voss, E. J.; Bauer, C. B. *Inorg. Chem.* **1993**, *32*, 3451−3462.

(21) Cragg, P. J.; Bott, S. G.; Atwood, J. L. *Lanthanide Actinide Res.* **1988**, *2*, 265−277.

(22) Cotton, S. *Lanthanides and Actinides*; MacMillan: London, 1991.

(23) Duffield, J. R.; Williams, D. R. *Chem. Soc. Rev.* **1986**, *15*, 291−307.

(24) Taesler, I.; Lundgren, J.-O. *Acta Crystallogr., Sect. B* **1978**, *34*, 2424−2428.

Table 1. Reactions of Ligands (L) with Metal Salts (M) According to Scheme 1

entry	L[a]	M	liquid clathrate formation	complex isolated
1	18-c-6	$LaCl_3\cdot 7H_2O$	with >5 equiv of 18-c-6	$(H_9O_4)[LaCl_2(H_2O)(18\text{-}c\text{-}6)]Cl_2$ (**1**)
2	18-c-6	$EuCl_3\cdot 6H_2O$	with >5 equiv of 18-c-6	$(H_3O)[EuCl(H_2O)_2(18\text{-}c\text{-}6)]Cl_3$ (**2**)
3	18-c-6	$YbCl_3\cdot 6H_2O$	with >5 equiv of 18-c-6	$(H_5O_2)[H_3O\cdot 18\text{-}c\text{-}6]Cl_2$
4	18-c-6	$EuCl_3\cdot 6H_2O + KCl$	with >5 equiv of 18-c-6	$[EuCl(H_2O)_2(18\text{-}c\text{-}6)]Cl_2\cdot 2H_2O$ (**4**)
5	18-c-6	$UO_2(CH_3CO_2)_2$	small lc[b] layer on heating with >5 equiv of 18-c-6	none
6	15-c-5	$LaCl_3\cdot 7H_2O$	no	
7	15-c-5	$EuCl_3\cdot 6H_2O$	no	
8	15-c-5	$YbCl_3\cdot 6H_2O$	small lc layer on heating with >5 equiv of 15-c-5	$[Yb(H_2O)_8]Cl_3\cdot(15\text{-}c\text{-}5)$ (**5**)
9	15-c-5	$UO_2(CH_3CO_2)_2$	yellow lc layer with >5 equiv of 15-c-5	$(H_5O_2)[UO_2(H_2O)_2Cl_3]\cdot 2(15\text{-}c\text{-}5)$ (**6**) $[UO_2(H_2O)_3Cl_2]_{16}\cdot(15\text{-}c\text{-}5)_{16}$ (**7**)

[a] 18-c-6 = 18-crown-6; 15-c-5 = 15-crown-5. [b] Liquid clathrate.

Table 2. O···Cl Hydrogen-Bonded Contacts in **1**

	Cl(1)	Cl(3)	Cl(4)
O(1S)			3.108(8) 3.161(8)
O(2S)		3.043(6)	
O(3S)	3.051(7)		
O(4S)		3.107(8)	3.009(8)
O(7)		3.106(5)	

oxygen atoms in the trigonal $H_9O_4^+$ ion in $(H_9O_4)(H_7O_3)Br_2\cdot 2H_2O$ are found to be 2.587, 2.588, and 2.496 Å,[25] in agreement with calculated values of 2.59 Å,[26] and indeed ab initio methods suggest that the trigonal $H_9O_4^+$ is more stable in the gas phase.[19] The trigonal form of $H_9O_4^+$ has been observed in a wide range of other studies.[24,27,28] In complex **1** the $H_9O_4^+$ ion forms an additional five hydrogen bonds to the uncoordinated chloride anions, Table 2, with O···Cl distances in the range 3.01−3.16 Å, making a total of nine hydrogen bonds for the entire $H_9O_4^+$ unit, consistent with the presence of the nine hydrogen atoms. The anion Cl(4) connects the oxonium ions together in a continuous two-dimensional hydrogen-bonded net via O(1S) and O(4S). The anion Cl(3) is hydrogen bonded to the oxonium ion via O(4S) and O(2S) and connects to the coordinated water molecule O(7). A more direct interaction between the lanthanide cation and the oxonium ion is provided by a hydrogen bond from the coordinated Cl(1) to O(3S), Figure 1.

The environment of the H_3O^+ cation, O(1S), in **2** (Figure 2) is pyramidal with hydrogen bonds to the coordinated water molecule O(7) [O···O 2.630(10) Å] and the two lattice chloride anions, O(1S)−Cl(4), 3.113(8) Å, O(1S)−Cl(5), 3.174(8) Å (cf. $H_3O\cdots O_{crown}$ contacts of 2.59−2.63 Å in $[H_3O\cdot$dicyclohexano-18-crown-6$]_2[Th(NO_3)_6]$[11]); angles subtended at O(1S), 122.6°, 101.4°, and 106.1° (cf. 95°, 102°, and 120° for the HOH angles in $[H_3O\cdot$tetraacetato-18-crown-6$]^+$ [6]). (N.B. The structure of **2** contains two formula units in the asymmetric unit. The data for the second independent complex are very similar.) In turn the anion Cl(4) is hydrogen bonded to a further europium-crown cation via O(8) [3.257(9) Å] while Cl(5) engages in interactions with both O(7B) and O(8B) of the second independent cation [3.022(8) and 3.048(8) Å].

Clearly the incorporation of the M^{3+} cations within the 18-crown-6 cavity in **1** and **2** is a striking contrast to the formation of oxonium ion species such as $[H_3O\cdot(18\text{-crown-}6)][MoOCl_4(H_2O)]$,[10] although unsurprising given the observation that binding constants for M^{2+} and M^{3+} ions with crown ethers are generally at least 10^3 times those for monovalent ions as a consequence of electrostatic effects.[29] The electrostatic nature of this preference for the higher charged cation, coupled with the hard, oxophilic nature of the lanthanides,[22] was confirmed by repeating the synthesis of **2** in the presence of 1 molar equiv of KCl (relative to $EuCl_3\cdot 6H_2O$). Oddly this resulted in the isolation of crystals of the europium crown complex **4**[20] instead of the closely related **2**. The fact that the K^+ is not incorporated is clear, however.

Reactions with 15-Crown-5. The above reactions were repeated in the presence of 15-crown-5 in place of 18-crown-6 in order to assess the effect of crown cavity size on the nature of the oxonium species formed. This has proved to be crucial in work involving transition metal centers.[12,13] Unfortunately, only in the case of $YbCl_3\cdot 6H_2O$ was any liquid clathrate formed, and even this layer was very small. After standing for ca. 2 weeks colorless crystals were deposited which proved to be of composition $[Yb(H_2O)_8]Cl_3\cdot(15\text{-crown-}5)$ (**5**) and surprisingly contained no oxonium ion. The structure of **5** is shown in Figure 3 and consists of $Yb(H_2O)_8^{3+}$ cations sandwiched by hydrogen bonding to two symmetry equivalent, disordered 15-crown-5 macrocycles via the coordinated water molecules O(1) and O(3); closest $O_{water}\cdots O_{crown}$ distance 2.67(2) Å. The remaining water molecules hydrogen bond to the chloride anions in pairs with O···Cl contacts in the range 3.04(1)−3.14(1) Å. Yb−O distances are in the range 2.297(4)−2.417(4) Å, which compares to an average value of 2.353 Å[30] and a distance of 2.341(3) Å (av) found in the *p*-sulfonatocalix[5]arene complex $Na_2[Yb(H_2O)_6(ONC_5H_5)(p\text{-sulfonatocalix[5]arene})]\cdot 13H_2O$.[31] The structure is isostructural with a number of other complexes of general formula $[M(H_2O)_8]Cl_3\cdot(15\text{-crown-}5)$ (M = Y, Gd, Lu, Nd),[32−36] though it is noteworthy that several lanthanide complexes of 15-crown-5 have been prepared in which the lanthanide metal cation is actually bound to the crown ether.[37,38]

Reaction of 15-crown-5 was also attempted with $UO_2(CH_3CO_2)_2$ within a toluene/HCl medium. Uranyl acetate was chosen because it was anticipated that the acetate ligands may enhance

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(25) Lundgren, J.-O.; Olovsson, I. *J. Chem. Phys.* **1968**, *49*, 1068−1074.
(26) Yeh, L. I.; Okumura, M.; Myers, J. D.; Price, J. M.; Lee, Y. T. *J. Chem. Phys.* **1989**, *91*, 7319−7330.
(27) Lundgren, J.-O. *Acta Crystallogr., Sect. B* **1978**, *34*, 2428−2431.
(28) Haser, R.; Pierrot, M. *Acta Crystallogr., Sect. B* **1972**, *28*, 2542−2547.
(29) Jong, F. d.; Reinhoudt, D. N. *Stability and Reactivity of Crown Ether Complexes*; Academic Press: London, 1981.
(30) Orpen, G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.
(31) Steed, J. W.; Johnson, C. P.; Barnes, C. L.; Juneja, R. K.; Atwood, J. L.; Reilly, S.; Hollis, R. L.; Smith, P. H.; Clark, D. L. *J. Am. Chem. Soc.* **1995**, *117*, 11426−11433.
(32) Rogers, R. D. *J. Chem. Crystallogr.* **1994**, *24*, 531.
(33) Rogers, R. D. Kurihara, L. K. *Inorg. Chim. Acta* **1986**, *116*, 171−177.
(34) Rogers, R. D. *Inorg. Chim. Acta* **1987**, *129*, 277−282.
(35) Rogers, R. D.; Kurihara, L. K. *Inorg. Chim. Acta* **1987**, *130*, 131−137.
(36) Rogers, R. D. *Inorg. Chim. Acta* **1988**, *149*, 307−314.
(37) Atwood, D. A.; Atwood, J. L.; Bott, S. G. *J. Coord. Chem.* **1987**, *17*, 93.
(38) Bunzli, J.-C. G.; Klein, B.; Chapuis, G.; Schenk, K. J. *Inorg. Chem.* **1982**, *21*, 808−812.

Table 3. Crystallographic Data for New Complexes

	1	**2**	**5**	**6**	**7**
formula	$C_{12}H_{35}Cl_4LaO_{11}$	$C_{24}H_{60}Cl_8Eu_2O_{18}$	$C_{10}H_{36}Cl_3O_{13}Yb$	$C_{20}H_{29}Cl_3O_{16}U$	$C_{10}H_{26}Cl_2O_{10}U$
fw (g mol^{-1})	636.11	1224.24	643.78	869.81	615.24
temp (°C)	20	−113	20	20	−100
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
space group	$P2_1/c$	$Pbn2_1$	$P2_1/n$	$Pmcn$	$P3_2$
unit cell dimens					
a (Å)	7.6950(2)	10.2267(6)	9.1740(3)	12.1740(5)	35.3500(2)
b (Å)	21.2160(16)	14.7231(9)	17.1900(3)	14.7740(7)	
c (Å)	15.8650(10)	29.8565(18)	15.2450(5)	18.4920(11)	21.3755(2)
α (deg)	90	90	90	90	90
β (deg)	92.866(2)	90	92.643(2)	90	90
γ (deg)	90	90	90	90	120
vol (Å^3)	2586.8(3)	4495.5(5)	2401.60(12)	3325.9(3)	23132.7(3)
Z	4	4	4	4	48
D_c (g cm^{-3})	1.633	1.809	1.781	1.737	2.120
μ (cm^{-1})	21.07	33.03	42.79	51.84	87.38
F(000)	1280	2440	1284	1680	14016
cryst size (mm)	0.6 × 0.05 × 0.05	0.33 × 0.18 × 0.15	0.4 × 0.1 × 0.1	0.1 × 0.05 × 0.05	0.2 × 0.2 × 0.2
θ range (deg)	3.73−25.0	1.99−28.37	3.75−25.0	3.41−23.5	2.76−25.0
index ranges	$0 \le h \le 8$, $0 \le k \le 25$, $-18 \le l \le 18$	$-13 \le h \le 13$, $-18 \le k \le 17$, $-38 \le l \le 28$	$0 \le h \le 10$, $0 \le k \le 20$, $-18 \le l \le 18$	$0 \le h \le 13$, $0 \le k \le 15$, $0 \le l \le 20$	$-42 \le h \le 42$, $-35 \le k \le 35$, $-23 \le l \le 25$
reflns collected	36 955	27 100	27 012	32 451	153 662
indep reflns	4397	8788	4191	2434	51 913
params	249	470	326	204	3305
goodness-of-fit on F^2	1.095	1.076	1.027	1.084	1.093
final R indices, $I > 2\sigma(I)^a$	R1 0.0446, wR2 0.0930	R1 0.0416, wR2 0.1002	R1 0.0332, wR2 0.0811	R1 0.0417, wR2 0.1061	R1 0.072, wR2 0.1500
R indices (all data)^a	R1 0.0633, wR2 0.0992	R1 0.0462, wR2 0.1022	R1 0.0409, wR2 0.0865	R1 0.0482, wR2 0.1109	R1 0.0866, wR2 0.1575
largest diff peak (e Å^{-3})	0.84	4.62^b	0.87	0.71	3.95^b

[a] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] Close to metal atom.

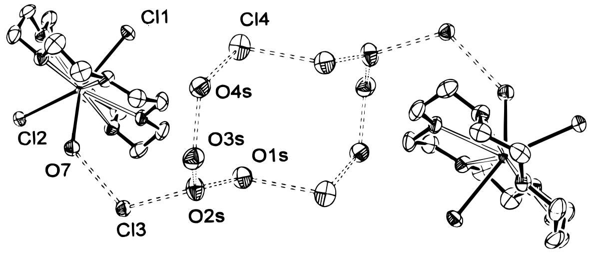

Figure 1. Hydrogen-bonding network in the $H_9O_4^+$ complex **1**.

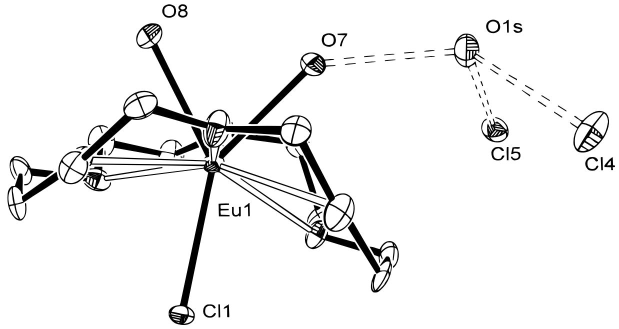

Figure 2. Structure of complex **2** showing the environment of the H_3O^+ cation.

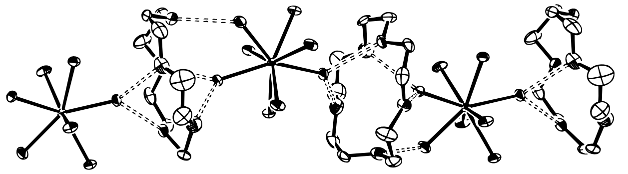

Figure 3. Alternating $[Yb(H_2O)_8]Cl_3$ and 15-crown-5 units in the structure of **5**.

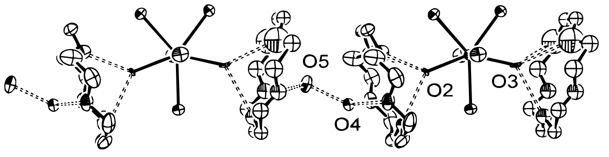

Figure 4. Structure of complex **6** showing alternating $H_5O_2^+$ cations and $[UO_2Cl_3(H_2O)_2]^-$ anions separated by 15-crown-5 molecules.

the initial solubility of the inorganic salt in the toluene phase. This resulted in the formation of a yellow liquid clathrate phase from which crystals of formulation $(H_5O_2)[UO_2(H_2O)_2Cl_3]\cdot 2$(15-crown-5) (**6**) were deposited on standing over a period of ca. 12 h. The crystal structure of complex **6** is shown in Figure 4 and consists of a linear, zigzag chain of alternating $H_5O_2^+$ cations and $[UO_2Cl_3(H_2O)_2]^-$ anions separated by 15-crown-5 molecules, in a fashion more generally reminiscent of transition metal containing liquid clathrate products in which an oxonium ion−crown ether array is stabilized by the presence of a large inorganic anion. The zigzag structure is a direct consequence of the nonlinear $H_2O-U-OH_2$ angle, 146.4(9)°. Within the $H_5O_2^+$ cation the O(4)−O(5) distance is extremely short at 2.371(8) Å (cf typical values of O···O separations 2.40−2.45 Å[5,12,15,16,19]) although Cotton et al. have observed a distance as low as 2.336(14) Å.[18] In **6** the $H_5O_2^+$ cation is apparently planar as a result of crystallographic symmetry, presumably resulting from disorder of the hydrogen atoms, which were not located. Intermolecular hydrogen-bonded contacts from the oxonium ion to the crown ether are in the range 2.70−3.20 Å. The opposite face of each crown ether is hydrogen bonded to coordinated water molecules O(2) and O(3) at distances 2.92−3.04 Å. The $[UO_2Cl_3(H_2O)_2]^-$ anion itself exhibits normal bond lengths and angles with U=O 1.743(6) Å, $U-OH_2$ 2.37(3) and 2.45(5) Å [the high esd values are a consequence of the disorder of O(2)

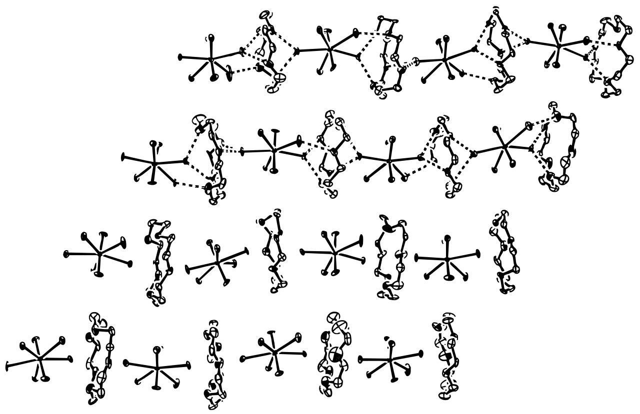

Figure 5. The unique 4 × 4 hydrogen-bonded array in $[UO_2Cl_2(H_2O)_3]_{16}$·(15-crown-5)$_{16}$ (**7**). (Hydrogen bonds omitted from second half for clarity.)

and O(3)], and U−Cl 2.708(3) and 2.709(3) Å. Typical distances are 1.763, 2.455, and 2.653 Å, respectively.[30]

In an attempt to carry out more detailed studies on the oxonium ion in complex **6**, the X-ray crystal structure of a second sample from the same reaction mixture was determined after a period of ca. 6 weeks. Surprisingly, loss of HCl from the reaction mixture coupled with the long "annealing" time had resulted in the formation of a new compound of empirical formula $[UO_2Cl_2(H_2O)_3]$·(15-crown-5) (**7**) which adopted the trigonal space group $P3_2$. The asymmetric unit of this species was observed to contain a total of 16 crystallographically unique pentagonal bipyramidal uranium complexes and 15-crown-5 molecules, arranged in a 4 × 4 array, repeating in infinite hydrogen bonded chains in the crystallographic *a* direction, with water···crown O···O distances in the range 2.60(2)−2.92(2), Figure 5. The highly complex structure is a direct result of the conflicting symmetry requirements of the nonlinear $H_2O-U-OH_2$ vectors (ca. 140° and 152°) and the 15-crown-5 conformation in which each macrocycle presents two faces, one with three accessible oxygen atoms and the other with two. In the case of **6** this mismatch is buffered by the presence of the $H_5O_2^+$ cation, but for **7** it results in an irregular 4-fold chain of four uranium complex−crown pairs in which the orientation of the previous member fixes the direction of approach of the next. No significant interchain interactions in the *c* direction were observed, while along the *b* direction the crown rings of one 4-fold chain interlock unsymmetrically with the adjacent arrays, again resulting in a pattern which is unable to replicate itself until the fifth chain.

Conclusions

The present work has highlighted the importance of metal complex and crown ether size and shape in determining the degree of hydration of the proton in the solid state, and the bulk crystal architecture. By introduction of lanthanide and actinide salts a number of interesting oxonium ion species have been observed including an unusual example of a well-defined, linear chain $H_9O_4^+$ exhibiting no disorder or crystallographic pseudosymmetry. A particularly short O···O distance of 2.371(8) Å has also been observed for the more common $H_5O_2^+$. In addition, the large metal complexes with solely hydrogen bond donor ability and the crown ethers with hydrogen bond acceptor ability represent rigid, noncomplementary supramolecular synthons from which surprising crystalline architectures result in the absence of buffering oxonium species. Use of the liquid clathrate medium not only provides for an unusual, highly acidic solvent but also greatly aids sample crystallization as the medium gradually becomes less polar due to loss of gaseous HCl. Clearly a great deal of rich oxonium, lanthanide and actinide coordination chemistry exists in liquid clathrate media, and this will be the subject of further studies.

Experimental Section

Instrumental. Mass spectra were run at King's College London in the FAB mode in a thioglycerol matrix. NMR spectra were recorded on a Bruker ARX-360 spectrometer operating at 360.1 MHz. Microanalyses were performed at University College London. All reactions were carried out in an atmosphere of HCl, and products generally displayed a high degree of moisture sensitivity when exposed to the atmosphere, generally dissolving in absorbed atmospheric moisture within a few minutes. For this reason yields were not measured in order to protect crystals for the X-ray experiment, but they are estimated to be ca. 30−40% based on $MCl_3·nH_2O$.

Preparations. $(H_9O_4)[LaCl_2(H_2O)(18\text{-crown-6})]Cl_2$ (1). $LaCl_3·7H_2O$ (0.24 g, 0.65 mmol), 18-crown-6 (1.00 g, 3.78 mmol), and water (0.15 cm^3, 8.3 mmol) were placed in a Schlenk tube containing toluene (30 cm^3). Gaseous HCl was bubbled through the mixture for 2 h, during which time all of the metal salt dissolved, to give a liquid clathrate layer of volume ca. 4 cm^3. The tube was loosely stoppered and the mixture allowed to stand for a period of ca. 1 week, resulting in the deposition of the compound as colorless blocks in the presence of featherlike crystals, identified as $(H_5O_2)[H_3O·(18\text{-crown-6})]Cl_2$ by X-ray crystallography and elemental analysis (Calcd for $C_{12}H_{32}O_9Cl_2$: C, 36.85; H, 8.24. Found: C, 36.98; H, 8.59). Anal. Calcd for $C_{12}H_{35}O_{11}Cl_4La$: C, 22.65; H, 5.50. Found: C, 25.60; H, 5.50. These figures suggest ca. 20% contamination of the sample by $(H_5O_2)[H_3O·(18\text{-crown-6})]Cl_2$. Attempts to obtain purer samples were frustrated by the complex's extreme moisture sensitivity.

$(H_3O)[EuCl(H_2O)_2(18\text{-crown-6})]Cl_3$ (2). $EuCl_3·6H_2O$ (0.50 g, 1.36 mmol), 18-crown-6 (1.00 g, 3.78 mmol), and water (0.15 cm^3, 8.3 mmol) were placed in a Schlenk tube containing toluene (30 cm^3). Gaseous HCl was bubbled through the mixture for 2 h, during which time all of the metal salt dissolved, to give a liquid clathrate layer of volume ca. 4 cm^3. The tube was loosely stoppered and the mixture allowed to stand for a period of ca.>3 days, resulting in the deposition of the compound as colorless blocks in the presence of featherlike crystals, identified as $(H_5O_2)[H_3O·(18\text{-crown-6})]Cl_2$ by X-ray crystallography. Anal. Calcd for $C_{12}H_{31}O_9Cl_4Eu$: C, 23.50; H, 5.10. Found: C, 25.18; H, 5.85. These figures suggest ca. 15% contamination of the sample by $(H_5O_2)[H_3O·(18\text{-crown-6})]Cl_2$. Attempts to obtain purer samples were frustrated by the complex's extreme moisture sensitivity.

$[Yb(H_2O)_8]Cl_3·(15\text{-crown-5})$ (5). $YbCl_3·6H_2O$ (0.20 g, 0.52 mmol), 15-crown-5 (0.50 g, 2.27 mmol), and water (0.05 cm^3, 2.8 mmol) were placed in a Schlenk tube containing toluene (30 cm^3). Gaseous HCl was bubbled through the mixture for 4 h, during which time most of the metal salt dissolved, to give a liquid clathrate layer of volume ca. 0.5 cm^3. The tube was loosely stoppered and the mixture allowed to stand for a period of ca. 3 weeks, resulting in the deposition of the compound as colorless blocks. Anal. Calcd for $C_{10}H_{36}O_{13}Cl_3Yb$: C, 18.66; H, 5.64. Found: C, 20.43; H, 5.77. These figures suggest ca. 10% contamination of the sample by $(H_5O_2)[H_3O·(18\text{-crown-6})]Cl_2$. Attempts to obtain purer samples were frustrated by the complex's extreme moisture sensitivity.

$(H_5O_2)[UO_2(H_2O)_2Cl_3]·2(15\text{-crown-5})$ (6). $UO_2(CH_3CO_2)_2$ (0.25 g, 0.64 mmol), 15-crown-5 (0.98 g, 4.45 mmol) and water (0.30 cm^3, 16.8 mmol), were placed in a Schlenk tube containing toluene (30 cm^3). Gaseous HCl was bubbled through the mixture for 12 h with gentle heating, during which time all of the metal salt dissolved, to give a yellow liquid clathrate layer of volume ca. 2 cm^3. The tube was loosely stoppered and the mixture allowed to stand for a period of ca. 12 h, resulting in the deposition of the compound as bright yellow blocks. Anal. Calcd for $C_{20}H_{29}O_{16}Cl_3U·2H_2O$: C, 26.00; H, 5.80. Found: C, 25.86; H, 6.26. Attempts to obtain samples uncontaminated by adventitious water were frustrated by the complex's extreme moisture sensitivity.

$[UO_2(H_2O)_3Cl_2]_{16}\cdot(15\text{-crown-}5)_{16}$ (7). The reaction mixture from **6** was allowed to stand for a period of ca. 6 weeks, resulting in the dissolution of **6** and deposition of **7** as large, bright yellow prisms. Anal. Calcd for $C_{10}H_{26}O_{10}Cl_2U$: C, 19.56; H, 4.23. Found: C, 19.88; H, 4.37.

Crystallography. Crystal data and data collection parameters are summarized in Table 2. Crystals were mounted using a fast-setting epoxy resin on the end of a glass fiber and, in the case of **2** and **7**, cooled on the diffractometer to −113 or −100 °C, respectively. All crystallographic measurements were carried out with a Nonius KappaCCD equipped with graphite-monochromated Mo Kα radiation using ϕ rotations with 2° frames (1° for **7**) and a detector to crystal distance of 25 mm (30 mm for **7**). Data for **2** were collected on a Siemens SMART diffractometer using ω rotations with narrow frames). Integration was carried out by the program DENZO-SMN[39] or by the Siemens suite of programs. Data sets were corrected for Lorentz and polarization effects and for the effects of absorption using the program Scalepack[39] (**1** and **5**−**7**) or a pseudo-ψ-scan method (**2**). Structures were solved using the direct methods option of SHELXS-86[40] and developed using conventional alternating cycles of least-squares refinement and difference Fourier synthesis (SHELXL-97[41]). In general all non-hydrogen atoms were refined anisotropically, while hydrogen atoms were fixed in idealized positions and allowed to ride on the atom to which they were attached. Hydrogen atom thermal parameters were tied to those of the atom to which they were attached. For complex **6** both crown ethers (which reside upon a crystallographic mirror plane) were found to be disordered and were modeled in terms of two different positions for O(3A) of 50% occupancy each and a number of minor contributions to crown “B” each of 25% occupancy. Disorder was also present for the water ligands O(3) and O(4) and was treated in terms of three positions each (across the mirror plane) of occupanices 25%, 50%, and 25%, respectively. Despite this disorder refinement converged satisfactorily with R1 = 0.0417. All calculations were carried out either on a Silicon Graphics Indy R5000 workstation or on an IBM-PC compatible personal computer. For details of refinements see Table 3.

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Supporting Information Available: Five X-ray crystallographic files in, CIF format, are available on the Internet only. Access information is given on any current masthead page.

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(39) Otwinowski, Z.; Minor, W. In *DENZO*; Otwinowski, Z., Minor, W., Eds.; Academic Press: New York, 1996; Vol. 276.

(40) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(41) Sheldrick, G. M. In *SHELX-97*; Sheldrick, G. M., Ed.; University of Göttingen: Göttingen, Germany, 1997.