homologues respectives dans les esters (Watson, Vicković & Ternay, 1985). La longueur de O(4)—C(13) [1,359 (5) Å] s'explique par la conjugaison des doublets non partagés de O(4) avec les électrons π du noyau phényle et celle, un peu trop grande, trouvée pour O(6)—C(20) [1,472 (8) Å] par les faits déjà évoqués à propos de C(20)—C(21).

La Fig. 2 représente la structure vue selon l'axe *c*. La cohésion intermoléculaire est due aux forces de van der Waals. Si l'on admet pour rayons de van der Waals des atomes de carbone et d'oxygène les valeurs suivantes (Bondi, 1964): r(C aliphatique) = 1,70, r(C aromatique) = 1,77 et r(O) = 1,50 Å, on constate que les distances indiquées ci-après sont très proches de la somme des rayons des deux atomes concernés. Il s'agit de $O(2)—O(3^{i})$ [3,103 (5) Å] [(i) $x, \frac{1}{2}-y, -\frac{1}{2}+z$], de $O(3)—C(2^{ii})$ [3,113 (5) Å] [(ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$], de $O(5)—C(16^{iii})$ [3,276 (5) Å] [(iii) $1+x, y, z$] et de $C(5)—C(15^{iv})$ [3,435 (6) Å] [(iv) $1-x, -y, 2-z$].

Références

Binger, P., Cetinkaya, B. & Krüger, C. (1978). *J. Organomet. Chem.* **159**, 63–72.

Bondi, A. (1964). *J. Phys. Chem.* pp. 441–451.

Busing, W. R., Martin, K. O. & Levy, H. A. (1971). *ORFFE*3. Rapport ORNL-TM-306. Oak Ridge National Laboratory, Tennessee, EU.

Cunliffe, W. J. & Miller, A. J. (1984). Dans *Retinoid Therapy*. Lancaster: MTP Press.

De Cian, A., L'Huillier, P. M. & Weiss, R. (1973). *Bull. Soc. Chim. Fr.* pp. 451–457.

Ducrey, P. (1985). Thèse de 3^{e} cycle de Doctorat en Pharmacie. Univ. de Nantes, France.

Frenz, B. A. (1982). *Structure Determination Package*. B. A. Frenz & Associates Inc., College Station, Texas, EU, et Enraf–Nonius, Delft, Pays-Bas.

Herbstein, F. H. & Reisner, M. G. (1977). *Acta Cryst.* B**33**, 3304–3317.

International Tables for X-ray Crystallography (1974). Tome IV, pp. 99 et 149. Birmingham: Kynoch Press. (Distributeur actuel Kluwer Academic Publishers, Dordrecht.)

Ito, T. & Sugawara, Y. (1983). *Best-Plane Program*, 3^{e} version (*BP7C*). The Institute of Physical and Chemical Research, Wako-Shi, Saitama 351, Japon.

Johnson, C. K. (1976). *ORTEP*II. Rapport ORNL-5138. Oak Ridge National Laboratory, Tennessee, EU.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univ. de York, Angleterre, et de Louvain, Belgique.

Mills, O. S. & Robinson, G. (1963). *Acta Cryst.* **16**, 758–761.

Nugent, J. & Clark, S. (1985). Dans *Ciba Foundation Symposium,* Tome 113: *Retinoids, Differentiation and Disease.* Londres: Pitman.

Sporn, A. B., Roberts, A. B. & Goodman, D. S. (1984). Dans *The Retinoids,* Tomes I et II. Londres: Academic Press.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 159–166.

Watson, W. H., Vicković, I. & Ternay, A. L. Jr (1985). *Acta Cryst.* C**41**, 1090–1092.

Acta Cryst. (1988). C**44**, 1397–1399

Preparation and Structure of Bis(1,4,7,10,13,16-hexaoxacyclooctadecaneammonium) Hexachlorouranate(IV)–Acetonitrile (1/2), $[(NH_4)(18\text{-crown-}6)]_2[UCl_6].2CH_3CN$[*]

By Robin D. Rogers[†] and Matthew M. Benning

Department of Chemistry, Northern Illinois University, DeKalb, IL 60115, *USA*

(*Received* 23 *February* 1988; *accepted* 5 *April* 1988)

Abstract. $[(NH_4)(C_{12}H_{24}O_6)]_2[UCl_6].2C_2H_3N$, M_r = 1098, rhombohedral, $R\bar{3}$ (the non-centrosymmetric $R3$ was investigated but not utilized), $a = 13{\cdot}888$ (6), $c = 21{\cdot}215$ (9) Å, $V = 3543{\cdot}7$ Å^3, $Z = 3$, $D_x = 1{\cdot}54$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 36{\cdot}3$ cm^{-1}, $F(000) = 1356$, $T = 293$ K, final $R = 0{\cdot}027$ for 1394 observed [$F_o \geq 5\sigma(F_o)$] reflections. The uranium atoms reside on crystallographic $\bar{3}$ symmetry sites. The ammonium cations reside on and the 18-crown-6 molecules around threefold crystallographic axes. The solvent molecules interact weakly with one side of the ethers and are disordered about the threefold axes. The ammonium cations are hydrogen bonded to three 18-crown-6 oxygen atoms [N(1)···O(2) = 2·887 (4) Å] with single hydrogen bonds and the fourth hydrogen atom of each cation is directed down a threefold axis towards three Cl atoms of an anion [N(1)···Cl = 3·510 (6) Å]. The closest NCMe···O contact is 3·70 (1) Å and the unique U—Cl separation is 2·6099 (7) Å.

Introduction. We have recently reported the preparation and structural characterization of complexes isolated from the reactions of 18-crown-6, dibenzo-18-crown-6, 15-crown-5, benzo-15-crown-5, and 12-crown-4 with UCl_4 in 3:1 mixtures of acetonitrile and

---

[*] *f*-Element/Crown Ether Complexes 23. Part 22: Rogers, Rollins & Benning (1988).

[†] To whom all correspondence should be addressed.

0108-2701/88/081397-03$03.00

methanol under conditions in which aerial oxidation of U^{IV} may take place (Rogers, Kurihara & Benning, 1988). In several cases crystallization resulted from the production or abstraction of a suitable counterion: either the ammonium ion in $[(NH_4)(15\text{-crown-}5)_2]_2$-$[UO_2Cl_4].2CH_3CN$, $[(NH_4)(\text{benzo-}15\text{-crown-}5)_2]_2$-$[UCl_6].4CH_3CN$ and $[(NH_4)(\text{dibenzo-}18\text{-crown-}6)]_2$-$[UO_2Cl_4].2CH_3CN$, or a sodium ion as found in $[Na(12\text{-crown-}4)_2]_2[UO_2Cl_4].2OHMe$ (Rogers, 1988). We have been able to isolate a similar ammonium ion complex of 18-crown-6 and report here the similarities to and dissimilarities from the previously determined ammonium ion/crown ether complexes of the title complex.

Experimental. 1·32 mmol of 18-crown-6 in 3 mL of CH_3CN/CH_3OH (3:1) was added to a stirring solution of 1·32 mmol of UCl_4 in 3 mL of the same solvent. The reaction mixture was heated to 333 K for 1 h, centrifuged and the volume reduced by $\frac{1}{3}$. The solution flask was then slowly cooled (0·1 K min^{-1}) to 268 K. Large green crystals of the title complex formed. Anal. calcd. for $[(NH_4)(18\text{-crown-}6)]_2[UCl_6].2CH_3CN$: C, 30·63; H, 5·69; N, 5·10; found: C, 29·50; H, 5·42; N, 4·18%. D_m not determined. Crystal 0·25 × 0·35 × 0·40 mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$. Cell constants from setting angles of 25 reflections ($\theta > 19°$). Corrections for Lorentz–polarization effect and for absorption (empirical), range of relative transmission factors 55/100%. $\theta_{max} = 25°$; h 0 to 16, k −16 to 16, l −25 to 25; $-h + k + l \neq 3n$ not collected ($R_{int} = 0·048$). 4169 reflections measured, 1394 independent observed reflections [$F_o \geq 5\sigma(F_o)$]. Structure solved *via* Patterson function and subsequent difference Fourier techniques. Crown-ether H atoms placed 0·95 Å from bonded C atom with a fixed isotropic thermal parameter, $B = 5·5$ Å^2, and allowed to ride with the C—H distance fixed. The two unique ammonium-ion H atoms were located from a difference Fourier map and included with fixed contributions ($B = 5·5$ Å^2). The solvent molecules are disordered about crystallographic threefold axes and were refined [N(2), C(5) and C(6)] with occupancy factors of 33%; methyl H atoms were not located. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); structure refined with *SHELX*76 (Sheldrick, 1976). $\sum w(|F_o| - |F_c|)^2$ minimized, weights = $[\sigma(F_o)^2]^{-1}$, 80 parameters varied. $R = 0·027$, $wR = 0·032$, $S = 2·5$. Δ/σ in final least-squares refinement cycle <0·01, $\Delta\rho = 0·6$ e Å^{-3} in final difference map.*

Discussion. Fractional coordinates and U_{eq} values are given in Table 1, distances and angles in Table 2, and an *ORTEP* (Johnson, 1976) illustration of the formula unit and atom labelling in Fig. 1. The $[UCl_6]^{2-}$ anion resides on a crystallographic $\bar{3}$ position and is essentially octahedral. The unique U—Cl separation, 2·6099 (7) Å, is identical to the average U—Cl distance of 2·61 (4) Å in $[(NH_4)(\text{benzo-}15\text{-crown-}5)_2]_2[UCl_6]$.-$4CH_3CN$ (Rogers, Kurihara & Benning, 1988).

The 18-crown-6 molecules reside around threefold axes on which lie the ammonium cations. The crown ether displays its full D_{3d} symmetry with O(1) and its two symmetry-related positions in the molecule forming

Table 1. *Final fractional coordinates for* $[(NH_4)$-$(18\text{-}\mathit{crown}\text{-}6)]_2[UCl_6].2CH_3CN$

	x	y	z	U_{eq}*
U	0·6667	0·3333	0·3333	0·026
Cl(1)	0·8416 (1)	0·4189 (1)	0·26049 (6)	0·045
O(1)	0·8935 (3)	0·3974 (3)	0·0715 (2)	0·056
O(2)	0·8278 (3)	0·5575 (3)	0·0915 (2)	0·052
N(1)	0·6667	0·3333	0·1281 (3)	0·045
C(1)	0·9672 (4)	0·5082 (5)	0·0918 (3)	0·058
C(2)	0·9331 (5)	0·5844 (4)	0·0655 (3)	0·057
C(3)	0·7919 (5)	0·6332 (4)	0·0719 (3)	0·062
C(4)	0·6808 (5)	0·5980 (4)	0·0995 (3)	0·058
N(2)	0·738 (3)	0·263 (2)	−0·123 (1)	(iso)
C(5)	0·709 (3)	0·289 (3)	−0·082 (1)	(iso)
C(6)	0·6667	0·3333	−0·0417 (9)	(iso)
H(1)[N(1)]	0·667	0·333	0·172	(iso)
H(2)[N(1)]	0·605	0·325	0·116	(iso)

* U_{eq} is equal to $(U_{11} + U_{22} + U_{33})/3$.

Table 2. *Bond distances* (Å) *and angles* (°) *for* $[(NH_4)(18\text{-}\mathit{crown}\text{-}6)]_2[UCl_6].2CH_3CN$

U—Cl(1)	2·6099 (7)		
O(1)—C(1)	1·423 (4)	O(2)—C(2)	1·426 (4)
O(2)—C(3)	1·432 (4)	O(1)—C(4^{i})	1·414 (7)
C(1)—C(2)	1·468 (5)	C(3)—C(4)	1·486 (5)
N(2)—C(5)	1·09 (2)	C(5)—C(6)	1·35 (2)
Cl(1)—U—Cl(1^{ii})	88·55 (3)	Cl(1)—U—Cl(1^{iii})	91·49 (3)
Cl(1)—U—Cl(1^{iv})	180·0		
C(1)—O(1)—C(4^{i})	112·7 (5)	C(2)—O(2)—C(3)	112·6 (3)
O(1)—C(1)—C(2)	110·3 (3)	O(2)—C(2)—C(1)	108·8 (3)
O(2)—C(3)—C(4)	109·2 (3)	O(1^{ii})—C(4)—C(3)	108·4 (5)
N(2)—C(5)—C(6)	167 (2)		

Symmetry codes: atoms related to those in Table 1 by (i) $1-x+y$, $1-x$, z; (ii) $1-y$, $x-y$, z; (iii) $\frac{1}{3}+y$, $\frac{2}{3}-x+y$, $\frac{2}{3}-z$; (iv) $\frac{4}{3}-x$, $\frac{2}{3}-y$, $\frac{2}{3}-z$.

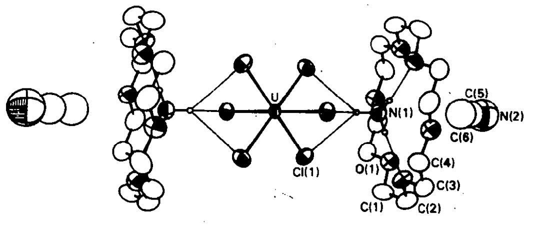

Fig. 1. $[(NH_4)(18\text{-crown-}6)]_2[UCl_6].2CH_3CN$. 50% probability ellipsoids for thermal motion. H atoms arbitrarily reduced, all but those for N(1) omitted.

---

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares-planes results have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44937 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

a plane deviating from the mean plane of all six O atoms towards the solvent molecule, and the three remaining oxygen atoms [O(2) and related positions] deviating towards the cation. The latter three O atoms are hydrogen bonded to the ammonium cation: H(2)[N(1)]···O(2) = 2·06 Å, N(1)–H(2)[N(1)]···O(2) = 167·9°, N(1)···O(2) = 2·887 (4) Å. The N(1)···O(1) separations are 3·058 (5) Å. These values and the deviation of the N atoms from the mean plane of the crown O atoms, 0·99 Å, are almost identical to those observed for $[(NH_4)(18\text{-crown-}6)][Br].2H_2O$ (Nagano, Kobayashi & Sasaki, 1978): N···O contacts closest to the ammonium ion average 2·871 Å, the remainder 3·064 Å, and the ammonium ion is 1·00 Å from the mean plane of all six O atoms. The average crown ether bonding parameters in the title complex are normal: O—C = 1·424 (6), C—C = 1·477 (9) Å, O—C—C = 109·2 (7), C—O—C = 112·6 (1)°.

The solvent molecules are disordered about the threefold axes (with the methyl groups residing on the symmetry axes) and may interact weakly if at all with the back side of the crown ether. The closest contact, C(6)···O(1), is 3·70 (1) Å [C(6)···O(2) = 3·96 (1) Å]. These values are much longer than observed in complexes of acetonitrile and crown ethers where C—H acidic hydrogen bonding does exist: 18-crown-6.-$2CH_3CN$ (Rogers, Richards & Voss, 1988), C···O separations average 3·25 (4) Å for those three oxygens which deviate towards the methyl group; dibenzo-18-crown-6.$2CH_3CN$ (Rogers, Kurihara & Richards, 1987), C···O average 3·42 (9) Å; $[UO_2(OH_2)_5]$-$[ClO_4]_2.2(18\text{-crown-}6).2CH_3CN.H_2O$ (Rogers, Kurihara & Benning, 1987), C···O average 3·29 (5) Å. The N(1)···C(6) through the ring contact is 3·60 (2) Å, with C(6) 2·61 Å out of the mean plane of the six crown O atoms.

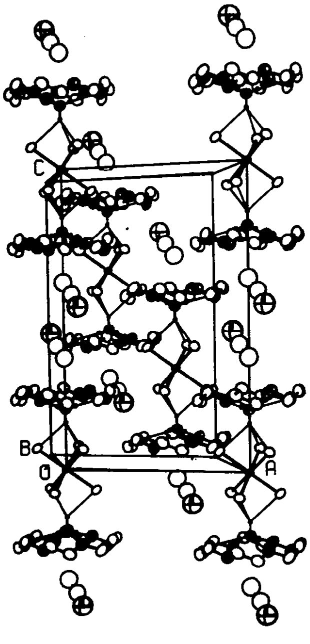

Fig. 2. Cell packing revealing the regular repetition of the formula units in chains along **c**.

Of the five complexes of this type we have structurally characterized, $[Na(12\text{-crown-}4)_2]_2[UO_2Cl_4]$.-2OHMe (Rogers, 1988), $[(NH_4)(15\text{-crown-}5)_2]_2[UO_2Cl_4].2CH_3CN$, $[(NH_4)(\text{benzo-}15\text{-crown-}5)_2]_2[UCl_6]$.-$4CH_3CN$, $[(NH_4)(\text{dibenzo-}18\text{-crown-}6)]_2[UO_2Cl_4]$.-$2CH_3CN$ (Rogers, Kurihara & Benning, 1988), and the title complex, the first three with the smaller crown ether achieve complete charge separation by forming sandwich cations. The title complex and the dibenzo-18-crown-6 structure, utilizing the larger crown ethers, crystallize with the ammonium ion hydrogen bonded to the crown ether on one side and the anion on the other. In this case the result is polymeric chains of the formula unit along **c** (Fig. 2). The ammonium cation presents a single hydrogen along the threefold axis to three chloride ions: H(1)[N(1)]···Cl = 2·81 Å, N(1)–H(1)-[N(1)]···Cl = 131·6°, N(1)···Cl = 3·510 (6) Å. In $[(NH_4)(\text{dibenzo-}18\text{-crown-}6)]_2[UO_2Cl_4].2CH_3CN$ a similar hydrogen-bonding pattern was observed although the cations are on twofold axes and interact with only two chlorine atoms in the $[UO_2Cl_4]^{2-}$ ions. As a consequence, the H···Cl and N···Cl contacts are slightly smaller [2·65, 3·401 (5) Å, respectively].

We thank the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this work and the NSF Chemical Instrumentation Program for funds used to purchase the diffractometer.

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

NAGANO, O., KOBAYASHI, A. & SASAKI, Y. (1978). *Bull. Chem. Soc. Jpn*, **51**, 790–793.

ROGERS, R. D. (1988). *Acta Cryst.* C**44**, 638–641.

ROGERS, R. D., KURIHARA, L. K. & BENNING, M. M. (1987). *J. Inclusion Phenom.* **5**, 645–658.

ROGERS, R. D., KURIHARA, L. K. & BENNING, M. M. (1988). *Inorg. Chem.* **26**, 4346–4352.

ROGERS, R. D., KURIHARA, L. K. & RICHARDS, P. D. (1987). *J. Chem. Soc. Chem. Commun.* pp. 604–606.

ROGERS, R. D., RICHARDS, P. D. & VOSS, E. J. (1988). *J. Inclusion Phenom.* **6**, 65–71.

ROGERS, R. D., ROLLINS, A. N. & BENNING, M. M. (1988). *Inorg. Chem.* In the press.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.