The crystals were supplied by Dr R. W. M. ten Hoedt, Dr J. G. Noltes and Professor G. van Koten.

The X-ray data were collected by Dr A. J. M. Duisenberg.

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Structure of Bis[(18-crown-6)ammonium]* Aquadioxotetrathiocyanatouranate

BY WANG MING AND ZHENG PEI-JU

Center of Analysis and Measurement, Fudan University, Shanghai, People's Republic of China

AND ZHANG JING-ZHI, CHEN ZHONG, SHEN JIN-MING AND YANG YONG-HUI

Department of Chemistry, Shandong University, Jinan, Shandong, People's Republic of China

Abstract. $[NH_4(C_{12}H_{24}O_6)]_2[UO_2(NCS)_4(H_2O)]$, $M_r = 1085 \cdot 09$, orthorhombic, $Fdd2$, $a = 29 \cdot 927$ (3), $b = 34 \cdot 527$ (3), $c = 8 \cdot 724$ (1) Å, $V = 9014 \cdot 5$ Å^3, $Z = 8$, $D_x = 1 \cdot 599$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0 \cdot 71073$ Å, $\mu = 36 \cdot 539$ cm^{-1}, $F(000) = 4352$, $T = 293$ K, $R = 0 \cdot 042$ for 1877 observed reflections with $F^2 > 3\sigma(F^2)$. The uranyl group does not enter into the 18-crown-6 cavity, but presents the usual pentacoordination in the equatorial plane with four linear NCS$^-$ ions and one water molecule. The NH$_4^+$ cation is anchored in the crown ether ring by hydrogen bonds and ion–dipolar interactions *via* oxygen atoms of the crown ether.

Introduction. Recently several systems for the extraction of uranium with crown ethers have been studied. It was reported that the extractability of uranium with crown ethers is different in various thiocyanate solutions (Jin & Xu, 1982). However, little is known about the structures and properties of these complexes. It is also of interest to know how uranium and crown ethers link up when some thiocyanates coexist. We synthesized some complexes and determined their struc-

tures. As part of these studies we report here the structure of the title compound.

Experimental. Yellow crystal ($0 \cdot 12 \times 0 \cdot 18 \times 0 \cdot 24$ mm). D_m not determined. Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell constants refined from 25 reflections ($14 < \theta < 15°$). Three standard reflections every 3600 s, $2\theta_{max} = 60°$, $h = 0$ to 42, $k = 0$ to 48, $l = 0$ to 12. 3684 independent reflections but only 1877 with $F^2 > 3\sigma(F^2)$ were used in the refinement. Variation of standard reflections $12,\overline{12},4$, $\overline{6}46$ and $\overline{11},\overline{17},3$, $\pm 0 \cdot 7\%$. Data corrected for Lorentz–polarization but not absorption. Systematic absences, hkl: $h+k$, $k+l$, ($h+l$) $= 2n+1$, $0kl$: $k+l = 4n \pm 1$, $h0l$: $h+l = 4n \pm 1$. Structure solved by Patterson method, ΔF syntheses. No attempts were made to locate the H atoms. Full-matrix least-squares refinement with anisotropic temperature factors. 254 variables, $(\Delta/\sigma)_{max} < 0 \cdot 06$, $R = 0 \cdot 042$, $wR = 0 \cdot 047$ where $w = 1$, $F^2 > 3\sigma(F^2)$; $w = 0$, $F^2 < 3\sigma(F^2)$. Correction for isotropic extinction, extinction coefficient $= 7 \cdot 47 \times 10^{-8}$. Max. value in final difference density map was $1 \cdot 976$ e Å^{-3} located near the U atom. Calculation performed on a PDP 11/44 computer

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* 18-Crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane.

with *SDP* program supplied by Enraf–Nonius (1983). Neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Table 1. *Atomic coordinates and thermal parameters with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab\cos\gamma B(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)].$

	x	y	z	$B_{eq}(\text{Å}^2)$
U	0·250	0·250	0·250	3·91 (1)
S(1)	0·2367 (1)	0·3272 (1)	0·7404 (6)	5·70 (9)
S(2)	0·1424 (2)	0·3608 (1)	0·1928 (6)	6·4 (1)
O(1)	0·2957 (4)	0·2813 (3)	0·250 (2)	6·8 (2)
O(2)	0·250	0·250	−0·036 (2)	6·1 (4)
O(3)	0·0717 (3)	0·3332 (3)	0·675 (1)	4·6 (2)
O(4)	0·1050 (3)	0·2601 (3)	0·775 (1)	4·9 (2)
O(5)	0·1195 (3)	0·2022 (3)	0·550 (1)	5·2 (2)
O(6)	0·0670 (3)	0·2026 (3)	0·285 (1)	4·9 (2)
O(7)	0·0349 (3)	0·2751 (3)	0·180 (1)	4·4 (2)
O(8)	0·0211 (3)	0·3331 (3)	0·403 (1)	4·4 (2)
N(1)	0·2235 (5)	0·2856 (4)	0·476 (2)	8·4 (5)
N(2)	0·2035 (5)	0·3020 (4)	0·158 (2)	6·3 (3)
N(3)	0·0997 (4)	0·2784 (3)	0·435 (1)	3·8 (2)
C(1)	0·2301 (6)	0·3030 (4)	0·586 (2)	5·6 (4)
C(2)	0·1780 (5)	0·3265 (4)	0·171 (2)	4·6 (3)
C(3)	0·0734 (6)	0·3211 (5)	0·834 (2)	6·2 (4)
C(4)	0·1129 (5)	0·2958 (5)	0·854 (2)	5·5 (4)
C(5)	0·1426 (5)	0·2345 (5)	0·776 (2)	6·3 (4)
C(6)	0·1315 (5)	0·1960 (5)	0·711 (2)	5·5 (4)
C(7)	0·1049 (5)	0·1667 (4)	0·482 (2)	5·6 (4)
C(8)	0·1010 (5)	0·1738 (4)	0·309 (2)	5·6 (4)
C(9)	0·0643 (6)	0·2117 (4)	0·129 (2)	5·2 (4)
C(10)	0·0242 (5)	0·2393 (4)	0·104 (2)	5·1 (3)
C(11)	−0·0017 (5)	0·3013 (4)	0·174 (2)	4·7 (3)
C(12)	0·0116 (5)	0·3396 (4)	0·243 (2)	5·1 (3)
C(13)	0·0326 (5)	0·3681 (4)	0·474 (2)	4·9 (3)
C(14)	0·0364 (5)	0·3608 (4)	0·646 (2)	5·7 (4)

Table 2. *Bond distances (Å) and angles (°) with e.s.d.'s in parentheses*

U–O(1)	1·743 (3)	O(5)–C(7)	1·426 (6)
U–O(2)	2·493 (4)	O(6)–C(8)	1·436 (6)
U–N(1)	2·452 (5)	O(6)–C(9)	1·399 (6)
U–N(2)	2·410 (5)	O(7)–C(10)	1·436 (5)
S(1)–C(1)	1·599 (6)	O(7)–C(11)	1·423 (5)
S(2)–C(2)	1·602 (6)	O(8)–C(12)	1·442 (6)
N(1)–C(1)	1·151 (7)	O(8)–C(13)	1·399 (5)
N(2)–C(2)	1·145 (6)	C(3)–C(4)	1·482 (9)
O(3)–C(3)	1·457 (6)	C(5)–C(6)	1·482 (8)
O(3)–C(14)	1·444 (6)	C(7)–C(8)	1·538 (9)
O(4)–C(4)	1·433 (6)	C(9)–C(10)	1·548 (7)
O(4)–C(5)	1·430 (6)	C(11)–C(12)	1·506 (7)
O(5)–C(6)	1·464 (6)	C(13)–C(14)	1·524 (8)

O(1)–U–O(1')	180·00 (0)	C(12)–O(8)–C(13)	110·0 (4)
O(1)–U–O(2)	89·9 (2)	U–N(1)–C(1)	151·2 (6)
O(1)–U–N(1)	86·8 (2)	U–N(2)–C(2)	154·2 (5)
O(1)–U–N(1')	93·3 (2)	S(1)–C(1)–N(1)	177·2 (7)
O(1)–U–N(2)	89·5 (2)	S(2)–C(2)–N(2)	179·3 (6)
O(1)–U–N(2')	90·4 (2)	O(3)–C(3)–C(4)	108·1 (5)
O(2)–U–N(1)	143·4 (1)	O(4)–C(4)–C(3)	108·6 (5)
O(2)–U–N(2)	70·5 (1)	O(4)–C(5)–C(6)	112·1 (4)
N(1)–U–N(1')	73·2 (3)	O(5)–C(6)–C(5)	106·9 (5)
N(1)–U–N(2)	73·0 (2)	O(5)–C(7)–C(8)	107·1 (5)
N(1)–U–N(2')	145·9 (2)	O(6)–C(8)–C(7)	107·7 (4)
N(2)–U–N(2')	141·0 (2)	O(6)–C(9)–C(10)	108·8 (4)
C(3)–O(3)–C(14)	112·5 (5)	O(7)–C(10)–C(9)	106·9 (4)
C(4)–O(4)–C(5)	113·6 (4)	O(7)–C(11)–C(12)	110·0 (4)
C(6)–O(5)–C(7)	110·2 (5)	O(8)–C(12)–C(11)	107·6 (4)
C(8)–O(6)–C(9)	109·7 (4)	O(8)–C(13)–C(12)	108·1 (4)
C(10)–O(7)–C(11)	111·1 (4)	O(3)–C(14)–C(13)	109·6 (4)

Discussion. The atomic parameters are given in Table 1.* The structure is shown in Fig. 1. Table 2 gives bond distances and angles for the complex.

The structure consists of a $[UO_2(NCS)_4(H_2O)]^{2-}$ complex anion and two $[(18\text{-crown-}6)NH_4]^+$ complex cations. The U atom is located on the 2 axis. The linear O=U=O ion is perpendicular to a nearly planar pentagon formed by four N atoms of the linear thiocyanate ions and one O atom of the water molecule around its equator. The bond distances U−N are close to those of Alcock, Roberts & Brown (1982).

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* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43647 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
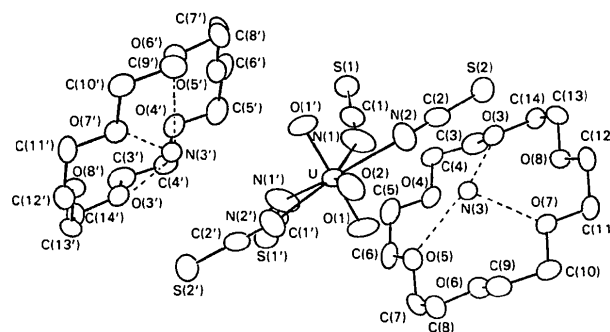

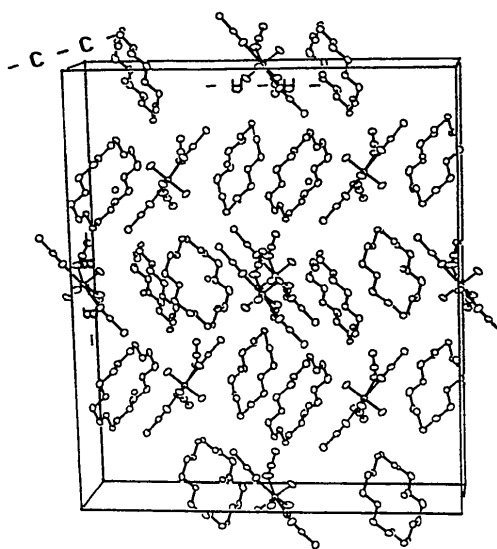Fig. 1. View and atomic numbering of the title compound.

Fig. 2. A view of the unit cell.

In the complex cation the distances from nitrogen atom N(3) of the ammonium ion to O(3), O(5) and O(7) of the crown ether are 2·94, 2·88 and 2·96 Å respectively. This means that three hydrogen bonds are formed (Behr, Dumas & Moras, 1982). Further stabilization may arise from ion–dipolar interactions; the distances from N(3) to the other three oxygen atoms O(4), O(6) and O(8) of the crown ether are 3·03, 3·09 and 3·03 Å respectively. The six O atoms are alternately about 0·20 Å above and below their mean plane to form a nearly planar hexagon. The twelve C atoms of the crown ether are nearly located in two planes which are parallel to the oxygen mean plane. The symmetry of the crown ether is close to D_{3d} as in (18-crown-6) complexes with potassium (Seiler, Dobler & Dunitz, 1974) and rubidium (Dobler & Phizackerley, 1974) thiocyanates.

In the crown ether ring, the average bond distance of C—C is 1·523 Å, C—O is 1·432 Å. The average angle of O—C—C is 109·3°, C—O—C is 111·2°. The torsion angles about C—C bonds are close to 65°. Those about C—O bonds are close to 175°. All these data are similar to those published in other papers (Dunitz, Dobler, Seiler & Phizackerley, 1974).

Complex anions and cations are attracted to each other. Only two NH_4^+ ions are 4·88 Å distant from the

U atom; others are more than 8 Å. Thus the complex anion is sandwiched between two NH_4^+ complexes of crown ether. Besides Coulomb forces, there are van der Waals forces formed by some atoms between complex anions and cations. The crystal is stabilized by these forces. Fig. 2 shows a view of the unit cell.

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Structure of Diethylammonium Enneaiododibismuthate(III)

BY F. LAZARINI

Department of Chemistry and Chemical Technology, Edvard Kardelj University of Ljubljana, Murnikova 6, 61000 Ljubljana, Yugoslavia

Abstract. $[NH_2(C_2H_5)_2]_3[Bi_2I_9]$, $M_r = 1782·54$, monoclinic, $P2_1/c$, $a = 12·919$ (4), $b = 14·718$ (3), $c = 19·975$ (5) Å, $\beta = 102·04$ (2)°, $V = 3714·53$ Å³, $Z = 4$, $D_m = 3·15$ (7), $D_x = 3·187$ g cm⁻³, $\lambda(Mo\,K\alpha) = 0·71069$ Å, $\mu = 161·3$ cm⁻¹, $F(000) = 3088$, $T = 293$ (1) K, $R = 0·077$ for 2202 diffractometer data $[I > 2·5\sigma(I)]$. The structure consists of $[NH_2(C_2H_5)_2]^+$ cations and binuclear $[Bi_2I_9]^{3-}$ anions composed of face-sharing octahedra with Bi—I(terminal) distances in the range between 2·934 (4) and 3·032 (3) Å and Bi—I(bridging) distances in the range between 3·169 (3) and 3·277 (3) Å. An isomorphous bromine compound also exists.

Introduction. The results of the systematic study of halobismuthates(III) show a great variety of different

halobismuthate(III) anions in the crystalline state, most of them bi- or polynuclear (see Lazarini, 1985, and references cited therein). The investigations were extended to the five existing diethylammonium halobismuthates(III) in order to examine the effect of a flexible cation on the geometry of the hexahalobismuthate(III) groups in these compounds (Lazarini, 1985; Blažič & Lazarini, 1985; Lazarini, 1987). The structural analysis of the title compound completes these investigations.

Experimental. Crystals of suitable dimensions for X-ray structural analysis were grown by slow evaporation at room temperature from a saturated solution of $(C_2H_5)_2NH$ and BiI_3 (molar ratio 3:2) in *n*-propanol–acetone–40% HI (90:9:1). D_m determined pycnometrically in CCl_4 at 293 K. A well developed