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 $D_{3a}$ as in (18-crown-6) complexes with potassium (Seller, 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, Seller & 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.

The authors are grateful for the financial support of The Science Fund of The Chinese Academy of Sciences.

References


crystal, selected for diffraction measurements, was characterized by the following planes (the distances in parentheses are from the crystal face to the centre of the crystal): ±(010)(0.009 mm), ±(001)(0.116 mm), ±(100)(0.118 mm). Intensities of three standard reflexions were averaged (agreement factor for 186 reflexions 0.016) and reflexions having I< 2.50(/) were rejected, 2202 reflexions remained for the structural analysis. Corrections applied for Lorentz and polarization effects, and for absorption [transmission factors, A/a=0.63 and 0.05 respectively in the final cycle.

For Bi and I the equivalent isotropic thermal parameter is given

\[ U_{eq} = \left( U_{11} + U_{22} + U_{33} \right)/3 \]

Table 1. Final positional parameters (×10⁴) and isotropic thermal parameters (×10³) with e.s.d.'s in parentheses

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

Fig. 1. Projection of the structure along b.
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(2.2 ≥ Δρ ≥ −2.0). Calculations performed on the DEC-10 computer at the Edvard Kardelj University, Ljubljana, with SHELX76 (Sheldrick, 1976). Interatomic distances and angles calculated using the XRAY system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Atomic scattering factors for neutral atoms from Cromer & Mann (1968) and values of $f'$ and $f''$ for the anomalous-dispersion correction from Cromer & Liberman (1970).

**Discussion.** The positional and thermal parameters are listed in Table 1;* equivalent isotropic thermal parameters are given for Bi and I atoms and isotropic thermal parameters for N and C atoms. The projection of the structure along b is shown in Fig. 1. The interatomic distances and angles are given in Table 2.

The crystal structure consists of diethylammonium cations and binuclear [Bi$_2$I$_6$]$_2$ anions with face-sharing octahedra. The Bi–I(terminal) distances are in the range 2.934 (4)–3.032 (3) Å, the Bi–I(bridging) distances in the range 3.169 (3)–3.277 (3) Å. The [Bi$_2$I$_6$]$_2$ species ($X = Cl, Br, I$) seem to be very stable. They are present in many crystal structures with large cations (Lazarini, 1985, and references cited therein). These compounds usually crystallize from solutions with a wide Bi:cation ratio.

The bond lengths and angles within the [NH$_2$(C$_5$H$_7$)$_2$]$^+$ cations are determined with lower accuracy, but they are in agreement with the values found in related compounds. Contacts between I atoms of different anions and between I and N atoms slightly shorter than the sum of van der Waals radii (4.30 and 3.65 Å respectively) are present (Table 2).

An isomorphous bromine compound also exists (Lazarini, 1985).

The author thanks Professor L. Golič for his help in this investigation. The financial support of the Research Council of Slovenia is also gratefully acknowledged.

**References**


