

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  $\text{NH}_4^+$  ions are 4.88 Å distant from the

U atom; others are more than 8 Å. Thus the complex anion is sandwiched between two  $\text{NH}_4^+$  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.

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*Acta Cryst.* (1987). **C43**, 875–877

## Structure of Diethylammonium Enneaiodibismuthate(III)

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(Received 3 November 1986; accepted 11 December 1986)

**Abstract.**  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]_3[\text{Bi}_2\text{I}_9]$ ,  $M_r = 1782.54$ , monoclinic,  $P2_1/c$ ,  $a = 12.919$  (4),  $b = 14.718$  (3),  $c = 19.975$  (5) Å,  $\beta = 102.04$  (2)°,  $V = 3714.53$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 3.15$  (7),  $D_x = 3.187$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu = 161.3$  cm<sup>-1</sup>,  $F(000) = 3088$ ,  $T = 293$  (1) K,  $R = 0.077$  for 2202 diffractometer data [ $I > 2.5\sigma(I)$ ]. The structure consists of  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]^+$  cations and binuclear  $[\text{Bi}_2\text{I}_9]^{3-}$  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  $(\text{C}_2\text{H}_5)_2\text{NH}$  and  $\text{BiI}_3$  (molar ratio 3:2) in *n*-propanol-acetone-40% HI (90:9:1).  $D_m$  determined pycnometrically in  $\text{CCl}_4$  at 293 K. A well developed

crystal, selected for diffraction measurements, was characterized by the following planes (the distances in parentheses are from the crystal faces to the centre of the crystal):  $\pm(010)(0.009 \text{ mm})$ ,  $\pm(001)(0.116 \text{ mm})$ ,  $\pm(100)(0.118 \text{ mm})$ . Intensity data collected at 293 (1) K with an Enraf-Nonius CAD-4 diffractometer and graphite-monochromatized Mo K $\alpha$  radiation,  $\omega-2\theta$  scan,  $\theta_{\min}=1^\circ$ ,  $\theta_{\max}=25^\circ$ ,  $2\theta$  scan width  $(0.9+0.3 \tan\theta)^\circ$ , aperture  $(2.5+0.9 \tan\theta) \text{ mm}$ , max. scan time 40 s, background  $\frac{1}{4}$  of the scan time at each of the scan limits. 7089 reflexions recorded ( $0 \leq h \leq 15$ ,  $0 \leq k \leq 17$ ,  $-23 \leq l \leq 23$ ). Intensities of three standard reflexions (12 $\bar{6}$ , 1 $\bar{1}6$ , 2 $\bar{4}4$ ) varied  $\pm 8\%$ . After symmetry-related reflexions were averaged (agreement factor for 186 reflexions 0.016) and reflexions having  $I < 2.5\sigma(I)$  (calculations based on counting statistics) were rejected, 2202 reflexions remained for the structural analysis. Corrections applied for Lorentz and polarization effects, and for absorption [transmission factors, calculated with the measured crystal dimensions (512 grid points, crystal volume 0.00101 mm<sup>3</sup>), range from 0.052 to 0.748]. Unit-cell parameters obtained from a least-squares fit of the  $\theta$  values of 36 reflexions ( $8 < \theta < 12^\circ$ ) measured on the diffractometer. The systematic absences  $h0l: l = 2n+1$ ,  $0k0: k = 2n+1$  indicated the space group  $P2_1/c$ . The positions of the Bi and I atoms were determined using the procedure of direct phase determination in the SHELX76 program (Sheldrick, 1976), the N and C atoms were located from successive difference Fourier summations; H atoms were not located. The structure was refined by full-matrix least squares with anisotropic thermal parameters for Bi and I, isotropic thermal parameters for N and C atoms and with anomalous-dispersion correction.  $\sum w(|F_o| - |F_c|)^2$  minimized in the least-squares procedure. Weighting function applied in the final cycle:  $w = 6.08/[\sigma(F)^2 + 0.0005F^2]$ . Empirical extinction parameter included in the final stage of the refinement:  $7(1) \times 10^{-5}$ . Final  $R = 0.077$ ,  $wR = 0.060$  for 162 parameters and 2202 reflexions. Max. and av.  $\Delta/\sigma = 0.63$  and 0.05 respectively in the final cycle. Final difference Fourier map featureless

Table 1. Final positional parameters ( $\times 10^4$ ) and isotropic thermal parameters ( $\times 10^3$ ) with e.s.d.'s in parentheses

For Bi and I the equivalent isotropic thermal parameter is given [ $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$ ]; for N and C the isotropic thermal parameter is given.

	x	y	z	$U_{eq}/U(\text{\AA}^2)$
Bi(1)	837 (1)	2501 (1)	4192 (1)	45 (1)
Bi(2)	3875 (1)	2404 (1)	5396 (1)	44 (1)
I(1)	370 (3)	1594 (3)	2836 (2)	75 (3)
I(2)	-327 (3)	4159 (3)	3685 (2)	74 (3)
I(3)	-1001 (3)	1634 (3)	4624 (2)	67 (2)
I(4)	2274 (2)	763 (2)	4861 (2)	52 (2)
I(5)	3063 (2)	3293 (2)	3936 (1)	57 (2)
I(6)	1762 (2)	3343 (2)	5696 (1)	54 (2)
I(7)	4328 (3)	1507 (3)	6793 (1)	67 (2)
I(8)	5631 (2)	1427 (3)	4941 (2)	66 (2)
I(9)	5245 (3)	3979 (2)	5900 (2)	68 (2)
N(1)	2000 (32)	4968 (34)	1749 (20)	95 (14)
C(11)	1423 (46)	4328 (46)	2098 (26)	107 (20)
C(12)	592 (43)	3903 (41)	1519 (25)	97 (18)
C(13)	2706 (40)	5497 (40)	2370 (24)	85 (17)
C(14)	3148 (47)	6217 (46)	2112 (27)	113 (22)
N(2)	7337 (32)	3678 (28)	4821 (20)	79 (12)
C(21)	6863 (39)	4136 (38)	4264 (24)	91 (16)
C(22)	6213 (38)	3582 (37)	3724 (23)	82 (17)
C(23)	8037 (38)	4213 (38)	5349 (23)	82 (17)
C(24)	8498 (38)	3596 (36)	5989 (22)	77 (15)
N(3)	6722 (31)	4850 (30)	1558 (18)	76 (12)
C(31)	6368 (53)	5840 (54)	1849 (33)	147 (27)
C(32)	6256 (45)	5907 (44)	2514 (29)	110 (21)
C(33)	7563 (57)	4336 (56)	1946 (31)	138 (27)
C(34)	7562 (57)	3441 (57)	1812 (31)	145 (28)

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

Bi(1)-I(1)	2.967 (4)	Bi(2)-I(4)	3.214 (3)
Bi(1)-I(2)	2.934 (4)	Bi(2)-I(5)	3.169 (3)
Bi(1)-I(3)	2.978 (5)	Bi(2)-I(6)	3.225 (3)
Bi(1)-I(4)	3.277 (3)	Bi(2)-I(7)	3.032 (3)
Bi(1)-I(5)	3.241 (3)	Bi(2)-I(8)	2.983 (4)
Bi(1)-I(6)	3.239 (3)	Bi(2)-I(9)	2.962 (3)
I(1)-Bi(1)-I(2)	93.8 (1)	I(4)-Bi(2)-I(5)	86.43 (9)
I(1)-Bi(1)-I(3)	92.8 (1)	I(4)-Bi(2)-I(6)	82.70 (8)
I(1)-Bi(1)-I(4)	90.6 (1)	I(4)-Bi(2)-I(7)	88.1 (1)
I(1)-Bi(1)-I(5)	92.1 (1)	I(4)-Bi(2)-I(8)	90.8 (1)
I(1)-Bi(1)-I(6)	169.9 (1)	I(4)-Bi(2)-I(9)	176.7 (1)
I(2)-Bi(1)-I(3)	94.3 (1)	I(5)-Bi(2)-I(6)	82.16 (7)
I(2)-Bi(1)-I(4)	174.9 (1)	I(5)-Bi(2)-I(7)	172.0 (1)
I(2)-Bi(1)-I(5)	93.1 (1)	I(5)-Bi(2)-I(8)	92.6 (1)
I(2)-Bi(1)-I(6)	93.7 (1)	I(5)-Bi(2)-I(9)	92.8 (1)
I(3)-Bi(1)-I(4)	88.0 (1)	I(6)-Bi(2)-I(7)	91.4 (1)
I(3)-Bi(1)-I(5)	170.9 (1)	I(6)-Bi(2)-I(8)	171.9 (1)
I(3)-Bi(1)-I(6)	93.3 (1)	I(6)-Bi(2)-I(9)	94.0 (1)
I(4)-Bi(1)-I(5)	84.22 (8)	I(7)-Bi(2)-I(8)	93.3 (1)
I(4)-Bi(1)-I(6)	81.51 (9)	I(7)-Bi(2)-I(9)	92.4 (1)
I(5)-Bi(1)-I(6)	80.84 (7)	I(8)-Bi(2)-I(9)	92.4 (1)
I(3)-I(4)	4.113 (5)	I(4)-N(3 <sup>iii</sup> )	3.61 (4)
I(4)-I(8 <sup>iv</sup> )	4.174 (5)	I(3)-N(1 <sup>ii</sup> )	3.69 (4)
		I(7)-N(1 <sup>v</sup> )	3.69 (5)
N(1)-C(11)	1.48 (8)	C(11)-N(1)-C(13)	101 (4)
N(1)-C(13)	1.59 (6)	N(1)-C(11)-C(12)	104 (4)
C(11)-C(12)	1.54 (7)	N(1)-C(13)-C(14)	107 (4)
C(13)-C(14)	1.36 (9)		
N(2)-C(21)	1.34 (6)	C(21)-N(2)-C(23)	116 (4)
N(2)-C(23)	1.47 (6)	N(2)-C(21)-C(22)	115 (5)
C(21)-C(22)	1.47 (7)	N(2)-C(23)-C(24)	110 (4)
C(23)-C(24)	1.58 (7)		
N(3)-C(31)	1.67 (9)	C(31)-N(3)-C(33)	121 (4)
N(3)-C(33)	1.41 (8)	N(3)-C(31)-C(32)	120 (6)
C(31)-C(32)	1.37 (9)	N(3)-C(33)-C(34)	116 (6)
C(33)-C(34)	1.34 (12)		

Symmetry code: (i)  $-x, -y, 1-z$ ; (ii)  $1-x, -y, 1-z$ ; (iii)  $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$ ; (iv)  $-x, -\frac{1}{2}+y, \frac{1}{2}-z$ ; (v)  $x, \frac{1}{2}-y, \frac{1}{2}+z$ .

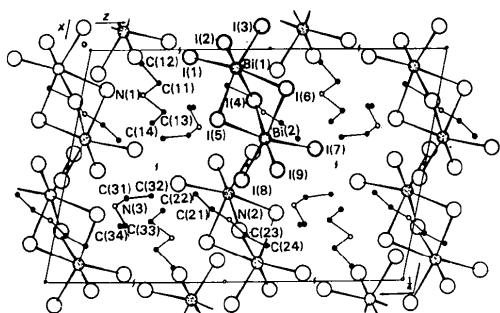


Fig. 1. Projection of the structure along b.

( $2.2 \geq \Delta\rho \geq -2.0$ ). 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  $[\text{Bi}_2\text{I}_9]^{3-}$  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  $[\text{Bi}_2\text{X}_9]^{3-}$  species ( $X = \text{Cl}, \text{Br}, \text{I}$ ) seem to be very stable. They are present in many crystal structures with large

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43636 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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  $[\text{NH}_2(\text{C}_2\text{H}_5)_2]^+$  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.

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*Acta Cryst.* (1987). **C43**, 877–880

## The Structure of Tetrachlorobis- $\mu$ -[dimethylenediphenylphosphato(V)- $C',C'$ ]-digold(III) Dihydrate, $[\text{Au}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ , an Organometallic Dinuclear Gold(III) Ylide Complex Containing Chloride Ligands

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(Received 28 April 1986; accepted 7 January 1987)

**Abstract.**  $[\text{Au}_2\text{Cl}_4\{\text{P}(\text{CH}_2)_2(\text{C}_6\text{H}_5)_2\}_2] \cdot 2\text{H}_2\text{O}$ ,  $M_r = 998.3$ , triclinic,  $P\bar{1}$ ,  $a = 11.927$  (7),  $b = 8.282$  (4),  $c = 8.829$  (6) Å,  $\alpha = 82.75$  (4),  $\beta = 106.67$  (5),  $\gamma = 100.24$  (4)°,  $V = 819.5$  (8) Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 2.02$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 9.61$  mm<sup>-1</sup>,  $F(000) = 472$ ,  $T = 298$  K. Convergence to final conventional  $R$  values of  $R = 0.0637$  and  $wR = 0.0666$

was obtained using 139 variable parameters and 1651 reflections with  $F_o^2 > 3\sigma(F_o^2)$ . The structure consists of discrete dinuclear gold(III) ylide dimers containing four-coordinate gold centers with *trans* chloride ligands. The Au atoms have square-planar coordination geometries and are symmetrically bridged by the ylide anion ligands. The unit cell consists of one complete centrosymmetric dimer and two molecules of water. The eight-membered heterocyclic ring of the complex is in a chair conformation, with the metal centers separated by a distance of 3.087 (2) Å.

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