The crystal structure of diethylammonium hexabromobismuthate(III) consists of $[NH_2(C_2H_5)_2]^+$ cations and $[BiBr_6]^{3-}$ anions. In contrast to the mainly ionic structure of $Rb_3[BiBr_6]$ (Lazarini, 1978), in the title compound the cations and anions are also attracted by hydrogen bonds of the type N—H···Br. Each $[NH_2(C_2H_5)_2]^+$ cation is linked to two different $[BiBr_6]^{3-}$ anions by two relatively weak hydrogen bonds: N—Br(2^{iii}) 3·30 (2) and N—Br(2^{iv}) 3·44 (2) Å; the sum of the van der Waals radii of N and Br is 3·45 Å. The arrangement of C(1), C(3), Br(2^{iii}) and Br(2^{iv}) atoms around the N atom is nearly tetrahedral. The hydrogen bonds seem to have a strong influence on the geometry of the anions. While in $Rb_3[BiBr_6]$ the anions, surrounded more regularly by Rb^+ cations, are relatively undistorted {the Bi—Br distances within two $[BiBr_6]^{3-}$ anions of the asymmetric unit are in the range 2·824 (8) to 2·884 (7) Å}, the $[BiBr_6]^{3-}$ anions in the title compound are rather distorted. In the C_3-distorted octahedron there are three shorter [2·749 (2) Å] and three longer Bi—Br distances [3·006 (2) Å]. Each Br atom at the longer distance is linked by two hydrogen bonds to two different $[NH_2(C_2H_5)_2]^+$ cations. The shorter distances fall in the range of Bi—Br(terminal) distances; the longer distances fall in the range of Bi—Br(bridging) distances of other bromobismuthates(III) containing bi- or polynuclear anions (Lazarini, 1977*a,c,d*, 1980*a,b*; Lazarini & Leban, 1980; McPherson & Meyers, 1968; Robertson, McPherson & Meyers, 1967). The values of the Bi—Br distances in $Rb_3[BiBr_6]$ and in $[NH_2(C_2H_5)_2]_3[BiBr_6]$ indicate that the bond strengths within the hexahalobismuthate(III) groups are significantly influenced by crystal-packing forces.

The bond angles within the $[BiBr_6]^{3-}$ anion of the title compound, listed in Table 3, do not indicate stereochemical activity of the Bi lone electron pair, which, however, has not been observed in other halobismuthates(III) either. The angles between the shorter Bi—Br bonds are larger, 92·79 (9)°; the angles between the longer Bi—Br bonds are smaller, 89·59 (6)°.

The bond lengths and angles within the $[NH_2(C_2H_5)_2]^+$ cations are determined with lower accuracy, but they are in agreement with the values found in related compounds.

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Structure of Diethylammonium Tetrachlorobismuthate(III)

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Abstract. $[NH_2(C_2H_5)_2][BiCl_4]$, $M_r = 424{\cdot}94$, monoclinic, $C2/c$, $a = 16{\cdot}522$ (9), $b = 11{\cdot}132$ (4), $c = 13{\cdot}353$ (6) Å, $\beta = 106{\cdot}16$ (5)°, $V = 2358{\cdot}88$ Å^3, $Z = 8$, $D_m = 2{\cdot}27$ (7), $D_x = 2{\cdot}393$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 152{\cdot}0$ cm^{-1}, $F(000) = 1504$, $T = 293$ (1) K, $R = 0{\cdot}055$ for 1367 diffractometer data $[I > 3\sigma(I)]$ and 68 parameters. The structure consists of $[NH_2(C_2H_5)_2]^+$ cations and polynuclear anions in which $BiCl_6$ octahedra, sharing *cis* edges, are interconnected into chains parallel to the *c* axis. The

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Bi—Cl(terminal) distances are 2·493 (6) and 2·559 (6) Å; the Bi—Cl(bridging) distances are in the range between 2·688 (8) and 3·003 (6) Å.

Introduction. The results of the systematic study of halobismuthate(III) compounds show a great variety of different halobismuthate(III) anions, most of them bi- or polynuclear, to occur in the crystalline state [see the references in the preceding paper (Lazarini, 1985)]. 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 (compare the preceding paper).

Experimental. Crystals of suitable dimensions for X-ray structural analysis were grown by slow evaporation at room temperature from a saturated aqueous solution obtained by dissolving equimolar quantities of $(C_2H_5)_2NH$ and $Bi(OH)_3$ in 36% HCl. D_m determined pycnometrically in CCl_4 at 293 K. A well developed crystal, selected for the diffraction measurements, was characterized by the following planes (in parentheses are the distances from the crystal faces to the centre of the crystal): $\pm(12,1,\overline{12})$ (0·10 mm), $(1\bar{2}\bar{1})$ (0·19 mm), $\pm(1,\bar{1},12)$ (0·16 mm), $\pm(44\bar{1})$ (0·20 mm) and $\pm(12\bar{1})$ (0·16 mm). Intensity data collected at 293 (1) K with an Enraf–Nonius CAD-4 diffractometer and graphite-monochromatized Mo $K\alpha$ radiation. ω–2θ scan, $\theta_{\min} = 1°$, $\theta_{\max} = 27°$, 2θ scan width $(0{\cdot}9 + 0{\cdot}3\tan\theta)°$, aperture $(2{\cdot}5 + 0{\cdot}9\tan\theta)$ mm, max. scan time 40 s, background $\frac{1}{4}$ of the scan time at each of the scan limits. 2795 reflexions recorded ($-21 \le h \le 21$, $0 \le k \le 14$, $0 \le l \le 17$). Intensities of three standard reflexions (442, $44\bar{4}$, 046) varied ±7%. After some symmetry-related reflexions were averaged (agreement factor 0·11 for 91 reflexions), and reflexions having $I < 3\sigma(I)$ (calculations based on counting statistics) were rejected, 1367 reflexions remained for the structural analysis. Corrections applied for Lorentz and polarization effects, and for absorption [transmission factors, calculated with the measured crystal dimensions (2052 grid points, crystal volume 0·0280 mm^3), range from 0·020 to 0·104]. Unit-cell parameters obtained from a least-squares fit of the θ values of 25 reflexions measured on the diffractometer. The systematic absences (hkl: $h + k = 2n + 1$; $h0l$: $l = 2n + 1$) and the clearly centrosymmetric distribution of the normalized structure factors indicated space group $C2/c$, which was subsequently confirmed by successful refinement. The position of the Bi atom was taken from the Patterson map; the Cl, N and C atoms were located from successive Fourier and difference Fourier summations; H atoms were not located. The structure was refined by full-matrix least-squares technique with anisotropic thermal parameters for Bi and Cl, 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: $w = 0{\cdot}978/[\sigma(F)^2 + 0{\cdot}00622F^2]$. Empirical extinction parameter included in the final stage of the refinement: $4{\cdot}0\,(4) \times 10^{-4}$. Final $R = 0{\cdot}055$, $wR = 0{\cdot}058$ for 68 parameters and 1367 reflexions. Max. and av. $\Delta/\sigma = 0{\cdot}89$ and 0·19 respectively in the final cycle. Final difference Fourier map featureless ($3{\cdot}8 \ge \Delta\rho \ge -1{\cdot}9$ e Å^{-3}). Calculations performed on the DEC-10 computer at the Edvard Kardelj University, Ljubljana, with *SHELX*76 (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 Cl atoms and isotropic for N and C atoms. Part of the unit cell in a projection along **b** is shown in Fig. 1. The interatomic distances and angles are given in Table 2.

The crystal structure of diethylammonium tetrachlorobismuthate(III) consists of $[NH_2(C_2H_5)_2]^+$ cations and polynuclear anions, in which slightly distorted $BiCl_6$ octahedra, sharing *cis* edges, are interconnected into chains parallel to the *c* axis. As in some other tetrachlorobismuthates(III) (Kruss & Ziegler, 1972; Mammano, Zalkin, Rheingold & Landers, 1977) three types of Bi—Cl distances are present within the $BiCl_6$ group: two short Bi—Cl(terminal) distances [2·493 (6) and 2·559 (6) Å], two longer Bi—Cl(bridging) distances [2·688 (8) and 2·747 (7) Å] and two other long Bi—Cl(bridging) distances [2·919 (6) and 3·003 (6) Å]. The geometry of the $BiCl_6$ group is also influenced slightly by weak hydrogen bonds between the cations and some of the Cl atoms of the anions: N—Cl(4) 3·27 (2) Å and N—Cl(1$^{\text{iii}}$) 3·26 (2) Å; the sum of the van der Waals radii of N and Cl is 3·30 Å. Each of the $[NH_2(C_2H_5)_2]^+$ cations interconnects two $BiCl_4$ chains. The lengthening of the corresponding Bi—Cl distances within $BiCl_6$ groups, caused by hydrogen bonds, is smaller than in the related compound $[NH_2(C_2H_5)_2]_3[BiBr_6]$ (see preceding paper).

The bond lengths and angles within the $[NH_2(C_2H_5)]^+$ cation are determined with lower accuracy, but they correspond approximately to the values found in related compounds.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42413 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters* ($\times 10^4$, *for* Bi $\times 10^5$) *and isotropic thermal parameters* ($\times 10^3$, *for* Bi $\times 10^4$) *with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}/U(Å^2)
Bi	54349 (4)	63800 (6)	41948 (5)	494 (4)
Cl(1)	5416 (5)	8677 (5)	4265 (6)	81 (5)
Cl(2)	6859 (4)	6332 (6)	5472 (6)	81 (4)
Cl(3)	4619 (4)	6235 (5)	5674 (5)	86 (3)
Cl(4)	3845 (4)	6400 (6)	2428 (5)	76 (4)
N	1857 (14)	5718 (20)	1430 (18)	94 (6)
C(1)	1879 (20)	4421 (31)	1592 (28)	126 (11)
C(2)	2010 (40)	3845 (43)	601 (49)	174 (21)
C(3)	1591 (45)	6303 (42)	2395 (56)	204 (26)
C(4)	838 (51)	6432 (42)	2369 (58)	182 (28)

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

Bi–Cl(1)	2·559 (6)	Cl(1)–Bi–Cl(2)	90·9 (2)
Bi–Cl(2)	2·493 (6)	Cl(1)–Bi–Cl(3)	91·1 (2)
Bi–Cl(3)	2·688 (8)	Cl(1)–Bi–Cl(4)	90·2 (2)
Bi–Cl(4)	3·003 (6)	Cl(1)–Bi–Cl(3$^{\rm i}$)	173·3 (2)
Bi–Cl(3$^{\rm i}$)	2·919 (6)	Cl(1)–Bi–Cl(4$^{\rm ii}$)	91·9 (2)
Bi–Cl(4$^{\rm ii}$)	2·747 (7)	Cl(2)–Bi–Cl(3)	93·8 (2)
		Cl(2)–Bi–Cl(4)	172·1 (2)
N–Cl(4)	3·27 (2)	Cl(2)–Bi–Cl(3$^{\rm i}$)	88·6 (2)
N–Cl(1$^{\rm iii}$)	3·26 (2)	Cl(2)–Bi–Cl(4$^{\rm ii}$)	90·4 (2)
		Cl(3)–Bi–Cl(4)	94·0 (2)
N C(1)	1·46 (4)	Cl(3)–Bi–Cl(3$^{\rm i}$)	82·3 (2)
N–C(3)	1·61 (8)	Cl(3)–Bi–Cl(4$^{\rm ii}$)	174·8 (2)
C(1)–C(2)	1·54 (8)	Cl(4)–Bi–Cl(3$^{\rm i}$)	91·1 (2)
C(3)–C(4)	1·24 (12)	Cl(4)–Bi–Cl(4$^{\rm ii}$)	81·7 (2)
		Cl(3$^{\rm i}$)–Bi–Cl(4$^{\rm ii}$)	94·7 (2)
C(1)–N–C(3)	106 (3)		
N–C(1)–C(2)	107 (3)		
N–C(3)–C(4)	121 (6)		

Symmetry code: (i) $1-x$, $1-y$, $1-z$; (ii) $1-x$, y, $\frac{1}{2}-z$; (iii) $-\frac{1}{2}+x$, $\frac{3}{2}-y$, $-\frac{1}{2}+z$.

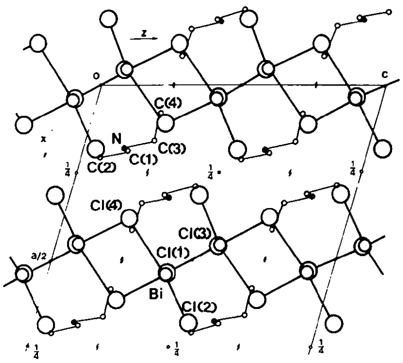

Fig. 1. Projection of the structure down **b**.

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Structure of the Monosodium Salt of D-Glucose 6-Hydrogenphosphate

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Abstract. $Na^+.C_6H_{12}O_9P^-$, $M_r = 282·1$, monoclinic, $P2_1$, $a = 5·762$ (1), $b = 7·163$ (2), $c = 12·313$ (1) Å, $\beta = 99·97$ (1)°, $U = 500·5$ Å^3, $Z = 2$, $D_m = 1·86$, $D_x = 1·87$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 3·3$ mm^{-1}, $F(000) = 292$, $T = 300$ K, final R for 922 observed reflections is 0·042. The phosphate ester bond, P—O(6), is 1·575 (5) Å, slightly shorter than the P~O bond in monopotassium phosphoenolpyruvate [1·612 (6) Å] [Hosur & Viswamitra (1981). *Acta Cryst.* B**37**, 839–843]. The pyranose sugar ring takes a $^4C_1$ chair conformation. The conformation about the exocyclic C(5)—C(6) bond is *gauche–trans*. The endocyclic C—O bonds in the glucose ring are nearly equal with C(5)—O(5) = 1·435 (8) and C(1)—O(5) = 1·436 (9) Å. The sodium ion has seven near neighbours within a distance of 2·9 Å. The crystal structure is stabilized by hydrogen bonds between the O atoms of symmetry-related molecules.