Structure of Diethylammonium Hexachlorobismuthate(III)

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Abstract. $[NH_2(C_2H_5)_2]_3[BiCl_6]$, $M_r = 644.14$, rhombohedral, $R3c$, hexagonal unit cell: $a = 14.822$ (6), $c = 19.380$ (8) Å, $V = 3687.21$ Å^3, $Z = 6$, $D_m = 1.7$ (1), $D_x = 1.740$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 75.1$ cm^{-1}, $F(000) = 1884$, $T = 293$ (1) K, $R = 0.089$ for 1146 diffractometer data $[I > 3\sigma(I)]$. The structure consists of $[NH_2(C_2H_5)_2]^+$ cations and $[BiCl_6]^{3-}$ anions. In the C_3-distorted $BiCl_6$ octahedron there are three short $[2.583$ (8) Å] and three longer Bi–Cl distances $[2.892$ (7) Å]. The elongation of these distances is caused by hydrogen bonds between the cations and anions.

Introduction. The results of systematic structural investigations of halobismuthates(III) show a great variety of different halobismuthate(III) anions in the crystalline state, most of them bi- or polynuclear. The role of the size and shape of the cation, as well as the role of the Bi lone electron pair, in the process of formation of polynuclear anions has been studied (see Lazarini, 1985, and references cited therein). The title compound is isomorphous with diethylammonium hexabromobismuthate(III) (Lazarini, 1985), which contains isolated octahedral $[BiBr_6]^{3-}$ anions. It has been assumed that a larger distortion of the octahedral anions, caused by the Bi lone electron pair, will be found in hexachlorobismuthate(III) with smaller Cl ligands than in hexabromobismuthate(III) with larger Br ligands. In fact, the $[BiBr_6]^{3-}$ anions were C_3-distorted by hydrogen bonds between the cations and anions rather than by lone electron pair repulsion. This article presents the crystal structure of diethylammonium hexachlorobismuthate(III); the geometries of the hexahalobismuthate(III) anions in both isomorphous compounds are compared.

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 $[NH_2(C_2H_5)_2]Cl$ and $Bi_2O_2CO_3$ (molar ratio 6:1) in 36% HCl. D_m determined pycnometrically in 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 an

arbitrary origin inside the crystal): $\pm(110)$ (0.17 mm), $\pm(\bar{1}20)$ (0.17 mm), $\pm(\bar{2}10)$ (0.10 mm), $\pm(012)$ (0.17 mm), $\pm(10\bar{2})$ (0.21 mm) and $\pm(1\bar{1}2)$ (0.23 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 $(0.9 + 0.3\tan\theta)°$, aperture $(2.5 + 0.9\tan\theta)$ mm, max. scan time 40 s, background $\frac{1}{4}$ of the scan time at each of the scan limits. 5583 reflexions recorded $(-20 \leq h \leq 20, 0 \leq k \leq 20, -26 \leq l \leq 26)$. Intensities of three standard reflexions $(\bar{1}38, 1\bar{4}8, 416)$ varied $\pm 8\%$. After symmetry-related reflexions were averaged [agreement factor R_{int} (calculated on F^2) 0.22] and reflexions having $I < 3\sigma(I)$ (calculations based on counting statistics) were rejected, 1146 reflexions remained for the structural analysis. Corrections applied for Lorentz and polarization effects, and for absorption [transmission factors, calculated with the measured crystal dimensions (2188 grid points, crystal volume 0.0245 mm^3), range from 0.12 to 0.26]. Unit-cell parameters obtained from a least-squares fit of the θ values of 25 reflexions $(8 < \theta < 12°)$ measured on the diffractometer. The space group $R3c$ (extinction conditions: $khil, -h + k + l = 3n + 1; h\bar{h}0l, l = 2n + 1$) was assumed to be the same as in the case of the isomorphous Br compound (Lazarini, 1985) and confirmed by successful refinement. The positions of all atoms have been taken from the isomorphous compound and refined by full-matrix least squares with anisotropic thermal parameters for Bi and Cl, isotropic thermal parameters for N and C atoms and with anomalous-dispersion correction. H atoms were not located. $\sum w(|F_o| - |F_c|)^2$ minimized in the least-squares procedure; weighting function applied in the final cycle: $w = 1.00/[\sigma(F)^2 + 0.0325F^2]$. Empirical extinction parameter included in the final stage of the refinement: 7.9 (6) $\times 10^{-4}$. Final $R = 0.089$, $wR = 0.081$ for 43 parameters and 1146 reflexions. Max. and av. $\Delta/\sigma = 0.122$ and 0.034 respectively in the final cycle. Final difference Fourier map featureless $(8.8 \geq \Delta\rho \geq -3.5$ e Å$^{-3})$. Surface hydrolysis of the crystal, observed after data collection, seems to be the reason for the high R value in this structure determination. 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 Cl atoms and isotropic thermal parameters for N and C atoms. Part of the unit cell in a projection along **c** is shown in Fig. 1. The interatomic distances and angles are given in Table 2.

In the predominantly ionic structure each $[NH_2-(C_2H_5)_2]^+$ cation is linked to two $[BiCl_6]^{3-}$ anions by weak hydrogen bonds: $N-Cl(2^{iii})$ 3·18 (2) and

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43570 (9 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* (× 10⁴) *and isotropic thermal parameters* (× 10⁴ *for* Bi; ×10³ *for* Cl, N *and* C) *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 the isotropic thermal parameter is given.

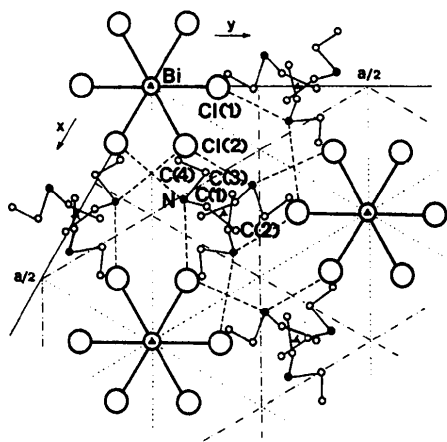|	x	y	z	$U_{eq}/U(\text{Å}^2)$
Bi	0	0	0	239 (6)
Cl(1)	188 (5)	1543 (4)	730 (4)	46 (5)
Cl(2)	1577 (4)	1624 (3)	−853 (4)	34 (2)
N	3009 (13)	2197 (13)	3490 (9)	40 (4)
C(1)	3176 (21)	2790 (19)	4146 (16)	61 (7)
C(2)	3888 (22)	3968 (22)	4064 (20)	70 (7)
C(3)	2330 (15)	2386 (17)	2990 (13)	40 (4)
C(4)	1953 (20)	1516 (22)	2433 (15)	58 (7)

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

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

Bi–Cl(1),Cl(1ⁱ),Cl(1ⁱⁱ)	2·583 (8)	Cl(1)–Bi–Cl(1ⁱ)	92·9 (3)
Bi–Cl(2),Cl(2ⁱ),Cl(2ⁱⁱ)	2·892 (7)	Cl(1)–Bi–Cl(1ⁱⁱ) Cl(1ⁱ)–Bi–Cl(1ⁱⁱ)	
N–Cl(2ⁱⁱⁱ)	3·18 (2)	Cl(2)–Bi–Cl(2ⁱ)	90·6 (2)
N–Cl(2ⁱᵛ)	3·26 (2)	Cl(2)–Bi–Cl(2ⁱⁱ) Cl(2ⁱ)–Bi–Cl(2ⁱⁱ)	
N–C(1)	1·49 (4)	Cl(1)–Bi–Cl(2ⁱⁱ)	173·3 (3)
N–C(3)	1·52 (3)	Cl(2)–Bi–Cl(1ⁱ)	
C(1)–C(2)	1·53 (4)	Cl(2ⁱ)–Bi–Cl(1ⁱⁱ)	
C(3)–C(4)	1·56 (4)	Cl(1)–Bi–Cl(2) Cl(1ⁱ)–Bi–Cl(2ⁱ)	83·8 (2)
C(1)–N–C(3)	111 (2)	Cl(1ⁱⁱ)–Bi–Cl(2ⁱⁱ)	
N–C(1)–C(2)	114 (2)	Cl(1)–Bi–Cl(2ⁱ)	93·1 (3)
N–C(3)–C(4)	107 (2)	Cl(2)–Bi–Cl(1ⁱⁱ) Cl(1ⁱ)–Bi–Cl(2ⁱⁱ)	

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

$N-Cl(2^{iv})$ 3·26 (2) Å; the sum of the van der Waals radii of N and Cl is 3·30 Å. The arrangement of C(1), C(3), Cl(2ⁱⁱⁱ) and Cl(2ⁱᵛ) is nearly tetrahedral. The hydrogen bonds have a strong influence on the geometry of the anions. They are C_3-distorted, with three shorter Bi—Cl distances [2·583 (8) Å], which fall in the range of Bi—Cl terminal distances, and three longer Bi—Cl distances [2·892 (7) Å], which fall in the range of Bi—Cl bridging distances of other chlorobismuthates(III) containing bi- or polynuclear anions (see Blažič & Lazarini, 1985, and references cited therein). In contrast to the assumption that the distortion of hexahalobismuthate(III) octahedra caused by the stereochemical activity of the Bi lone electron pair will be larger in the case of $[BiCl_6]^{3-}$ than in the case of $[BiBr_6]^{3-}$, the geometry of both species is essentially the same (Table 2). It seems that the bond strengths within the hexahalobismuthate(III) groups are influenced by crystal packing forces, e.g. hydrogen bonds, rather than by lone electron pair repulsion. The bond lengths and angles within the $[NH_2(C_2H_5)_2]^+$ cations were determined with lower accuracy, but they are in agreement with the values found in related compounds.

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