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Structure of Diethylammonium Hexabromobismuthate(III)

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Abstract. $[NH_2(C_2H_5)_2]_3[BiBr_6]$, $M_r = 910{\cdot}87$, rhombohedral, $R3c$, hexagonal unit cell: $a = 15{\cdot}213$ (5), $c = 20{\cdot}137$ (9) Å, $V = 4036{\cdot}03$ Å^3, $Z = 6$, $D_m = 2{\cdot}22$ (8), $D_x = 2{\cdot}248$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 150{\cdot}5$ cm^{-1}, $F(000) = 2532$, $T = 293$ (1) K, $R = 0{\cdot}038$ for 840 diffractometer data $[I > 3\sigma(I)]$. The structure consists of $[NH_2(C_2H_5)_2]^+$ cations and $[BiBr_6]^{3-}$ anions. In the C_3-distorted $BiBr_6$ octahedron there are three short [2·749 (2) Å] and three longer Bi—Br distances [3·006 (2) Å]. The elongation of these distances seems to be caused by hydrogen bonds between the cations and anions.

Introduction. A systematic investigation of halobismuthates(III) was undertaken in order to establish the influence of different cations on the linking of halobismuthate(III) groups into polynuclear species. Using cations of different size and shape, a great variety of anions, most of them bi- or polynuclear, was obtained (Lazarini, 1977*a,b,c,d,* 1978, 1980*a,b*; Lazarini & Leban, 1980), but the role of the cation, as well as the role of the Bi lone electron pair, in the process of formation of polynuclear anions has not yet been identified. In this context the system diethylammonium halide–bismuth(III) halide, studied recently by nuclear quadrupole resonance (Landers & Brill, 1980), became of interest for crystallographic research. So far only three crystalline substances have been reported: $[NH_2(C_2H_5)_2][BiCl_4]$, $[NH_2(C_2H_5)_2]_3[BiCl_6]$ and $[NH_2(C_2H_5)_2]_3[BiBr_6]$. The linking of hexabromobismuthate(III) groups, in which the influence of the Bi lone electron pair should be smaller than in hexachlorobismuthate(III) groups, into polynuclear anions seemed not to occur.

In a series of experiments the diethylammonium halide–bismuth(III) halide ratio in the solution was varied over a wide range (from 4:1 to 1:2) in order to crystallize all existing compounds. Two new crystalline phases were obtained: $[NH_2(C_2H_5)_2]_3[Bi_2Br_9]$ and $[NH_2(C_2H_5)_2]_3[Bi_2I_9]$. According to the crystal data of these substances, listed in Table 1, $[NH_2(C_2H_5)_2]_3[BiCl_6]$ is isostructural with $[NH_2(C_2H_5)_2]_3[BiBr_6]$, and $[NH_2(C_2H_5)_2]_3[Bi_2Br_9]$ with $[NH_2(C_2H_5)_2]_3[Bi_2I_9]$. Accurate crystal structure determinations are planned in order to enable precise comparison of the geometry of hexahalobismuthate(III) groups in all these crystal structures.

Experimental. Crystals of suitable dimensions for X-ray structural analysis were grown by slow evaporation at room temperature from a saturated aqueous solution of $(C_2H_5)_2NH$ and $BiBr_3$ (molar ratio 3:1) in 40% HBr. D_m determined pycnometrically in CCl_4 at 293 K. A well developed crystal, selected for diffraction measurements, was characterized by the following planes (in parentheses are the distances from the crystal faces to an arbitrary origin inside the crystal): ±(110) (0·13 mm), $\pm(\bar{1}20)$ (0·20 mm), $\pm(\bar{2}10)$ (0·20 mm), ±(012) (0·31 mm), $\pm(1\bar{1}2)$ (0·30 mm) and $\pm(10\bar{2})$ (0·27 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,

Table 1. *The solid phases in the system* $[NH_2(C_2H_5)_2]X/BiX_3$ $(X = Cl,Br,I)$

	$[NH_2(C_2H_5)_2][BiCl_4]$	$[NH_2(C_2H_5)_2]_3[BiCl_6]$	$[NH_2(C_2H_5)_2]_3[BiBr_6]$	$[NH_2(C_2H_5)_2]_3[Bi_2Br_9]$	$[NH_2(C_2H_5)_2]_3[Bi_2I_9]$
	Monoclinic	Hexagonal	Hexagonal	Monoclinic*	Monoclinic*
a (Å)	16·522 (9)	14·822 (6)	15·213 (5)	12·36	12·86
b (Å)	11·132 (4)			13·91	14·57
c (Å)	13·353 (6)	19·380 (8)	20·137 (9)	18·94	19·37
β (°)	106·16 (5)			102·0	101·9
Space group	*C*2/*c*	*R*3*c*	*R*3*c*	$P2_1/c$	$P2_1/c$
$[NH_2(C_2H_5)_2]X/BiX_3$ ratio (in solution) at which the substance was obtained					
	2:1	4:1	4:1	2:1	3:1
	1:1	3:1	3:1	1:1	2:1
	1:2				1:1

* Data determined from Weissenberg and precession photographs.

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background $\frac{1}{4}$ of the scan time at each of the scan limits. 5553 reflexions recorded ($-19 \leq h \leq 19$, $-19 \leq k \leq 19$, $0 \leq l \leq 25$). Intensities of three standard reflexions ($\bar{3}66$, $\bar{2}43$, $3\bar{1}4$) varied ±6%. After symmetry-related reflexions were averaged (agreement factor 0·09), and reflexions having $I < 3\sigma(I)$ (calculations based on counting statistics) were rejected, 840 reflexions remained for the structural analysis. Corrections applied for Lorentz and polarization effects, and for absorption [transmission factors, calculated with the measured crystal dimensions (3264 grid points, crystal volume 0·0578 mm^3), range from 0·011 to 0·067]. Unit-cell parameters obtained from a least-squares fit of the θ values of 20 reflexions measured on the diffractometer. The positions of the Bi and Br atoms were taken from the Patterson map. The partial structure was then refined simultaneously in all possible space groups (indicated by the following extinction conditions: $hkil$, $-h + k + l = 3n + 1$; $h\bar{h}0l$, $l = 2n + 1$): $R\bar{3}c$, $R3c$ and $R32$. After three cycles of least-squares refinement quite different R values were achieved: 0·156, 0·095 and 0·130, respectively. The structural analysis was then continued in space group $R3c$ with lowest R value and also with reasonable temperature factors. The N and C atoms were located from a difference Fourier map. H atoms were not located. The structure was refined by full-matrix least-squares technique with anisotropic thermal parameters for Bi and Br, 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: $w = 3{\cdot}371/[\sigma(F)^2 + 0{\cdot}00158F^2]$. Empirical extinction parameter also included in the final stage of the refinement: 2·9 (2) $\times 10^{-4}$. Final $R = 0{\cdot}038$, $wR = 0{\cdot}037$ for 43 parameters and 840 reflexions. Max. and ave. $\Delta/\sigma = 0{\cdot}100$ and 0·012, respectively, in the final cycle. Final difference Fourier map flat ($1{\cdot}0 \geq \Delta\rho \geq -1{\cdot}4$ 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 2;* equivalent isotropic thermal parameters are given for Bi and Br atoms and isotropic thermal parameters for N and C atoms. Part of the unit cell in a projection along **c**, with the atom numbering system used, is shown in Fig. 1. The interatomic distances and angles are given in Table 3.

Table 2. *Final positional parameters* ($\times 10^4$) *and isotropic thermal parameters* ($\times 10^4$ *for* Bi *and* Br; $\times 10^3$ *for* N *and* C) *with e.s.d.'s in parentheses*

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

	x	y	z	$U_{\rm eq}/U$(Å^2)
Bi	0	0	0	320 (3)
Br(1)	175 (2)	1591 (1)	749 (1)	620 (11)
Br(2)	1601 (1)	1614 (1)	−868 (1)	482 (8)
N	2976 (13)	2280 (13)	3499 (9)	68 (4)
C(1)	3177 (23)	2871 (21)	4225 (15)	93 (8)
C(2)	3809 (29)	3842 (28)	4066 (21)	127 (10)
C(3)	2312 (17)	2375 (18)	3021 (12)	79 (6)
C(4)	1950 (23)	1625 (25)	2496 (16)	103 (9)

Table 3. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Bi–Br(1),Br(1$^{\rm i}$),Br(1$^{\rm ii}$)	2·749 (2)	Br(1)–Bi–Br(1$^{\rm i}$)	92·79 (9)
Bi–Br(2),Br(2$^{\rm i}$),Br(2$^{\rm ii}$)	3·006 (2)	Br(1)–Bi–Br(1$^{\rm ii}$)	
		Br(1$^{\rm i}$)–Bi–Br(1$^{\rm ii}$)	
N–Br(2$^{\rm iii}$)	3·30 (2)	Br(2)–Bi–Br(2$^{\rm i}$)	89·59 (6)
N–Br(2$^{\rm iv}$)	3·44 (2)	Br(2)–Bi–Br(2$^{\rm ii}$)	
		Br(2$^{\rm i}$)–Bi–Br(2$^{\rm ii}$)	
N–C(1)	1·66 (4)	Br(1)–Bi–Br(2$^{\rm ii}$)	174·43 (8)
N–C(3)	1·45 (3)	Br(2)–Bi–Br(1$^{\rm i}$)	
C(1)–C(2)	1·34 (4)	Br(2$^{\rm i}$)–Bi–Br(1$^{\rm ii}$)	
C(3)–C(4)	1·45 (4)	Br(1)–Bi–Br(2)	85·28 (8)
		Br(1$^{\rm i}$)–Bi–Br(2$^{\rm i}$)	
		Br(1$^{\rm ii}$)–Bi–Br(2$^{\rm ii}$)	
C(1)–N–C(3)	119 (2)	Br(1)–Bi–Br(2$^{\rm i}$)	92·52 (9)
N–C(1)–C(2)	103 (3)	Br(2)–Bi–Br(1$^{\rm ii}$)	
N–C(3)–C(4)	114 (3)	Br(1$^{\rm i}$)–Bi–Br(2$^{\rm ii}$)	

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

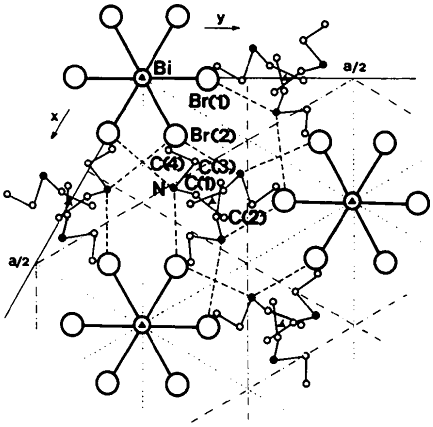

Fig. 1. Projection of the structure down **c**.

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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 42430 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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. $[NH_2(C_2H_5)_2][BiCl_4]$, $M_r = 424·94$, monoclinic, $C2/c$, $a = 16·522$ (9), $b = 11·132$ (4), $c = 13·353$ (6) Å, $\beta = 106·16$ (5)°, $V = 2358·88$ Å^3, $Z = 8$, $D_m = 2·27$ (7), $D_x = 2·393$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 152·0$ cm^{-1}, $F(000) = 1504$, $T = 293$ (1) K, $R = 0·055$ 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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