Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71095 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1035]

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Structure of $[(C_2H_5)_2NH_2]_3BiCl_6$

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Abstract

In diethylammonium hexachlorobismuthate(III) the Bi atoms form a slightly distorted cubic *I* arrangement, *i.e.* they occupy the corners and the midpoint (owing to the *c*-glide plane) of the pseudo-cubic rhombohedral unit cell defined by the transformation $\mathbf{a}'_1 = -\frac{1}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{1}{3}\mathbf{c}$, $\mathbf{a}'_2 = -\frac{1}{3}\mathbf{a}_1 - \frac{2}{3}\mathbf{a}_2 + \frac{1}{3}\mathbf{c}$, $\mathbf{a}'_3 = \frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{1}{3}\mathbf{c}$; each Bi atom is surrounded octahedrally by six Cl atoms. The octahedron occurs in two different orientations according to the *c*-glide plane. The centres of the organic groups are close to the midpoints of the edges and the faces of the *I*-centred cubic cell. The isolated octahedra are connected to form a three-dimensional framework by hydrogen bonding *via* three symmetrically equivalent atoms Cl(1), which form an octahedral face. The other three Cl(2) atoms are not involved in the bonding scheme. Each octahedron is surrounded by six $(C_2H_5)_2NH_2$ groups. The two H atoms connected to the N atom bridge to different octahedra; a third H atom connected to a non-methyl C atom also bridges to Cl(1), thus completing a distorted tetrahedral environment for Cl(1), set up by three H and one Bi atom. The distance Bi—Cl for the hydrogen bonded Cl(1) is 2.875 Å; it is diminished for Cl(2) to 2.587 Å.

Comment

The present investigation is part of a series of studies on the influence of organic cations on heavy-metal halogenides. The structure was originally solved by

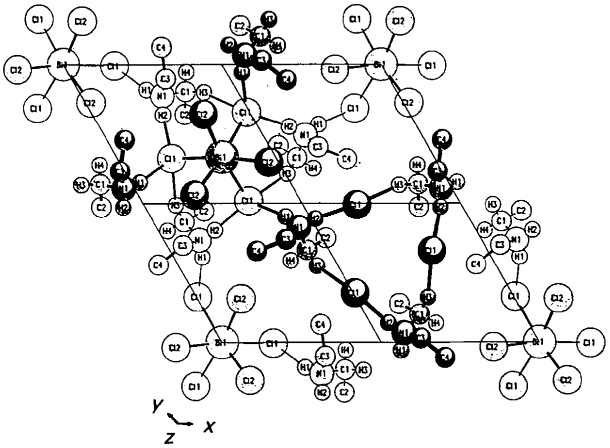
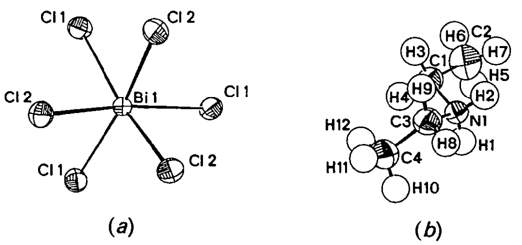


Fig. 1. Projection of part of the unit cell along **c**.



(*a*) (*b*)

Fig. 2. Displacement ellipsoids for (*a*) the $BiCl_6$ octahedron and (*b*) the $(C_2H_5)_2NH_2$ group.

Lazarini (1987); he recognized that three longer Bi—Cl distances occurred, evidently resulting from the presence of hydrogen bonding. However, the positions of the H atoms were not given. It is the intention of this paper to allow a clearer discussion by the aid of actual coordinates for H atoms.

The structure was solved approximately by Patterson methods in space group $R\bar{3}c$; the refinement process led to $R3c$. For the refinement of the H atoms in the methyl groups a constraint condition was used that implied equal distances and angles to the central atom for all three of them and equal angles between them. In addition to the description of the structural arrangement in the *Abstract*, the connection pattern is illustrated in Fig. 1. For the sake of clarity, only a suitable slice is projected. Displacement ellipsoids of the $BiCl_6$ octahedron and the organic cation are shown in Fig. 2. The distortion of the octahedron is small, the H-bridge bonds vary in length from 2.26 to 2.68 Å. The shortest H-atom distances to Cl(2) are larger than 2.9 Å. No unusual values could be found in distances and angles. The final difference map did not give experimental evidence for a located lone pair of electrons in the region of Bi; the distortion of the $[BiCl_6]^{3-}$ arises from hydrogen bonding, as suggested by Lazarini (1987).

Experimental

Crystal data

$3C_4H_{12}N^+.BiCl_6^{3-}$
$M_r = 644.135$
Hexagonal setting
$R3c$
$a = 14.7507\ (6)$ Å
$c = 19.373\ (1)$ Å
$V = 3650.5$ Å^3
$Z = 6$
$D_x = 1.758$ Mg m^{-3}

Mo $K\alpha_1$ radiation
$\lambda = 0.70926$ Å
Cell parameters from 65 reflections
$\theta = 7.6\text{-}19.4°$
$\mu = 7.889$ mm^{-1}
$T = 298$ K
Irregular
0.2 × 0.2 × 0.2 mm
Colourless

Data collection

Modified PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: *CAMEL JOCKEY* (modified) (Flack, 1975)
$T_{min} = 0.374$, $T_{max} = 0.442$
8648 measured reflections
1486 independent reflections
1486 observed reflections [all reflections observed]

$R_{int} = 0.0113$
$\theta_{max} = 25°$
$h = -17 \rightarrow 17$
$k = -17 \rightarrow 17$
$l = -23 \rightarrow 23$
4 standard reflections monitored every 100 reflections intensity variation: 0.95-1.09%

Refinement

Refinement on F
Final $R = 0.0177$
$wR = 0.0159$
$S = 2.27$
1486 reflections
92 parameters
$w = 1/\sigma(F)$
$(\Delta/\sigma)_{max} < 0.01$
$\Delta\rho_{max} = 1.03$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}

Extinction correction: Larson (1970)
Extinction coefficient: 12636 (397)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

U_{iso} is given for H atoms; for non-H atoms U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{iso}/U_{eq}
Bi(1)	0.00000	0.00000	0.00000 †	0.0277
Cl(1)	−0.16174 (7)	−0.15757 (8)	0.08504 (7)	0.0410
Cl(2)	0.13643 (9)	0.15472 (8)	0.07347 (7)	0.0513
N(1)	1.1125 (3)	0.3672 (3)	0.0160 (2)	0.0464
C(1)	1.0975 (4)	0.4337 (4)	−0.0345 (3)	0.0562
C(2)	1.1792 (5)	0.4716 (5)	−0.0883 (3)	0.0734
C(3)	1.0510 (4)	0.3481 (5)	0.0836 (3)	0.0631
C(4)	0.9378 (4)	0.2776 (4)	0.0721 (3)	0.0718
H(1)	1.091 (3)	0.306 (3)	−0.002 (2)	0.059 (5)
H(2)	1.180 (3)	0.403 (3)	0.032 (2)	0.059 (5)
H(3)	1.100 (3)	0.494 (3)	0.000 (2)	0.059 (5)
H(4)	1.027 (3)	0.401 (3)	−0.056 (2)	0.059 (5)
H(5)	1.172 (1)	0.425 (2)	−0.122 (1)	0.059 (5)
H(6)	1.18738	0.52672	−0.11444	0.059 (5)
H(7)	1.24611	0.49505	−0.07381	0.059 (5)
H(8)	1.061 (3)	0.302 (3)	0.114 (2)	0.059 (5)
H(9)	1.074 (3)	0.418 (3)	0.109 (2)	0.059 (5)
H(10)	0.923 (1)	0.206 (2)	0.057 (1)	0.059 (5)
H(11)	0.89666	0.26847	0.11588	0.059 (5)
H(12)	0.91039	0.30640	0.03526	0.059 (5)

† Coordinate fixed to define origin.

Table 2. *Geometric parameters* (Å, °)

Bi(1)—Cl(2)	2.587 (2)	C(2)—H(6)	0.912 (7)
Bi(1)—Cl(1)	2.875 (1)	C(2)—H(5)	0.91 (2)
Cl(1)—H(2)	2.26 (5)	C(2)—H(7)	0.912 (7)
Cl(1)—H(1)	2.45 (4)	C(2)—C(1)	1.475 (8)
Cl(1)—H(3)	2.68 (5)	C(3)—H(8)	0.97 (5)
N(1)—H(1)	0.87 (4)	C(3)—H(9)	1.03 (4)
N(1)—H(2)	0.92 (4)	C(3)—C(4)	1.478 (7)
N(1)—C(1)	1.478 (7)	C(4)—H(10)	1.01 (2)
N(1)—C(3)	1.536 (7)	C(4)—H(11)	1.012 (7)
C(1)—H(4)	0.99 (4)	C(4)—H(12)	1.012 (7)
C(1)—H(3)	1.09 (4)		
Cl(2)—Bi(1)—Cl(2)	92.63 (4)	N(1)—C(1)—H(3)	100. (2)
Cl(1)—Bi(1)—Cl(2)	93.07 (4)	N(1)—C(1)—C(2)	110.8 (5)
Cl(1)—Bi(1)—Cl(2)	173.59 (3)	H(5)—C(2)—H(6)	101. (2)
Cl(1)—Bi(1)—Cl(1)	90.42 (4)	H(7)—C(2)—H(6)	104.4 (6)
Cl(1)—Bi(1)—Cl(2)	84.18 (4)	H(7)—C(2)—H(5)	101. (2)
H(1)—Cl(1)—H(2)	125. (1)	C(1)—C(2)—H(6)	116.7 (6)
H(3)—Cl(1)—H(2)	118. (1)	C(1)—C(2)—H(5)	117. (1)
H(3)—Cl(1)—H(1)	94. (1)	C(1)—C(2)—H(7)	116.7 (5)
Bi(1)—Cl(1)—H(2)	112. (1)	H(9)—C(3)—H(8)	108. (3)
Bi(1)—Cl(1)—H(1)	97.4 (8)	C(4)—C(4)—H(8)	97. (2)
Bi(1)—Cl(1)—H(3)	107.2 (7)	C(4)—C(3)—H(9)	118. (2)
H(2)—N(1)—H(1)	118. (5)	N(1)—C(3)—H(8)	112. (3)
C(1)—N(1)—H(1)	109. (3)	N(1)—C(3)—H(9)	111. (2)
C(1)—N(1)—H(2)	109. (3)	N(1)—C(3)—C(4)	110.9 (4)
C(3)—N(1)—H(1)	106. (2)	H(11)—C(4)—H(10)	108. (1)
C(3)—N(1)—H(2)	101. (3)	H(12)—C(4)—H(10)	108. (1)
C(3)—N(1)—C(1)	114.5 (4)	H(12)—C(4)—H(11)	107.9 (6)
H(3)—C(1)—H(4)	105. (3)	C(3)—C(4)—H(10)	111. (1)
C(2)—C(1)—H(4)	110. (2)	C(3)—C(4)—H(11)	111.0 (5)
C(2)—C(1)—H(3)	115. (2)	C(3)—C(4)—H(12)	111.0 (5)
N(1)—C(1)—H(4)	115. (2)		

Crystals of suitable dimensions were grown by slow evaporation at room temperature from a saturated aqueous solution obtained by dissolving $[(C_2H_5)_2NH_2]Cl$ and $BiCl_3$ (molar ratio 3:1) in 36% HCl. Absolute configuration was determined by least-squares comparison of the two different forms. The R values obtained for the inverse structure are R = 0.05 and wR = 0.06. H atoms were located from a difference Fourier map; their positions were refined with a common displacement parameter. $\Delta\rho_{max}$ was exactly at the position of Bi; all other maxima in the difference map were smaller than 0.36 e Å^{-3}. All computations were performed on a PC'386 with an adapted version of the program system *ATARI CRYSTAN*88 (Burzlaff & Rothammel, 1989).

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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 71077 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1023]

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Structure of $[NH_3(C_2H_5)]_2[Hg(CN)_2Cl_2]$

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Abstract

The structure of bis(ethylammonium) dichlorodicyanomercurate consists of slightly deformed tetragonal nets of Cl atoms parallel to (100) at $x = 0.25$ and 0.75. Half of the chlorine squares are nearly centred by Hg atoms resulting in a chess-board arrangement. The environment of the Hg atom is augmented to a distorted octahedron by two CN groups nearly perpendicular to the chlorine net. The $C_2H_5NH_3$ groups are located above and below the non-centred chlorine squares. Two H atoms of the NH_3 group bridge to Cl atoms of the neighbouring net with distances of 2.233 (2) and 2.442 (2) Å. The shortest distance from the third H atom to the N atom of the CN group located in the next slice is 2.078 (7) Å. Thus the two slices may be regarded as being tied up by hydrogen bridges. The nets are shifted against each other in the **b** direction according to the glide operation **a**.

Comment

The reaction of substituted ammonium halogenides with metal halogenides leads to a series of compounds of the general formula $(R_xNH_{4-x})_2MX_4$, with R being an aliphatic or aromatic hydrocarbon, M a divalent metal and X a halogen Cl, Br, I. Most of these compounds show interesting structural and physical properties such as ferroelectricity or ferroelasticity. Many of them show successive phase transitions and quite often incommensurate phases {*e.g.* $[N(CH_3)_4]_2ZnCl_4$, *cf.* Mashiyama (1980)}. The phase transitions are mainly a result of order–disorder effects for the substituted ammonium group. An example for interesting physical properties is the compound $[N(CH_3)_4]_2MnCl_4$ that was used by Dupas & Renard (1973) and Birgeneau, Shirane & Kitchens (1974) for studying low-dimensional magnetism.

Another point of interest is the investigation of the coordinative environment of Hg^{II}; because of the closed d shell and relatively large coordination distances it will be difficult to distinguish bonded and non-bonded neighbours. Preferred occurance of nearly linear $HgCl_2$ units is reported (*e.g.* Subramanian & Seff, 1980) with Hg—Cl distances from 2.28 (1) to 2.30 (1) Å. Additional weaker interactions are reported that range from 3.36 (1) to 3.48 (1) Å and augment the environment to a distorted hexagonal scalenohedron (coordination No. 8). Regular octahedral coordination is rare and has been observed for complexes with O atoms (Sandström, 1978) or ternary F atoms (Hoppe, Wilhelm & Müller, 1972) as ligands. Other coordination numbers can be three, four (tetrahedral) and five (trigonal bipyramidal) as reported by Sandström (1978) and Grdenic (1965). In the special case of $(RNH_3)_2HgX_4$, perovskite-like structures with MX_6 octahedra are found (Ben Salah, Daoud, Constant, Jaud & Galy, 1983; Ben Salah, Daoud, Bats & Fuess, 1986).

The present investigation intends to study the effects of the substitution of Cl atoms by CN groups.