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Structure of Tetrakis(dimethylammonium) Chloride Hexachlorobismuthate(III), $\{[(CH_3)_2NH_2]^+\}_4.Cl^-.[BiCl_6]^{3-}$*

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Abstract. $M_r = 641.5$, orthorhombic, $P2_12_12$, $a = 10.342\,(1)$, $b = 13.510\,(1)$, $c = 8.693\,(1)$ Å, $V = 1215$ Å^3, $Z = 2$, $D_x = 1.754$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1.54184$ Å, $\mu = 200.1$ cm^{-1}, $F(000) = 620$, $T = 293$ K, $R = 0.059$, $wR = 0.068$, for 2059 observed reflections. The nearly perfect octahedral Cl coordination around the Bi atom shows crystallographic twofold symmetry. Both ionic interactions and strong hydrogen bridging including the N-bonded H atoms [H(11), H(12), H(21) and H(22)] and all covalent bonded Cl atoms [Cl(1), Cl(2), Cl(3)] together with an interstitial Cl atom [Cl(4)] build up a three-dimensional network with distances N—H···Cl in the range 3.02 (2)–3.57 (2) Å. The relatively high thermal parameters for Cl(4) are typical for non-coordinated atoms involved in strong hydrogen bonds. Although the site-specific symmetry allows distortion of the $[BiCl_6]^{3-}$ octahedron, no stereochemical activity of the lone pair is observed.

Experimental. The title compound was prepared by heating a mixture of 1.3 mmol bismuth subsalicylate and 5 ml dimethylformamide at 358 K for 0.5 h. After adding aqueous hydrochloric acid (0.1 ml; 1 n) the stirred suspension rapidly cleared. Cooling to 263 K over night yielded colourless crystals suitable for X-ray structure analysis. Elemental analysis:

Calculated	C 14.98, H 5.03, N 8.73, Bi 32.58, Cl 38.68%;
Found	C 15.55, H 5.29, N 8.92, Bi 30.9, Cl 38.5%.

A well shaped colourless prism (0.30 × 0.39 × 0.26 mm) was randomly mounted on a glass fibre. Preliminary examinations and data collection were carried out with Cu $K\alpha$ radiation on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. The observed extinctions ($h00$: $h = 2n + 1$; $0k0$: $k = 2n + 1$) together with the orthogonal crystal system confirmed the orthorhombic space group $P2_12_12$. Final cell constants were obtained by least-squares refinement of 25 automatically centred high-angle reflections ($80.7 < 2\theta < 85.5°$). Data were collected using $\theta/2\theta$ scans. Each reflection in the hemisphere h 12, k 15, l ±10 and $\theta_{\max} \le 65.0°$ was measured twice ($\psi \pm 1.5°$, check for Renninger effects). Three orientation control reflections were monitored every 200 reflections. A loss of 30.3% of intensity, indicated by three standards checked every 3600 s during the data collection, was corrected. Lorentz and polarization corrections (Müller, Schmidt, Massa & Herdtweck, 1986) together with a numerical absorption correction based on six indexed faces were applied. The transmission factors ranged from 0.0202 to 0.1645. 28 systematically absent data were rejected from the original data set of 4559 measured reflections. 89 reflections with negative measured intensities were assigned a positive value of $I = 1/100\sigma(I)$. After averaging ($R_{\mathrm{merge}} = 0.023$), 2059 ($I > 0.01$) out of 2060 unique reflections were used in the refinement. The structure was solved by Patterson methods and subsequent difference Fourier maps. Full-matrix least-squares refinement was carried out by minimizing $\sum w(||F_o| - |F_c||)^2$, where $w = 1/\sigma^2(F_o)$.

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* Main Principles in Solid State Coordination Chemistry of Sb and Bi Compounds. Part I.

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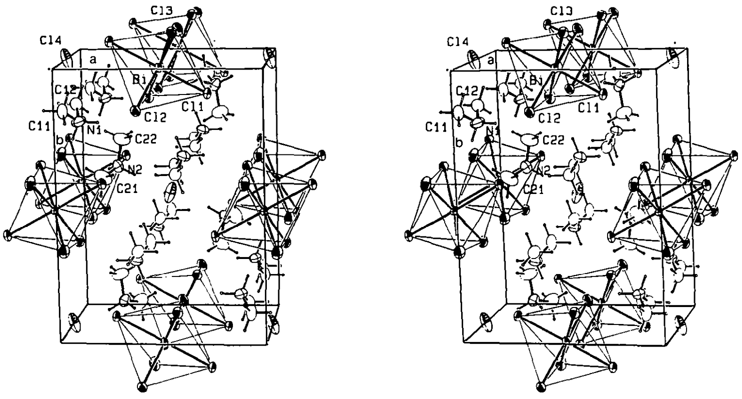

Fig. 1. *ORTEP*II (Johnson, 1976) stereo plot, viewed approximately down the *c* axis with **a** horizontal. Thermal ellipsoids are drawn at the 30% level, and H atoms are assigned arbitrary values.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* ($Å^2$) *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Bi	$\frac{1}{2}$	0	0.06444 (7)	0.0478 (2)
Cl(1)	0.7318 (3)	0.0939 (3)	0.0612 (5)	0.0714 (12)
Cl(2)	0.4103 (4)	0.1386 (3)	−0.1381 (5)	0.0724 (13)
Cl(3)	0.5749 (5)	−0.1210 (5)	0.2893 (6)	0.0979 (19)
Cl(4)	0	0	0.4991 (11)	0.152 (5)
N(1)	0.1205 (22)	0.1886 (14)	0.0083 (29)	0.118 (9)
C(11)	0.0625 (25)	0.1400 (21)	−0.1275 (31)	0.113 (10)
C(12)	0.0925 (23)	0.1386 (18)	0.1502 (33)	0.109 (10)
N(2)	0.2368 (17)	0.4056 (14)	0.5381 (17)	0.087 (6)
C(21)	0.1795 (29)	0.4324 (21)	0.3940 (29)	0.125 (11)
C(22)	0.2576 (33)	0.3048 (18)	0.5398 (30)	0.117 (11)

Table 2. *Selected bond distances* (Å), *bond angles* (°) *and possible intermolecular hydrogen contacts* (Å) *with e.s.d.'s in parentheses*

Bi—Cl(1)	2.713 (4) × 2	N(1)—H(11)···Cl(1)	3.21 (2)
—Cl(2)	2.732 (4) × 2	N(1)—H(11)···Cl(2)	3.38 (2)
—Cl(3)	2.663 (6) × 2	N(1)—H(12)···Cl(2)	3.33 (2)
N(1)—C(11)	1.48 (4)	N(2)—H(21)···Cl(3)	3.57 (2)
—C(12)	1.44 (4)	N(2)—H(22)···Cl(4)	3.02 (2)
N(2)—C(21)	1.43 (3)		
—C(22)	1.38 (3)		
Cl(1)—Bi—Cl(2)	88.5 (1)	C(11)—N(1)—C(12)	113 (2)
Cl(1)—Bi—Cl(3)	92.2 (2)	C(21)—N(1)—C(22)	109 (2)
Cl(2)—Bi—Cl(3)	172.9 (2)		

Anisotropic thermal parameters were introduced for all non-H atoms. All H atoms were calculated in their ideal positions, included in the parameter set with a collective isotropic thermal parameter per pivot atom and refined as a rigid body with U_{ij} free. Atomic scattering factors, f' and f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The refinement converged at $R = 0.059$, $wR = 0.068$ [$w = 1/\sigma^2(F_o)$], for 98 parameters; maximum shift/e.s.d. < 0.001. Final difference Fourier syntheses showed relatively high residual peaks (maximum/minimum $\Delta\rho$ 4.6/ − 3.3 e $Å^{-3}$) near the Bi atom. All calculations were performed on a VAX 3100 computer with the *STRUX*-III system (Kiprof, Herdtweck, Schmidt, Birkhahn & Massa, 1987) including the programs *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1982), *SCHAKAL* (Keller, 1988), *SDP* (Frenz, 1988), and *SHELX*76 (Sheldrick, 1976). Final positional parameters are given in Table 1, selected bond angles and distances in Table 2. Fig. 1 shows a stereoscopic representation of the unit cell.[*]

Related literature. Coordination chemistry of bismuth(III) and antimony(III) compounds together with physiologically relevant counterparts: Remy & Pellens (1928); Herrmann, Herdtweck & Pajdla (1991, 1992).

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[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55541 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1009]

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Structure of the Thallium-Rich Complex $[(Tl18\text{-crown-}6)_4CuBr_4][TlBr_4]_2$

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Abstract. Tetrakis[1,4,7,10,13,16-hexaoxacyclooctadecanethallium(I)] tetrabromocuprate(II) bis[tetrabromothallate(III)], $[TlC_{12}H_{24}O_6]_4[CuBr_4][TlBr_4]_2$, $M_r = 3306.0$, cubic, $F23$, $a = 20.897$ (2) Å, $V = 9125.6$ (9) Å^3, $Z = 4$, $D_m = 2.38$, $D_x = 2.406$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 161.6$ cm^{-1}, $F(000) = 6044$, $T = 295$ K, $R = 0.047$ for 604 unique observed $[I > \sigma(I)]$ reflections and 71 parameters. The two $TlBr_4^-$ [Tl—Br = 2.536 (2) and 2.553 (2) Å] and one $CuBr_4^{2-}$ [Cu—Br = 2.311 (2) Å] anions occupy sites of 23 symmetry, $CuBr_4^{2-}$ being tetrahedrally surrounded by Tl(18-crown-6)$^+$ cations on threefold axes. Thallium(I) in Tl(18-crown-6)$^+$ lies 0.9823 (7) Å out of the best plane of the six O atoms, towards $CuBr_4^{2-}$, forming contacts Tl···Br = 3.5629 (9) and Tl···Cu = 3.5893 (8) Å.

Experimental. The complex$[(Tl18c6)_4CuBr_4][TlBr_4]_2$ was prepared from 18-crown-6 (18c6), thallium(I) bromide and copper bromide in methanol using a method described previously for the chloro isomorphs (Kahwa, Miller, Mitchel, Fronczek, Goodrich, Williams, O'Mahoney, Slawin, Ley & Groombridge, 1992). The density was measured by the flotation technique using a mixture of diiodomethane ($D = 3.325$ g cm^{-3}) and bromochloromethane ($D = 1.991$ g cm^{-3}). A black square-prism crystal, 0.18 × 0.30 × 0.30 mm, was mounted on a CAD-4 diffractometer equipped with a graphite monochromator and Mo $K\alpha$ source. Cell dimensions were determined from the setting angles of 25 reflections having $10 < \theta < 12°$. Data were collected by ω–2θ scans of variable rate (0.63–4.0° min^{-1}) over an octant defined by $1 < \theta < 32°$, $0 \le h \le 31$, $0 \le k \le 31$, $0 \le l \le 31$, h, k and l all odd or all even. A total of 4358 reflections were measured, yielding 1419 unique data ($R_{\text{int}} = 0.034$), and 604 reflections having $I > 1\sigma(I)$ were considered observed and used in the refinement. Three standard reflections (600, 060,006) were monitored periodically and exhibited a 4.0% decrease in intensity, for which a linear correction was applied. Data reduction included corrections for background, Lorentz and polarization effects. Absorption corrections were based on ψ scans, with minimum relative transmission coefficient 78.1% and maximum 99.1%. The title compound was found to be isostructural with the complex $[(Tl18c6)_4CuCl_4][TlCl_4]_2$ (Kahwa *et al.*, 1992), and coordinates from that structure were used as an initial refinement model. The H atoms were idealized, assigned isotropic parameters ($B = 1.3$ B_{eq} of attached C atom) with C—H constrained to 0.95 Å, and allowed to ride on their parent C atoms. Non-H atoms were refined by full-matrix least squares, minimizing

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{\text{eq}} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Tl1	0.65083 (6)	$1 - x$	x	5.19 (1)
Tl2	1	1	1	3.65 (7)
Tl3	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	3.54 (7)
Cu	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	8.0 (4)
Br1	0.1861 (2)	$1 - x$	$1 - x$	12.92 (7)
Br2	0.9299 (1)	x	x	5.43 (3)
Br3	0.8205 (1)	x	x	5.18 (3)
O1	0.5260 (7)	0.2877 (7)	0.6530 (9)	5.4 (4)
O4	0.5917 (8)	0.2763 (8)	0.5355 (8)	5.6 (5)
C2	0.499 (1)	0.260 (1)	0.598 (1)	6.0 (6)
C3	0.552 (2)	0.228 (1)	0.561 (1)	12 (1)
C5	0.647 (1)	0.256 (2)	0.502 (1)	6.2 (7)
C6	0.679 (1)	0.313 (1)	0.474 (1)	4.5 (6)

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