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Key indicators

Single-crystal X-ray study
T = 292 K
Mean σ(C–C) = 0.020 Å
Disorder in main residue
R factor = 0.046
wR factor = 0.132
Data-to-parameter ratio = 22.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Bis(piperazinium) di-μ-chloro-pentachloro-triiododibismuthate(III) tetrahydrate

The title salt, $(C_4H_{12}N_2)_2[Bi_2Cl_7I_3]\cdot 4H_2O$, was prepared by the reaction of bismuth trichloride, potassium iodide and piperazine in a hydrochloric acid medium. It is composed of piperazinium dications and dimeric $[Bi_2Cl_7I_3]^{4-}$ tetraanions, together with water of crystallization. The halobismuthate(III) tetraanion is located on a center of inversion. Hydrogen bonds, including N—H···O, N—H···Cl, N—H···I, O—H···O, O—H···Cl and O—H···I interactions, are present in the crystal structure.

Comment

The chemistry and physics of halobismuthate(III) complexes have received considerable interest in recent years because of their anti-ulcer activity (Turel *et al.*, 1998) and their unique optical and electronic properties, including nonlinear optical activity, luminescence and semiconductivity (Goforth *et al.*, 2004). Therefore, we report the crystal structure of a new mixed halobismuthate(III) complex, bis(piperazinium) di-μ-chloropentachlorotriiododibismuthate(III) tetrahydrate, (I). Complex (I) is made up of diprotonated piperazine cations (2+) with a chair-like conformation and a dinuclear mixed haloanion of bismuth(III) (Fig. 1), $[Bi_2Cl_7I_3]^{4-}$, together with water molecules of crystallization. The $[Bi_2Cl_7I_3]^{4-}$ anion is built up of two edge-sharing $[BiX_6]$ octahedral units, resulting in a centrosymmetric $[Bi_2X_{10}]^{4-}$ fragment, and is located on a crystallographic inversion center. Although the $[Bi_2X_{10}]^{4-}$ fragment has been reported previously (Benetollo *et al.*, 2001; Bigoli *et al.*, 1984; Bowmaker *et al.*, 1998; Chaabouni *et al.*, 1998; Charmant *et al.*, 2002; Wu *et al.*, 2005), the mixed-halide $[Bi_2X_{10}]^{4-}$ anions are rarely mentioned in the literature (Goforth *et al.*, 2004). In (I), one of the five crystallographically independent halide sites is affected by halide disorder. This site (Cl2/I2) and that symmetry-related by an inversion center (designated *A*) are equatorial ligand sites in relation to the $Bi_2Cl_3I_3$ basal plane.


(I)
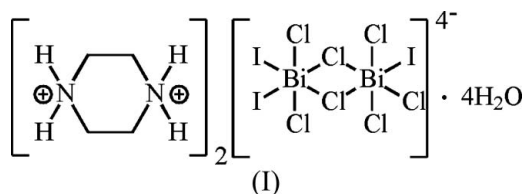
Within the basal plane, two chloride ligands bridge the bismuth centers; one bismuth center has a terminal iodide and three terminal chloride ligands, and the other has two terminal chloride and two terminal iodide ligands. Bond distances and angles for this anion are given in Table 1. There are compli-
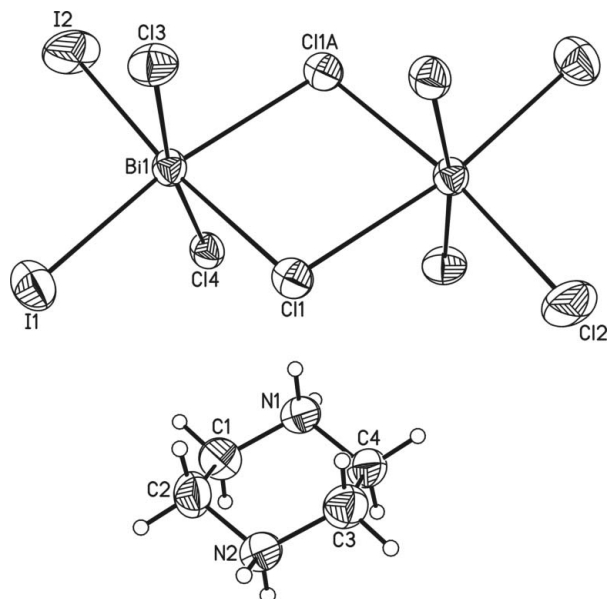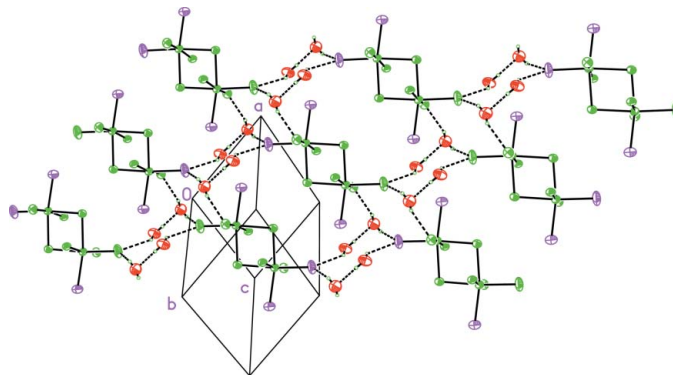
Figure 1
A perspective view of the $[Bi_2Cl_7I_3]^{4-}$ anion and the piperazium cation with the atomic numbering scheme. The disordered I/Cl sites are shown as I2 on one side of the inversion center and Cl2 on the other. Displacement ellipsoids are drawn at the 50% probability level [symmetry code: (A) $1 - x, 1 - y, 1 - z$].
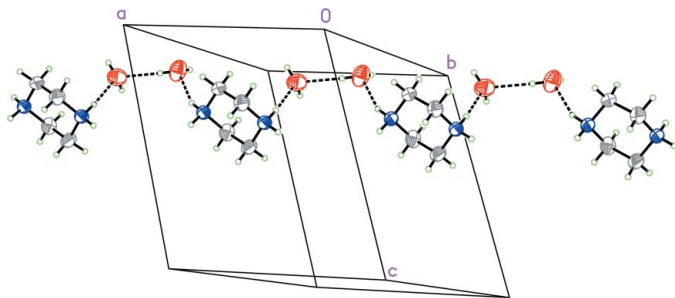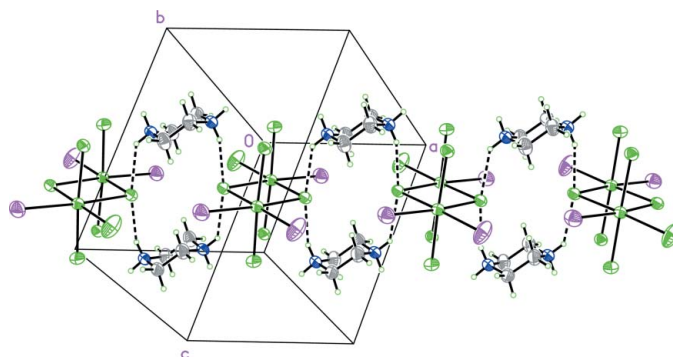

Figure 2
A view showing the chain propagated by water molecules *via* O—H⋯O hydrogen bonds and piperazium cations *via* N—H⋯O hydrogen bonds (hydrogen bonds shown as dashed lines).

cated hydrogen bonding interactions among the $[Bi_2Cl_7I_3]^{4-}$ anions, piperazinium cations and water molecules of crystallization, which result in various supramolecular assemblies. Two neighboring water molecules of crystallization aggregate into a dimer through O—H⋯O hydrogen bonds (Fig. 2). Such dimers are linked by N—H⋯O hydrogen bonds with their neighboring piperazium cations to form a one-dimensional chain along the *a* axis (Fig. 2). Furthermore, these water dimers and the $[Bi_2Cl_7I_3]^{4-}$ anions are assembled into two-dimensional layers parallel to the (011) plane through O—H⋯Cl and O—H⋯I hydrogen-bonding interactions (Fig. 3). In particular, the N—H⋯Cl and O—H⋯I hydrogen bonds between each of the $[Bi_2Cl_7I_3]^{4-}$ anions and its four neighboring piperazium cations result in another chain, formed by one row of halobismuthate anions sandwiched between two parallel rows of piperazium cations, along the *a* axis in the crystal structure (Fig. 4). These chains are then linked by hydrogen bonds involving water molecules, forming a three-

Figure 3
A hydrogen-bonded layer composed of water molecules and the $[Bi_2Cl_7I_3]^{4-}$ anions with O—H⋯Cl and O—H⋯I hydrogen bonds (dashed lines).

Figure 4
A cation–anion alternating chain composed of piperazium cations and $[Bi_2Cl_7I_3]^{4-}$ anions (dashed lines indicate hydrogen bonds).

dimensional extended structure. Detailed hydrogen bond parameters are given in Table 2.

Experimental

An aqueous solution of $BiCl_3$ (0.39 g, 1.2 mmol, dissolved in 2 ml of concentrated HCl) and piperazine hexahydrate (0.65 g, 3.3 mmol, dissolved in 15 ml of water) was refluxed for about 1 h, then KI (0.48 g, 1 mmol) was added. The resulting solution was refluxed for another 1 h. After filtering, yellow crystals of the title compound suitable for single-crystal X-ray diffraction were deposited over a period of about four days on slow evaporation at room temperature. IR (KBr, cm^{-1}): 3578 (*m*, O—H), 3493 (*m*, O—H), 3137 (*m*, N—H), 3003 (*m*, N—H), 2810 (*m*, C—H), 2360 (*w*), 2341 (*w*), 1613 (*s*, H_2O), 1575 (*s*, NH_2), 1453 (*vs*, CH_2), 1441 (*vs*, CH_2), 1318 (*m*), 1308 (*m*), 1200 (*w*), 1083 (*s*), 1053 (*s*), 1001 (*m*), 941 (*vs*), 864 (*s*), 682 (*s*). UV (in DMSO, nm): 222, 322.

Crystal data

$(C_4H_{12}N_2)_2[Bi_2Cl_7I_3]\cdot4H_2O$	$Z = 1$
$M_r = 1295.19$	$D_x = 2.725$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.2076$ (8) Å	Cell parameters from 1080
$b = 10.4721$ (11) Å	reflections
$c = 10.7474$ (11) Å	$\theta = 2.5$–26.0°
$\alpha = 97.328$ (2)°	$\mu = 14.68$ mm^{-1}
$\beta = 108.678$ (2)°	$T = 292$ (2) K
$\gamma = 110.504$ (2)°	Block, yellow
$V = 789.18$ (14) Å^3	$0.30 \times 0.20 \times 0.20$ mm

Data collection

Bruker APEX CCD area detector diffractometer	3026 independent reflections
	2828 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.027$
Absorption correction: multi-scan (*SADABS*; Sheldrick 1996)	$\theta_{max} = 26.0°$
	$h = -10 \rightarrow 10$
$T_{min} = 0.032$, $T_{max} = 0.053$	$k = -12 \rightarrow 10$
4283 measured reflections	$l = -12 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0801P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$+ 3.4558P]$
$wR(F^2) = 0.132$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
3026 reflections	$\Delta\rho_{max} = 2.61$ e Å^{-3}
132 parameters	$\Delta\rho_{min} = -1.82$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Bi1—Cl4	2.737 (3)	Bi1—I1	2.8879 (9)
Bi1—Cl3	2.749 (3)	Bi1—Cl1^i	2.969 (2)
Bi1—Cl2	2.8210 (14)		
Cl4—Bi1—Cl3	171.31 (8)	Cl2—Bi1—Cl1	172.69 (6)
Cl4—Bi1—Cl2	94.89 (7)	I1—Bi1—Cl1	88.07 (5)
Cl3—Bi1—Cl2	89.10 (7)	Cl4—Bi1—Cl1^i	86.54 (7)
Cl4—Bi1—I1	93.11 (5)	Cl3—Bi1—Cl1^i	85.57 (8)
Cl3—Bi1—I1	94.00 (6)	Cl2—Bi1—Cl1^i	92.61 (7)
Cl2—Bi1—I1	97.69 (4)	I1—Bi1—Cl1^i	169.69 (6)
Cl4—Bi1—Cl1	89.27 (7)	Cl1—Bi1—Cl1^i	81.62 (7)
Cl3—Bi1—Cl1	85.99 (8)	Bi1—Cl1—Bi1^i	98.38 (7)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O1···O2	0.85	2.04	2.888 (14)	178
O1—H2O1···I2^{ii}	0.85	2.91	3.582 (10)	137
O2—H1O2···Cl3^{iii}	0.85	2.35	3.167 (11)	161
O2—H2O2···Cl2^{iv}	0.85	2.60	3.453 (11)	175
N2—H2C···Cl1^v	0.90	2.54	3.258 (9)	137
N2—H2D···O2^{vi}	0.90	1.87	2.771 (13)	175
N1—H1C···O1	0.90	1.92	2.777 (13)	158
N1—H1D···Cl1	0.90	2.42	3.272 (9)	157

Symmetry codes: (ii) $x - 1, y, z - 1$; (iii) $x, y, z - 1$; (iv) $-x + 2, -y + 2, -z + 1$; (v) $-x, -y + 1, -z + 1$; (vi) $x - 1, y, z$.

The refinement of the Cl2/I2 site as single site fully occupied by either Cl or I alone resulted in a higher residual factor and unreasonably large or small displacement parameters and significantly elongated ellipsoids. This site was successfully modeled as a mixed Cl/I position. Initially, the occupancies of these atoms were allowed to refine freely. The resulting occupancies both approached 0.5, and correspondingly, their sum was close to unity, thereby supporting the assignment as a mixed Cl/I position. For the final cycles, the occupancies were constrained to 0.5, since the elemental analysis implies that the ratio of Bi to Cl and to I in the title compound is close to 2:7:3. No unusual problems were encountered for Cl1, I1, Cl3 or Cl4, and the final refined composition of the anion is then Bi$_2$Cl$_7$I$_3$. H atoms attached to O atoms were located in a difference Fourier map and other H atoms were positioned geometrically. All H atoms were refined using a riding model, with C—H = 0.97 Å, N—H = 0.90 Å and O—H = 0.85 Å. For all H atoms, U_{iso}(H) = 1.2U_{eq}(parent atom). The locations of the maximum and minimum difference density peaks are 1.01 and 0.63 Å from Bi1 and I1, respectively.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003); software used to prepare material for publication: *SHELXTL*.

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