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Halobismuth(III) salts with substituted aminopyridinium cations

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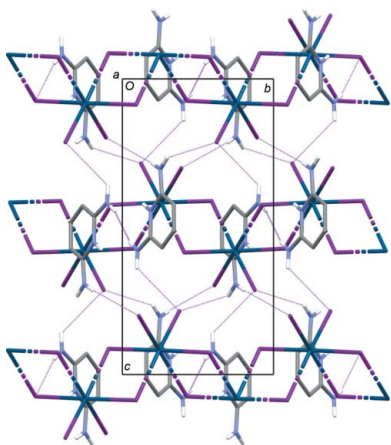
CCDC references: 2001365; 2001364; 2001363; 2001362; 2001361; 2001360

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The crystal structures of six halobismuth(III) salts of variously substituted aminopyridinium cations display discrete mononuclear $[\text{BiCl}_6]^{3-}$ and dinuclear $[\text{Bi}_2\text{X}_{10}]^{4-}$ anions ($X = \text{Cl}$ or Br), and polymeric *cis*-double-halo-bridged $[\text{Bi}_n\text{X}_{4n}]^{n-}$ anionic chains ($X = \text{Br}$ or I). Bis(2-amino-3-ammoniopyridinium) hexachloridobismuth(III) chloride monohydrate, $(\text{C}_5\text{H}_9\text{N}_3)_2[\text{BiCl}_6]\text{Cl}\cdot\text{H}_2\text{O}$, (1), contains discrete mononuclear $[\text{BiCl}_6]^{3-}$ and chloride anions. Tetrakis(2-amino-3-methylpyridinium) di- μ -chlorido-bis[tetrachloridobismuth(III)], $(\text{C}_6\text{H}_9\text{N}_2)_4[\text{Bi}_2\text{Cl}_{10}]$, (2), tetrakis(2-amino-3-methylpyridinium) di- μ -bromido-bis[tetrabromidobismuth(III)], $(\text{C}_6\text{H}_9\text{N}_2)_4[\text{Bi}_2\text{Br}_{10}]$, (3), and bis(4-amino-3-ammoniopyridinium) di- μ -chlorido-bis[tetrachloridobismuth(III)] dihydrate, $(\text{C}_5\text{H}_9\text{N}_3)_2[\text{Bi}_2\text{Cl}_{10}]\cdot 2\text{H}_2\text{O}$, (4), incorporate discrete $[\text{Bi}_2\text{X}_{10}]^{4-}$ anions ($X = \text{Cl}$ or Br), while *catena*-poly[2,6-diaminopyridinium [*cis*-diiodidobismuth(III)]-di- μ -iodido], $\{(\text{C}_5\text{H}_8\text{N}_3)[\text{BiI}_4]\}_n$, (5), and *catena*-poly[2,6-diaminopyridinium [*cis*-dibromidobismuth(III)]-di- μ -bromido], $\{(\text{C}_5\text{H}_7\text{N}_2)[\text{BiBr}_4]\}_n$, (6), include $[\text{Bi}_n\text{X}_{4n}]^{n-}$ anionic chains ($X = \text{Br}$ or I). Structures (2) and (3) are isostructural, while that of (5) is a pseudomerohedral twin. There is no discernible correlation between the type of anionic species obtained and the cation or halide ligand used. The Bi^{III} centres always have a slightly distorted octahedral geometry and there is a correlation between the $\text{Bi}-\text{X}$ bond lengths and the number of classic $\text{N}-\text{H}\cdots\text{X}$ hydrogen bonds that the X ligand accepts, with a greater number of interactions corresponding with slightly longer $\text{Bi}-\text{X}$ distances. The supramolecular networks formed by classic $\text{N}-\text{H}\cdots\text{X}$ hydrogen bonds include ladders, bilayers and three-dimensional frameworks.

1. Introduction

Metal–organic frameworks (MOFs) are of interest as porous materials because of their potential as hosts in a variety of purposes, one of which is as a drug-delivery system (Yang *et al.*, 2015). In such uses, toxicity is an important issue. Bismuth is a low-toxicity heavy metal, which has long been used as a treatment for gastrointestinal problems (DuPont, 1987) and is therefore a good candidate for the development of MOF hosts for drug delivery. During investigations of routes towards the synthesis of bismuth(III) coordination polymers with pyridine carboxylate derivatives as spacer ligands (Senior & Linden, 2020), bismuth halides, BiX_3 ($X = \text{Cl}$, Br or I), were mixed with a variety of aminopyridine derivatives. Six compounds were obtained, which were not the desired coordination polymers, but, instead, simple salts of the aminopyridinium cations with $[\text{BiX}_6]^{3-}$, $[\text{Bi}_2\text{X}_{10}]^{4-}$ or polymeric *cis*-double-halo-bridged $[\text{Bi}_n\text{X}_{4n}]^{n-}$ counter-ions. The crystal structures of these salts are described here, namely, bis(2-amino-3-ammoniopyridinium) hexachloridobismuth(III) chloride monohydrate, (1), tetrakis(2-amino-3-methylpyridinium) di- μ -chlorido-bis[tetrachloridobismuth(III)], (2), tetrakis(2-amino-3-methylpyridin-



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Table 1

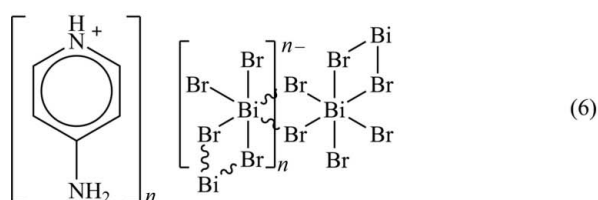
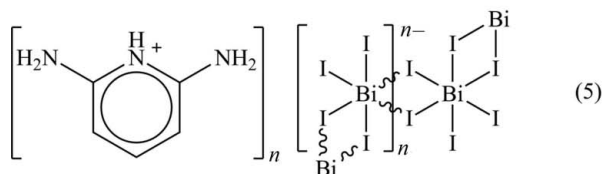
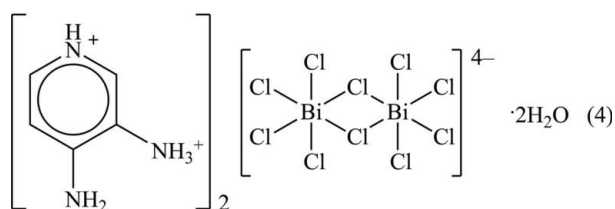
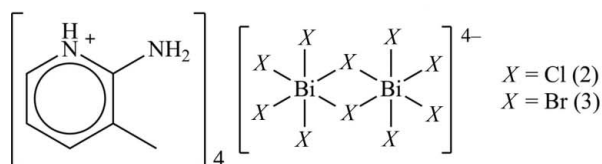
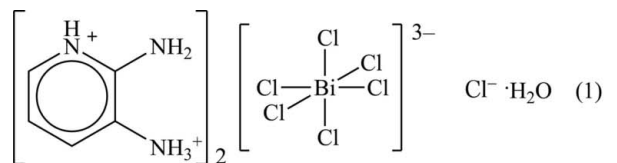
Experimental details.

Experiments were carried out using an Oxford Diffraction SuperNova dual radiation diffractometer.

	(1)	(2)	(3)
Crystal data			
Chemical formula	(C ₅ H ₉ N ₃) ₂ [BiCl ₆]Cl·H ₂ O	(C ₆ H ₉ N ₂) ₄ [Bi ₂ Cl ₁₀]	(C ₆ H ₉ N ₂) ₄ [Bi ₂ Br ₁₀]
<i>M_r</i>	697.45	1209.07	1653.67
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	160	160	160
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.1612 (4), 10.8591 (6), 11.7273 (7)	8.8144 (3), 8.9982 (3), 12.3440 (4)	9.2145 (3), 9.0678 (2), 12.6314 (4)
α , β , γ (°)	94.303 (4), 101.914 (4), 106.254 (4)	76.784 (3), 87.111 (3), 88.514 (3)	75.476 (3), 86.926 (3), 89.221 (2)
<i>V</i> (Å ³)	1084.89 (10)	951.80 (6)	1020.22 (5)
<i>Z</i>	2	1	1
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	9.00	9.96	18.43
Crystal size (mm)	0.25 × 0.20 × 0.10	0.25 × 0.15 × 0.07	0.15 × 0.14 × 0.07
Data collection			
Absorption correction	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2018)	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2018)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2018)
<i>T_{min}</i> , <i>T_{max}</i>	0.551, 1.000	0.660, 1.000	0.274, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	8459, 5056, 4589	8469, 4463, 4137	22534, 5122, 4575
<i>R_{int}</i>	0.040	0.026	0.046
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.691	0.692	0.694
Refinement			
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 0.075, 1.03	0.024, 0.049, 1.02	0.028, 0.059, 1.06
No. of reflections	5054	4463	5122
No. of parameters	237	201	202
No. of restraints	2	54	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	3.53, -1.74	0.89, -1.03	1.52, -1.77
	(4)	(5)	(6)
Crystal data			
Chemical formula	(C ₅ H ₉ N ₃) ₂ [Bi ₂ Cl ₁₀]·2H ₂ O	(C ₅ H ₉ N ₃)[BiL ₄]	(C ₅ H ₇ N ₂)[BiBr ₄]
<i>M_r</i>	1030.79	826.72	623.75
Crystal system, space group	Monoclinic, <i>C2/c</i>	Monoclinic, <i>P2₁/n</i>	Monoclinic, <i>P2₁/c</i>
Temperature (K)	160	160	160
<i>a</i> , <i>b</i> , <i>c</i> (Å)	18.0583 (2), 12.07450 (12), 13.43800 (15)	12.02106 (15), 7.80880 (9), 15.3298 (2)	11.66220 (15), 14.08143 (19), 7.35193 (9)
α , β , γ (°)	90, 104.0805 (11), 90	90, 90.0530 (11), 90	90, 94.7149 (13), 90
<i>V</i> (Å ³)	2842.05 (5)	1439.01 (3)	1203.25 (3)
<i>Z</i>	4	4	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	13.33	20.80	27.89
Crystal size (mm)	0.20 × 0.18 × 0.08	0.16 × 0.10 × 0.04	0.21 × 0.08 × 0.06
Data collection			
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2018)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2018)	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2018)
<i>T_{min}</i> , <i>T_{max}</i>	0.348, 1.000	0.259, 1.000	0.735, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	30758, 3742, 3505	35690, 4076, 3831	26081, 3128, 2794
<i>R_{int}</i>	0.034	0.041	0.040
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.693	0.712	0.692
Refinement			
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.016, 0.030, 1.08	0.020, 0.040, 1.05	0.023, 0.050, 1.05
No. of reflections	3742	4076	3127
No. of parameters	182	120	121
No. of restraints	12	0	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.66, -0.55	1.21, -1.04	1.26, -2.22

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT2018* (Sheldrick, 2015a), *OLEX2* (Dolomanov *et al.*, 2009), *Mercury* (Macrae *et al.*, 2020), *SHELXL2018* (Sheldrick, 2015b) and *PLATON* (Spek, 2015, 2020).

ium) di- μ -bromido-bis[tetrabromidobismuth(III)], (3), bis(4-amino-3-ammoniopyridinium) di- μ -chlorido-bis[tetrachlorido-bismuth(III)] dihydrate, (4), *catena*-poly[2,6-diaminopyridinium [[*cis*diiodidobismuth(III)]-di- μ -iodido]], (5), and *catena*-poly[2,6-diaminopyridinium [[*cis*dbromidobismuth(III)]-di- μ -bromido]], (6).



Scheme 1

The Cambridge Structural Database (CSD, Version 5.41, update of November 2019; Groom *et al.*, 2016) contains 604 entries for pure halobismuth(III) anions. Of these, 126 have $[\text{BiX}_6]^{3-}$ anions, 17 have single-halo-bridged $[\text{Bi}_2\text{X}_{11}]^{5-}$ anions, 109 have double-halo-bridged $[\text{Bi}_2\text{X}_{10}]^{4-}$ anions, and 94 have triple-halo-bridged $[\text{Bi}_2\text{X}_9]^{3-}$ anions. There are 88 examples with more exotic discrete multinuclear cluster anions with up to eight Bi^{III} centres, such as $[\text{Bi}_4\text{I}_{16}]^{4-}$ (Dennington & Weller, 2018), $[\text{Bi}_4\text{Br}_{18}]^{6-}$ (Kotov *et al.*, 2019), $[\text{Bi}_5\text{Cl}_{18}]^{3-}$ (Sharutin, 2016), $[\text{Bi}_6\text{I}_{22}]^{4-}$ (Liu *et al.*, 2006), $[\text{Bi}_6\text{Cl}_{26}]^{8-}$ (Leblanc *et al.*, 2010), $[\text{Bi}_7\text{I}_{24}]^{3-}$ (Hamdeh *et al.*, 2016) and $[\text{Bi}_8\text{Cl}_{28}]^{4-}$ (Adonin *et al.*, 2014), where single- and double-halo bridges are mainly found and, in some cases, halo bridges span three Bi^{III} centres. There are 84 polymeric examples with single-halo-bridged $[\text{Bi}_n\text{X}_{5n}]^{2n-}$ anions, 60 with

cis-double-halo-bridged $[\text{Bi}_n\text{X}_{4n}]^{n-}$ anions and 24 with more complex anionic systems; examples being $[\text{Bi}_{6n}\text{I}_{20n}]^{2n-}$ (Heine, 2015), $[\text{Bi}_{6n}\text{I}_{22n}]^{4n-}$ (Heine, 2015) and $[\text{Bi}_{2n}\text{Br}_{9n}]^{3n-}$ (Pandey *et al.*, 2017). There are no examples of double-halo-bridged $[\text{Bi}_n\text{X}_{4n}]^{n-}$ anionic chains where the terminal halo ligands are *trans*-disposed.

The CSD contains 2, 37, 119, 6 and 259 entries with 2-amino-3-ammoniopyridinium, 2-amino-3-methylpyridinium, 2,6-diaminopyridinium, 4-amino-3-ammoniopyridinium or 4-amino-pyridinium cations, respectively. Of these, 0, 8, 8, 0 and 40 are salts with pure halometallate anions (halometallate anions including non-halogen ligands are excluded). It is apparent that structures of any kind with the divalent 2-amino-3-ammoniopyridinium and 4-amino-3-ammoniopyridinium cations are scarce. There are 22 and 16 entries for the corresponding monovalent 2,3- and 3,4-diaminopyridinium cations, respectively, but none of these are pure halometallate salts.

2. Experimental

2.1. Synthesis and crystallization

Salts (1)–(6) were prepared by dissolving 0.3 mmol of the appropriate bismuth halide, BiX_3 ($X = \text{Cl}, \text{Br}$ or I), in a minimum quantity of the corresponding 2 M acid, HX , and then stirring in 0.3 mmol of the relevant aminopyridine. Crystals of each salt were obtained by allowing the solutions to evaporate slowly in the air at room temperature.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. For (2), rigid-body restraints were applied to the atoms of the cation containing atom N3. The asymmetric unit of salt (4) includes two sites for water molecules, which are disordered about twofold axes, so that each site is only half-occupied. The chosen crystal of (5) was a pseudomerohedral twin with a major twin fraction of 0.9278 (3). The twin arises through a twofold rotation about [001] with a twin matrix of $\bar{1}00/0\bar{1}0/001$. Of the 4076 unique reflections, 3989 overlap because the unit-cell b angle is essentially 90° [$90.0530(11)^\circ$], so it was not necessary to integrate the two twin components separately. The water H atoms in (1) and all the N-bound H atoms in (6) were located in a difference Fourier map and their positions were refined along with individual isotropic displacement parameters; the O–H distances in (1) were restrained to 0.84 (1) Å. The N- and O-bound H atoms in (4) were similarly located and refined, but with O–H and H...H distance restraints of 0.84 (1) and 1.40 (1) Å, respectively, for the disordered water molecules, and N–H distance restraints of 0.88 (1) Å for the pyridine and amine H atoms, and 0.91 (1) Å for the ammonium H atoms. Apart from this, the H atoms of the methyl group in (2) and the $-\text{NH}_3^+$ group in (1) were constrained to an ideal geometry ($\text{C–H} = 0.98$ Å and $\text{N–H} = 0.91$ Å), with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C,N})$, but were allowed to rotate freely about the C–C or C–N bonds. All other H atoms in the structures were placed in geometrically idealized positions and

Table 2
Selected bond lengths (Å) for (1).

Bi1—Cl1	2.6812 (12)	Bi1—Cl6	2.5896 (12)
Bi1—Cl2	2.7986 (14)	N2—C1	1.331 (6)
Bi1—Cl3	2.8899 (12)	N3—C2	1.454 (6)
Bi1—Cl4	2.6970 (13)	N5—C6	1.335 (6)
Bi1—Cl5	2.6312 (13)	N6—C7	1.455 (6)

constrained to ride on their parent atoms ($C-H = 0.95 \text{ \AA}$ and $N-H = 0.88 \text{ \AA}$), with $U_{iso}(H) = 1.2U_{eq}(C,N)$. One and two low-angle reflections were omitted from the final cycles of refinement for (6) and (1), respectively, because their observed intensities were much lower than the calculated values as a result of being partially obscured by the beam stop.

3. Results and discussion

The syntheses of compounds (1)–(6) involved mixing the chosen cation with BiX_3 in a 1:1 stoichiometric ratio in the corresponding 2 *M* HX acid ($X = Cl, Br$ or I). Nonetheless, the stoichiometric ratio of cation to bismuth was 2:1 in the crystal structures of salts (1)–(4), which all contain discrete halobismuth(III) anions, and 1:1 only in compounds (5) and (6), which contain polymeric halobismuth(III) anions.

3.1. Bis(2-amino-3-ammoniopyridinium) hexachloridobismuth(III) chloride monohydrate, (1)

The asymmetric unit of (1) contains two divalent 2-amino-3-ammoniopyridinium cations, one slightly distorted octahedral $[BiCl_6]^{3-}$ anion, one chloride anion and one water molecule (Fig. 1). The Bi—Cl bond lengths range from 2.5896 (12) to 2.8899 (12) Å (Table 2). The *cis* Cl—Bi—Cl angles range from 82.16 (4) to 97.59 (4)° and the *trans* Cl—Bi—Cl angles from 170.83 (4) to 179.68 (4)°. The longest Bi—Cl bond involves atom Cl3 in the $[BiCl_6]^{3-}$ anion, which is involved in two hydrogen bonds with cations. The only other Cl ligand in the $[BiCl_6]^{3-}$ anion involved in two hydrogen bonds is Cl4, but

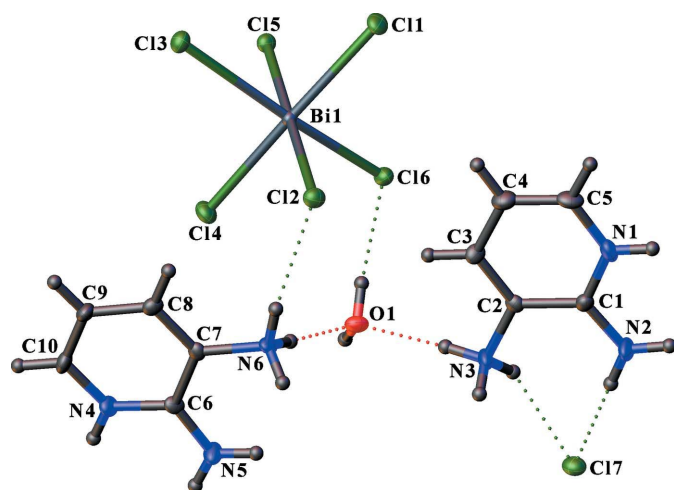


Figure 1
View of the asymmetric unit of (1), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

Table 3
Hydrogen-bond geometry (Å, °) for (1).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 \cdots Cl3 ⁱ	0.88	2.31	3.154 (5)	160
N2—H21 \cdots Cl4 ⁱ	0.88	2.43	3.215 (4)	150
N2—H22 \cdots Cl7	0.88	2.35	3.223 (5)	171
N3—H31 \cdots Cl7 ⁱⁱ	0.91	2.68	3.202 (5)	118
N3—H32 \cdots O1	0.91	1.94	2.848 (6)	176
N3—H33 \cdots Cl1 ⁱⁱⁱ	0.91	2.37	3.228 (5)	157
N4—H4 \cdots Cl7 ^{iv}	0.88	2.35	3.181 (4)	158
N5—H51 \cdots Cl7 ^{iv}	0.88	2.70	3.453 (5)	144
N5—H52 \cdots Cl5 ⁱⁱⁱ	0.88	2.43	3.290 (5)	167
N6—H61 \cdots O1	0.91	1.91	2.794 (6)	163
N6—H62 \cdots Cl3 ⁱⁱⁱ	0.91	2.29	3.167 (4)	163
N6—H63 \cdots Cl2	0.91	2.38	3.218 (4)	153
O1—H11 \cdots Cl4 ^v	0.84 (1)	2.36 (2)	3.177 (5)	165 (6)
O1—H12 \cdots Cl6	0.84 (1)	2.26 (2)	3.083 (4)	170 (6)

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

one of the donors is a water molecule; this is the third longest Bi—Cl bond. The longest Bi—Cl bond is *trans* to the shortest one, which involves atom Cl6. Similarly, the second longest Bi—Cl bond involving atom Cl2 is *trans* to the second shortest one, which involves atom Cl5. The N-bound H atoms for only one cation were unambiguously visible in a difference electron-density map, but this was enough to indicate that the 3-amino group was protonated, and not the 2-amino group. This was further confirmed by the C2—N3 and C7—N6 bond lengths of approximately 1.45 Å (Table 2), which are consistent with the C—N⁺ bond of the 3-ammonio group, while the shorter C1—N2 and C6—N5 bond lengths of about 1.33 Å

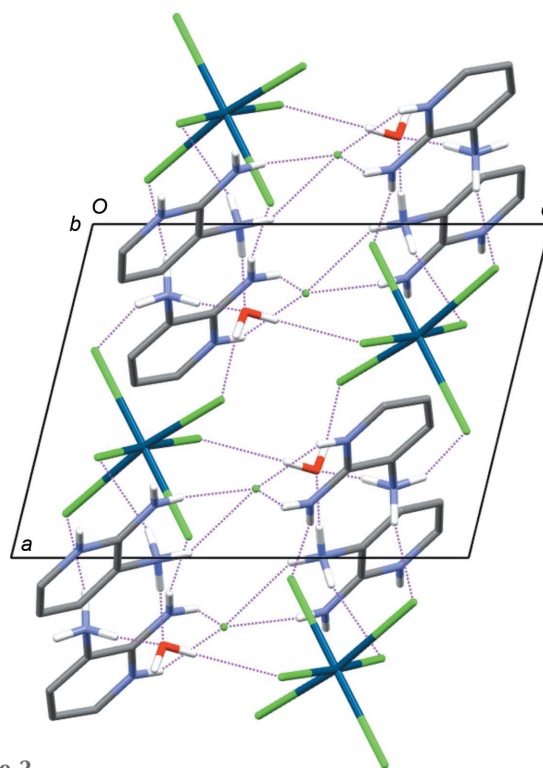


Figure 2
The hydrogen-bonded supramolecular bilayer in (1), viewed down the *b* axis. H atoms bonded to C atoms have been omitted for clarity.

Table 4
Selected geometric parameters (Å, °) for (2), (3) and (4).

	(2) ($X = \text{Cl}$)	(3) ($X = \text{Br}$)	(4) ($X = \text{Cl}$)
Bi1—X1	2.5533 (10)	2.7114 (4)	2.5247 (5)
Bi1—X2	2.5992 (9)	2.7491 (4)	2.6474 (5)
Bi1—X3	2.6342 (9)	2.7830 (4)	2.6840 (5)
Bi1—X4	2.7471 (8)	2.9043 (4)	2.7170 (5)
Bi1—X5	2.8300 (9)	2.9590 (4)	2.8136 (5)
Bi1—X5 ⁱ	2.9760 (10)	3.1172 (4)	2.9738 (6)
N2—C1	1.323 (4)	1.331 (5)	—
N4—C7	1.310 (5)	1.306 (6)	—
N2—C2	—	—	1.458 (3)
N3—C3	—	—	1.323 (3)
Bi1—X5—Bi1 ⁱ	97.40 (3)	95.335 (12)	97.096 (16)

Symmetry code (i) for (2) and (3): $-x + 1, -y + 1, -z$; for (4): $-x + \frac{1}{2}, -y + \frac{3}{2}, -z$.

indicate the sp^2 -hybridization character of the 2-amino N atoms and that they are neutral amino groups. Subsequently, this information was used to place all N-bound H atoms in appropriately calculated positions.

All species in the structure of (1) are involved in hydrogen bonds (Table 3). Each cation donates six hydrogen bonds. The cation containing atom N1 donates one hydrogen bond to the water molecule, two to the chloride ion, two to one $[\text{BiCl}_6]^{3-}$ anion and one to a second $[\text{BiCl}_6]^{3-}$ anion. The cation containing atom N4 has the same number of interactions with neighbouring species, but the donor/acceptor atom pairs are not always the same. The ammonio substituent at atom N3 interacts with a water molecule, a chloride ion and a $[\text{BiCl}_6]^{3-}$

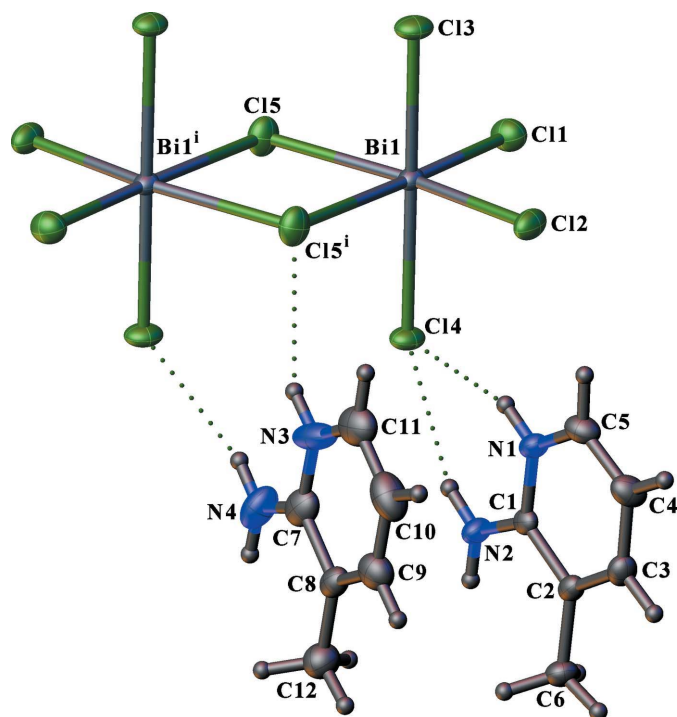


Figure 3
View of the core components of (2), showing the centrosymmetric dinuclear anion and the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

Table 5
Hydrogen-bond geometry (Å, °) for (2).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots Cl4	0.88	2.46	3.287 (3)	156
N2—H21 \cdots Cl4	0.88	2.52	3.324 (3)	153
N2—H22 \cdots Cl2 ⁱⁱ	0.88	2.49	3.345 (3)	165
N3—H3 \cdots Cl5 ⁱ	0.88	2.81	3.451 (4)	131
N4—H41 \cdots Cl3 ⁱ	0.88	2.57	3.360 (3)	150
N4—H42 \cdots Cl5 ⁱⁱⁱ	0.88	2.86	3.737 (4)	175

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $x - 1, y, z$; (iii) $-x, -y + 1, -z$.

anion, while that at atom N6 interacts with the same water molecule and two other $[\text{BiCl}_6]^{3-}$ anions. The pyridine group at atom N1 interacts with a $[\text{BiCl}_6]^{3-}$ anion, while that at atom N4 interacts with a chloride ion. The amino group of both cations interact with a chloride ion and a $[\text{BiCl}_6]^{3-}$ anion, albeit not with the same ones. The water molecule donates a hydrogen bond to each of two different $[\text{BiCl}_6]^{3-}$ anions and accepts a hydrogen bond from each of the symmetry-independent cations. The chloride anion accepts four hydrogen bonds, two from each of the symmetry-independent cations. The $[\text{BiCl}_6]^{3-}$ anion accepts eight hydrogen bonds from five surrounding cations and two water molecules. The result of these interactions is a two-dimensional (2D) supramolecular bilayer structure involving all species. The bilayers lie parallel to the (001) plane and their outer surfaces are composed of cations and $[\text{BiCl}_6]^{3-}$ anions with the chloride ions sandwiched in between. The water molecules also line the inner side of the individual layers (Fig. 2). There are no classic hydrogen-bonding interactions between the bilayers.

3.2. Tetrakis(2-amino-3-methylpyridinium) di- μ -chlorido-bis[tetrachloridobismuth(III)], (2)

The asymmetric unit of (2) contains two monovalent 2-amino-3-methylpyridinium cations and one half of a centrosymmetric double-chlorido-bridged $[\text{Bi}_2\text{Cl}_{10}]^{4-}$ anion (Fig. 3). The bridging Bi—Cl bonds in the anion are slightly asymmetric, differing by 0.1460 (9) Å, and significantly longer than all of the terminal Bi—Cl bonds, which range from 2.5533 (10) to 2.7471 (8) Å (Table 4). The two longest terminal Bi—Cl bonds are in axial positions and the longest of these involves atom Cl4, which accepts two hydrogen bonds from a cation, while the slightly shorter bond involving atom Cl3 has only one hydrogen-bonding interaction. Similarly, the longer of the equatorial terminal Bi—Cl bonds, which involves atom Cl2, is a hydrogen-bond acceptor, while the slightly shorter equatorial bond involving atom Cl1 does not participate in hydrogen bonds. The shorter of the equatorial Bi—Cl bonds is also *trans* to the longer of the bridging Bi—Cl bonds. The unique Bi^{III} centre has a slightly distorted octahedral geometry, with *cis* Cl—Bi—Cl angles ranging from 82.60 (3) to 96.18 (3)°; the smallest angle involving the two bridging Cl atoms. The *trans* Cl—Bi—Cl angles range from 169.86 (3) to 178.64 (3)°. The C1—N2 and C6—N5 bond lengths (Table 4) indicate the sp^2 -hybridization character of these 2-amino N atoms and that they have not been protonated.

Table 6
Hydrogen-bond geometry (Å, °) for (3).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots Br4	0.88	2.62	3.456 (3)	158
N2—H21 \cdots Br4	0.88	2.68	3.496 (3)	154
N2—H22 \cdots Br2 ⁱⁱ	0.88	2.65	3.504 (4)	165
N3—H3 \cdots Br5 ⁱ	0.88	3.02	3.653 (4)	130
N4—H41 \cdots Br3 ⁱ	0.88	2.72	3.521 (4)	152
N4—H42 \cdots Br5 ⁱⁱⁱ	0.88	3.04	3.912 (5)	173

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $x - 1, y, z$; (iii) $-x, -y + 1, -z$.

A complex series of hydrogen bonds (Table 5) links the cations and anions of (2) into one-dimensional (1D) supramolecular ladders, which lie parallel to the [100] direction (Fig. 4). Each upright of the ladder is composed of stacks of the two unique cations aligned with the ring planes parallel to the ladder direction. Each $[\text{Bi}_2\text{Cl}_{10}]^{4-}$ anion acts as the rung of the ladder and hydrogen bonds to eight cations, four from each upright and four above and below the anion in the ladder direction, so that the cations and anions stack in an alternating fashion along the ladder. All N—H donors are involved, but not all Cl atoms act as hydrogen-bond acceptors. The pyridinium group of one of the unique cations hydrogen bonds with one of the bridging Cl atoms of a neighbouring $[\text{Bi}_2\text{Cl}_{10}]^{4-}$ anion, while the amino group interacts with an axial terminal Cl atom of the same anion and with the same bridging Cl atom in the next anion along the ladder. These two Cl atoms accept one and two interactions, respectively. The pyridinium and one of the amino H atoms of the other unique cation interact with

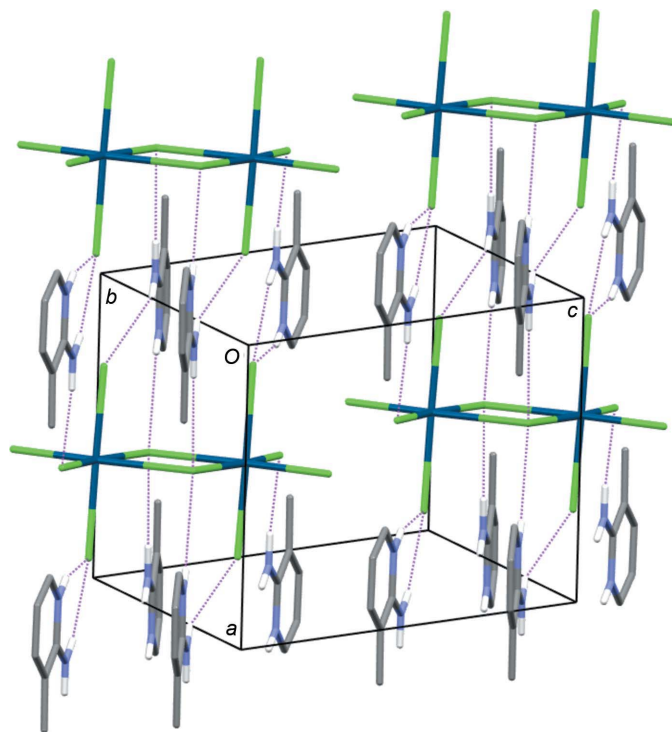


Figure 4
The hydrogen-bonded supramolecular ladders extending in the [100] direction in (2). H atoms bonded to C atoms have been omitted for clarity.

the other axial terminal Cl atom on the inversion-related side of the anion, while the other amino H atom interacts with an equatorial terminal Cl atom of the anion one step further along the ladder, as before. In this way, one cation only interacts with one axial Cl atom and two bridging Cl atoms from different anions, while the other cation interacts with one axial and one equatorial Cl atoms in different anions. The centrosymmetric nature of the $[\text{Bi}_2\text{Cl}_{10}]^{4-}$ anion means that the entire anion accepts 10 hydrogen bonds. Nonetheless, one equatorial terminal Cl atom on each side of the anion is not involved in such interactions.

3.3. Tetrakis(2-amino-3-methylpyridinium) di- μ -bromido-bis[tetrabromidobismuth(III)], (3)

Complex (3) is isostructural with (2) (Fig. 5), including the trends among the geometrical parameters (Table 4) and the supramolecular arrangement of the hydrogen bonds (Table 6). The structure of (3) is presented in a non-standard setting of the triclinic unit cell, so as to be able to overlay and compare conveniently the structure and unit-cell packing with those of (2). Unlike for (2), where the unit-cell a axis is slightly shorter than the b axis, the a axis in (3) is slightly longer than the b axis; this non-standard setting can be transformed to the proper reduced setting of the triclinic unit cell by interchanging the a and b axes with the matrix $0\bar{1}0/\bar{1}00/00\bar{1}$.

3.4. Bis(4-amino-3-ammoniopyridinium) di- μ -chlorido-bis[tetrachloridobismuth(III)] dihydrate, (4)

The asymmetric unit of (4) (Fig. 6) contains one divalent 4-amino-3-ammoniopyridinium cation, one half of a centrosymmetric double-chlorido-bridged $[\text{Bi}_2\text{Cl}_{10}]^{4-}$ anion and two

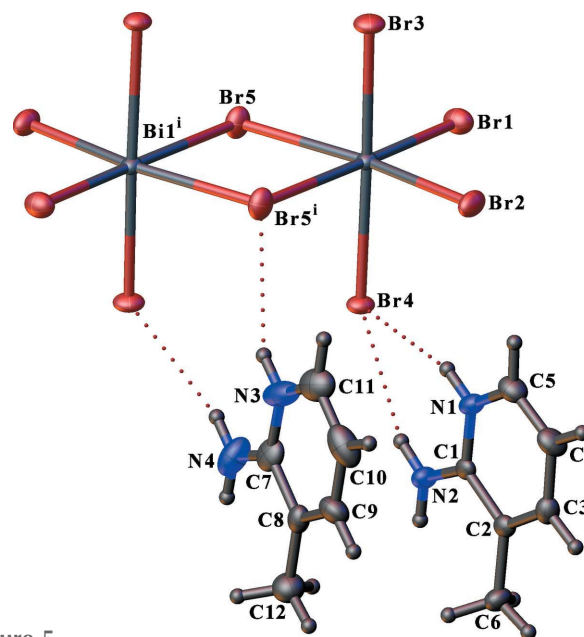


Figure 5
View of the core components of (3), showing the centrosymmetric dinuclear anion and the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

Table 7
 Hydrogen-bond geometry (Å, °) for (4).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1···Cl2 ⁱⁱ	0.88 (1)	2.56 (2)	3.300 (2)	142 (2)
N1—H1···Cl4 ⁱⁱⁱ	0.88 (1)	2.78 (2)	3.356 (2)	124 (2)
N2—H21···Cl2 ⁱⁱⁱ	0.90 (1)	2.67 (2)	3.438 (2)	144 (2)
N2—H21···Cl4	0.90 (1)	2.70 (2)	3.2570 (19)	121 (2)
N2—H22···O1	0.91 (1)	1.98 (1)	2.879 (5)	169 (3)
N2—H22···O1 ^{iv}	0.91 (1)	1.87 (1)	2.766 (5)	168 (3)
N2—H23···Cl3 ^v	0.91 (1)	2.28 (1)	3.1137 (19)	152 (2)
N3—H31···Cl5 ^{iv}	0.89 (1)	2.51 (2)	3.342 (2)	158 (3)
N3—H32···Cl3 ^{vi}	0.87 (1)	2.45 (2)	3.209 (2)	146 (3)
O1—H1A···Cl1 ^{iv}	0.84 (1)	2.66 (3)	3.418 (3)	151 (5)
O1—H1B···O2	0.84 (1)	1.94 (4)	2.661 (5)	143 (6)
O2—H2B···Cl1 ^{vi}	0.84 (1)	2.55 (4)	3.282 (7)	147 (7)

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

sites for water molecules, which are disordered about twofold axes and are therefore only half-occupied. The trends in the octahedral geometry about the unique Bi^{III} centre (Bi—Cl bond lengths: bridging > axial > equatorial, Table 4) and the asymmetry of the Bi—Cl bond lengths in the chlorido bridges through atom Cl5 [difference 0.1602 (7) Å] are akin to those observed for (2). The longest of the terminal equatorial Bi—Cl bonds is to atom Cl2, which accepts hydrogen bonds from two cations, whereas atom Cl1 participates only in a single hydrogen bond. The axial Bi—Cl bonds are similar in length in this structure, which is consistent with each of these Cl atoms, Cl3 and Cl4, accepting hydrogen bonds from two cations. As with (2), the shorter of the equatorial Bi—Cl bonds is *trans* to the longer of the bridging Bi—Cl bonds. The distortions from ideal octahedral angles in the [Bi₂Cl₁₀]⁴⁻ anion are slightly larger than in (2) and (3); the *cis* angles range from 82.042 (16) to 99.089 (18)° and the *trans* angles from 164.142 (18) to 178.756 (16)°. The C—N bond lengths for the 4-amino and 3-ammonio substituents of the cation (Table 4) are again consistent with the degree of protonation of these groups.

Hydrogen bonds between the cations, anions and water molecules of (4) link these entities into a three-dimensional

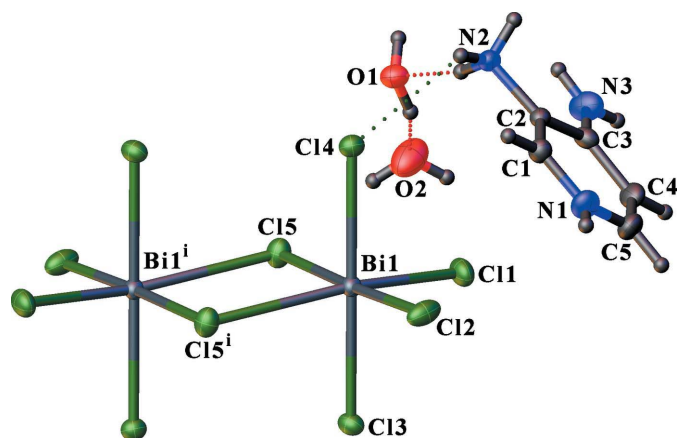


Figure 6
 View of the core components of (4), showing the centrosymmetric dinuclear anion and the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

(3D) supramolecular framework (Table 7 and Fig. 7). The pyridinium group of the cation forms bifurcated hydrogen bonds with an axial Cl atom in a neighbouring [Bi₂Cl₁₀]⁴⁻ anion and with an equatorial Cl atom in another anion. The amino group forms hydrogen bonds with a bridging Cl atom in a third anion and an axial Cl atom of a fourth anion. The ammonio substituent also has an interaction with an axial Cl atom of the third anion, plus a bifurcated interaction with an equatorial Cl atom of the first anion in this description and with an axial Cl atom of a fifth neighbouring anion. The third ammonio H atom interacts with both disordered sites of the O1 water molecule. This water molecule then donates hydrogen bonds to the O2 atom of the other water molecule, as well as to an equatorial and a bridging Cl atom of the third neighbouring [Bi₂Cl₁₀]⁴⁻ anion. One of the H atoms of the O2 water molecule is involved in a hydrogen bond to an equatorial Cl atom of a sixth anion, but the other H atom of this water molecule does not appear to be involved in any hydrogen-bonding interactions. In the [Bi₂Cl₁₀]⁴⁻ anion, the bridging Cl atoms accept two hydrogen bonds each, while all terminal Cl atoms, except for one equatorial Cl atom at each Bi^{III} centre, accept two hydrogen bonds. The latter Cl atoms accept a single hydrogen bond from a disordered water molecule.

3.5. *catena*-Poly[2,6-diaminopyridinium [[*cis*-diiodidobismuth(III)]-di-*μ*-iodido]], (5)

The chosen crystal of (5) was a pseudomerohedral twin (see §2.2). The asymmetric unit contains one monovalent 2,6-diaminopyridinium cation and a [BiI₄]⁻ unit, which is the unique

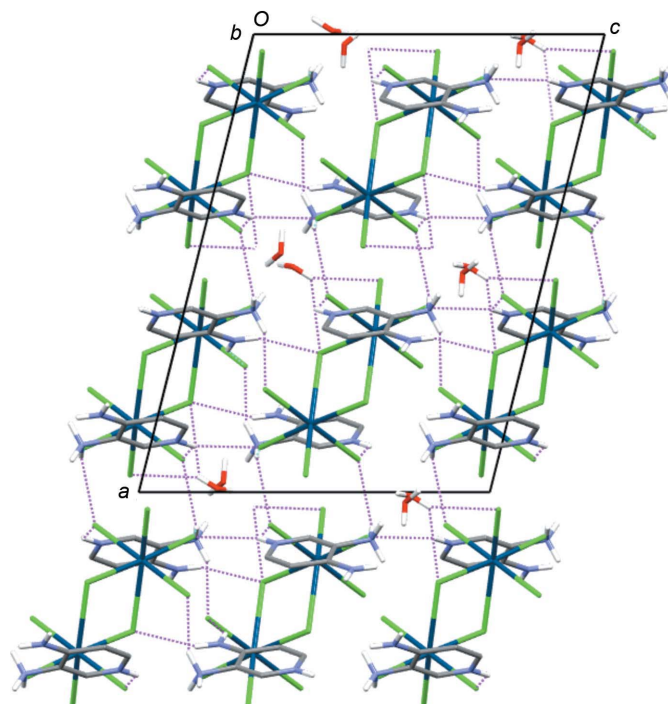


Figure 7
 The hydrogen-bonded 3D supramolecular structure of (4), viewed down the *b* axis. H atoms bonded to C atoms have been omitted for clarity.

Table 8
Selected geometric parameters (Å, °) for (5) and (6).

	(5) ($X = I$)	(6) ($X = Br$)
Bi1—X1	2.9432 (3)	2.7079 (4)
Bi1—X2	2.9187 (3)	2.6431 (4)
Bi1—X3	3.1003 (3)	2.8846 (4)
Bi1—X3 ⁱ	3.3348 (3)	3.1822 (4)
Bi1—X4	3.0660 (3)	2.8787 (4)
Bi1—X4 ⁱⁱ	3.2248 (3)	3.0620 (4)
N2—C1	1.342 (5)	—
N3—C5	1.325 (6)	—
N2—C3	—	1.326 (6)
Bi1—X3—Bi1 ⁱ	94.738 (7)	92.407 (11)
Bi1—X4—Bi1 ⁱⁱ	92.869 (8)	95.064 (11)

Symmetry codes for (5): (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; for (6): (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

segment of a polymeric *cis*-double-iodido-bridged $[Bi_nI_{4n}]^{n-}$ anionic zigzag chain (Fig. 8). The chains extend parallel to the [010] direction. Each of the double-iodido bridges links Bi^{III} centres across crystallographic centres of inversion, so the double-bridged Bi₂I₂ rings on each side of the unique Bi^{III} centre are symmetry independent and the chain is extended by sequential application of the inversion symmetry. The symmetry-unique Bi^{III} centre has a slightly distorted octahedral geometry. The terminal Bi—I bonds are the shortest (Table 8) and the bridging Bi—I bond lengths are asymmetric, differing by 0.2345 (4) and 0.1588 (4) Å for the bridges involving atoms I3 and I4, respectively. The Bi—I bonds involving atom I3 are longer than the corresponding bonds involving atom I4 and this continues to be consistent with the observation that atom I3 is an acceptor of two hydrogen bonds from a single cation, while atom I4 does not accept any hydrogen bonds. The terminal Bi—I bond involving atom I1, which accepts two

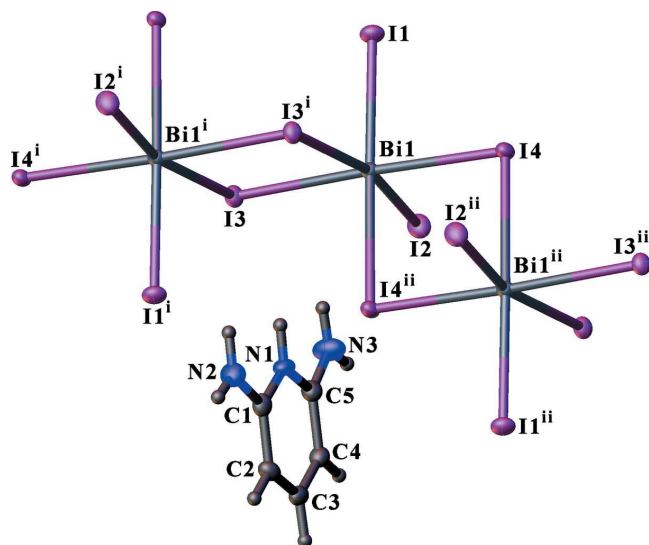


Figure 8
View of the core components of (5), showing the atom-labelling scheme and a short segment of the anionic chain. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

Table 9
Hydrogen-bond geometry (Å, °) for (5).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 ⁱ ···I3	0.88	3.12	3.941 (3)	157
N2—H2A···I3	0.88	2.92	3.773 (4)	165
N2—H2B···I1 ⁱⁱⁱ	0.88	3.16	3.811 (4)	132
N3—H3A···I2 ^{iv}	0.88	2.98	3.754 (4)	147
N3—H3B···I1 ^v	0.88	3.06	3.816 (4)	145

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

hydrogen bonds from two different cations, is marginally longer than that involving atom I2, which only accepts one hydrogen bond from a third cation. The *cis* I—Bi—I angles range from 80.483 (8) to 98.912 (9)°, with the largest angle involving the bonds to the *cis*-related terminal I atoms. The *trans* I—Bi—I angles range from 168.189 (9) to 177.843 (9)°. The angles at the bridging atoms, I3 and I4, differ by less than 2°. The short C1—N2 and C5—N3 bond lengths (Table 8) again preclude that the 2- and 6-amino groups have been protonated.

Hydrogen bonds, some quite weak, between the cations and the anionic chains of (5) link these entities into a 3D supramolecular framework (Table 9 and Fig. 9). Each anionic chain is surrounded by four columns of slant-stacked cations and *vice versa*. Each cation interacts with four different anionic chains. The pyridinium and one N2 amino H atom form hydrogen bonds with the same anionic chain, while all other

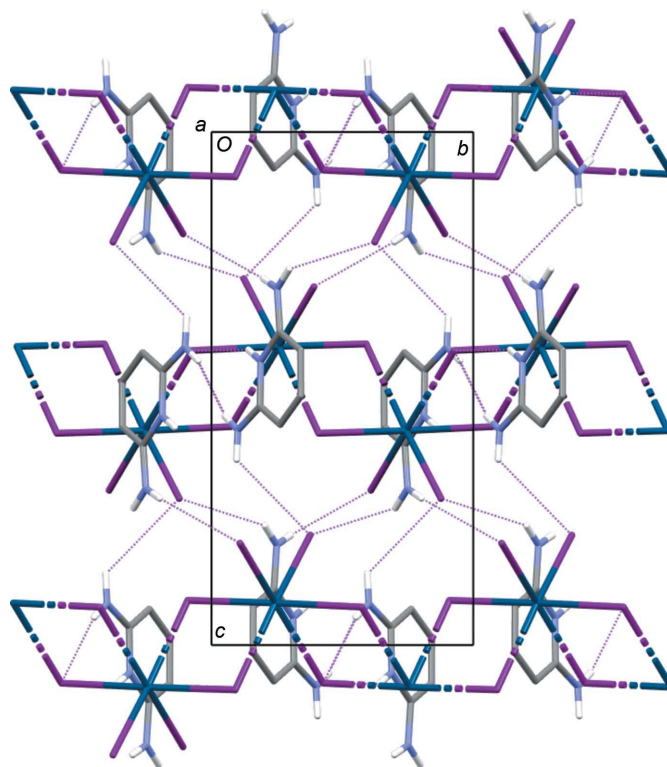


Figure 9
The hydrogen-bonded 3D supramolecular structure of (5), viewed down the *a* axis. H atoms bonded to C atoms have been omitted for clarity.

Table 10
 Hydrogen-bond geometry (Å, °) for (6).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots Br3$	0.81 (6)	2.74 (6)	3.521 (4)	163 (6)
$N2-H21\cdots Br1^{iii}$	0.85 (6)	2.76 (7)	3.605 (5)	173 (5)
$N2-H22\cdots Br4^{iv}$	0.84 (6)	2.78 (6)	3.620 (4)	179 (5)

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

amino H atoms interact with separate anionic chains. Each $[BiBr_4]^-$ unit in the anionic chains accepts five hydrogen bonds from four different cations, as already described above.

3.6. catena-Poly[4-aminopyridinium [[cis-dibromidobismuth(III)]-di- μ -bromido]], (6)

The asymmetric unit of (6) contains one monovalent 4-aminopyridinium cation and a $[BiBr_4]^-$ unit, which is the unique segment of a polymeric *cis*-double-bromido-bridged $[Bi_nBr_{4n}]^{n-}$ anionic zigzag chain (Fig. 10). The chains run parallel to the [001] direction. Unlike the centrosymmetric double-iodido bridges in (5), the double-bromido bridges in (6) have two symmetry-independent Br atoms, Br3 and Br4, and the linkages in the chain propagate through operation of the space-group *c*-glide plane, which passes through the middle of each double-bromido bridge and runs parallel to the chain direction. In (5), the propagation of the chains is *via* the centres of inversion and perpendicular to the glide plane (*n*-glide in this case). Thus, there is only one symmetry-independent Bi_2Br_2 ring in the structure, compared with the two in (5). Otherwise, the pattern of bond lengths and angles in (6) is similar to that in (5). The terminal Bi–Br bonds from the

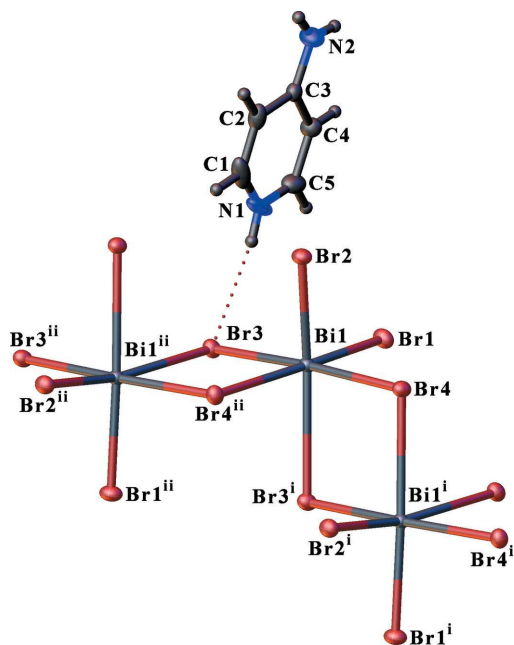


Figure 10
 View of the core components of (6), showing the atom-labelling scheme and a short segment of the anionic chain. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

slightly distorted octahedral Bi^{III} centre are the shortest (Table 8) and the bridging Bi–Br bond lengths are asymmetric, differing by 0.2976 (6) and 0.1833 (6) Å for the bridges involving atoms Br3 and Br4, respectively. The bridges involving atom Br3 are slightly longer than those involving atom Br4. Although each bridging Br atom accepts one hydrogen bond, Br3 accepts a slightly stronger hydrogen bond from a pyridinium group, while Br4 interacts with the amino group of another cation (Table 10), so the trend is consistent with that observed for the other structures. The terminal Bi–Br bond involving atom Br1, which accepts one hydrogen bond from the amino group of a different cation, is marginally longer than that involving atom Br2, which is not involved in any classic hydrogen-bonding interactions. The *cis* Br–Bi–Br angles range from 83.810 (12) to 95.756 (12)°, but only the second largest angle involves the bonds to the *cis*-related terminal Br atoms. The *trans* Br–Bi–Br angles range from 169.462 (12) to 176.605 (12)°. The angles at the bridging atoms, Br3 and Br4, differ by less than 3°. The C3–N2 bond length (Table 8) again confirms the sp^2 -hybridization character of the neutral 4-amino N atom.

The N–H \cdots Br hydrogen-bonding interactions in (6) link the cations and anionic chains into a 2D supramolecular bilayer network which lies parallel to the (100) plane (Table 10 and Fig. 11). All hydrogen-bond donors of the cation are involved and interact with three different anionic chains. The symmetry-unique $[BiBr_4]^-$ unit accepts a hydrogen bond from each of three different cations (the acceptor atoms are described above). Each layer in the bilayer is composed of anionic chains alternating with and hydrogen bonded to stacks of cations; adjacent cations in the stacks are slightly offset with respect to one another, but the planes of the cations are approximately perpendicular to the stacking direction. The second layer of the bilayer is the same as the first, except that it is slipped along so that an anionic chain is opposite to and

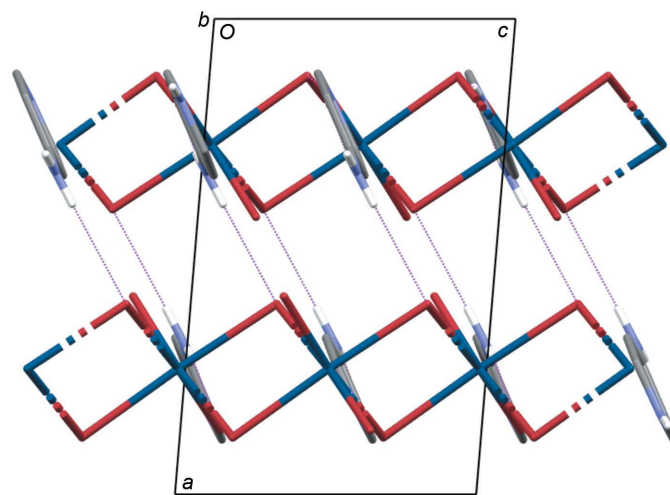


Figure 11
 The supramolecular structure of (6), viewed down the *b* axis, showing the hydrogen-bonded bilayer. H atoms bonded to C atoms have been omitted for clarity.

hydrogen bonded to a stack of cations in the first layer. There are no classic hydrogen-bonding interactions between adjacent bilayers.

3.7. Other halobismuth(III) salts with these substituted aminopyridinium cations

Structures (1) and (4) are the first reported crystal structures of pure halometallate salts involving any metal with 2-amino-3-ammoniopyridinium or 4-amino-3-ammoniopyridinium cations. The crystal structure of the salt of 2,6-diaminopyridinium with $[\text{Bi}_2\text{Cl}_{10}]^{4-}$ anions has been reported by Fredj *et al.* (2017).

As 4-aminopyridine is a popular reagent in syntheses, the 4-aminopyridinium cation appears in 259 entries in the CSD and eight of these entries involve halobismuth(III) salts. One of these involves $[\text{Bi}_n\text{I}_{4n}]^{n-}$ anionic chains, but the structure has the space group *Pbcn* and is thus not isostructural with that of (6) (Buikin *et al.*, 2018). Khelifi *et al.* (2010) reported an unusual structure involving $[\text{H}_n\text{Bi}_{2n}\text{Cl}_{11n}]^{n-}$ anionic chains with hydrido bridges between Cl atoms within the repeat unit. Kulicka *et al.* (2006) described polymorphs of salts involving 4-aminopyridinium and *cis*-double-chlorido-bridged $[\text{Bi}_n\text{Cl}_{4n}]^{n-}$ anionic zigzag chains at 100 and 250 K; the low-temperature form appears to be isostructural with that of (6). The structure of a single polymorph of the 4-aminopyridinium salt with dinuclear single-chlorido-bridged $[\text{Bi}_2\text{Cl}_{11}]^{5-}$ anions has been described at 100, 150 and 301 K by Kulicka *et al.* (2010). This structure also includes $[\text{Bi}_2\text{Cl}_9(\text{H}_2\text{O})_2]^{3-}$ anions. Finally, a structure of the 4-aminopyridinium salt with discrete $[\text{BiCl}_6]^{3-}$ anions and chloride ions has been reported by Mencil *et al.* (2019).

4. Conclusion

The crystal structures of six halobismuth(III) salts involving five different substituted aminopyridinium cations have been determined and described here. Three anionic Bi-containing species have been observed, namely, discrete mononuclear $[\text{BiCl}_6]^{3-}$ and dinuclear $[\text{Bi}_2\text{X}_{10}]^{4-}$ anions ($X = \text{Cl}$ or Br), and polymeric *cis*-double-halo-bridged $[\text{Bi}_n\text{X}_{4n}]^{n-}$ anionic chains ($X = \text{Br}$ or I). Although there are 94 entries in the CSD concerning $[\text{Bi}_2\text{X}_9]^{3-}$ anions, this frequently-occurring species was not observed in this work. There is no discernible correlation between the type of anionic species obtained and the cation or halide ligand used. There is a correlation, at least within the structures examined here, between the $\text{Bi}-X$ bond lengths and the number of classic $\text{N}-\text{H}\cdots X$ hydrogen bonds that the X ligand accepts, with a greater number of interactions corresponding with slightly longer $\text{Bi}-X$ distances.

The supramolecular networks formed by classic $\text{N}-\text{H}\cdots X$ hydrogen bonds include ladders, bilayers and 3D frameworks.

Acknowledgements

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supporting information

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Halobismuth(III) salts with substituted aminopyridinium cations

Levi Senior and Anthony Linden

Computing details

For all structures, data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: SHELXT2018 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *SHELXL2018* (Sheldrick, 2015b) and *PLATON* (Spek, 2015, 2020).

Bis(2-amino-3-ammoniopyridinium) hexachloridobismuth(III) chloride monohydrate (1)

Crystal data

(C₅H₉N₃)₂[BiCl₆]Cl·H₂O

M_r = 697.45

Triclinic, *P*1̄

a = 9.1612 (4) Å

b = 10.8591 (6) Å

c = 11.7273 (7) Å

α = 94.303 (4)°

β = 101.914 (4)°

γ = 106.254 (4)°

V = 1084.89 (10) Å³

Z = 2

F(000) = 664

D_x = 2.135 Mg m⁻³

Mo *Kα* radiation, *λ* = 0.71073 Å

Cell parameters from 5333 reflections

θ = 3.5–29.2°

μ = 9.00 mm⁻¹

T = 160 K

Prism, red

0.25 × 0.20 × 0.10 mm

Data collection

Oxford Diffraction SuperNova dual radiation diffractometer

Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray source

Mirror monochromator

Detector resolution: 10.3801 pixels mm⁻¹

ω scans

Absorption correction: gaussian (CrysAlis PRO; Rigaku OD, 2018)

T_{min} = 0.551, *T_{max}* = 1.000

8459 measured reflections

5056 independent reflections

4589 reflections with *I* > 2σ(*I*)

R_{int} = 0.040

θ_{max} = 29.4°, *θ_{min}* = 2.9°

h = -11→9

k = -14→14

l = -16→13

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.036

wR(*F*²) = 0.075

S = 1.03

5054 reflections

237 parameters

2 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: geom & difmap

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0172*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.002

Δρ_{max} = 3.53 e Å⁻³

$$\Delta\rho_{\min} = -1.74 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL2018
(Sheldrick, 2015b),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00175 (19)

Special details

Experimental. Data collection and full structure determination done by Prof. Anthony Linden:
anthony.linden@chem.uzh.ch

Solvent used: 2M HCl Cooling Device: Oxford Instruments Cryojet XL Crystal mount: on a glass fibre Frames collected: 272 Seconds exposure per frame: 1.5 Degrees rotation per frame: 1.0 Crystal-detector distance (mm): 55.0 Client: Levi Senior Sample code: LS009

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The water H-atoms were refined isotropically with O-H distance restraints of 0.84 (1) Å. All other H atoms were placed in calculated positions and allowed to ride on their parent atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Bi1	0.33379 (2)	0.65001 (2)	0.77021 (2)	0.01333 (8)
Cl1	0.30114 (15)	0.87093 (12)	0.86367 (13)	0.0217 (3)
Cl2	0.62022 (15)	0.67918 (13)	0.92734 (13)	0.0205 (3)
Cl3	0.13301 (14)	0.50002 (12)	0.90309 (12)	0.0197 (3)
Cl4	0.35744 (16)	0.43435 (12)	0.65545 (13)	0.0234 (3)
Cl5	0.06380 (14)	0.62274 (12)	0.62347 (12)	0.0165 (3)
Cl6	0.47286 (14)	0.77900 (12)	0.62570 (13)	0.0190 (3)
Cl7	1.20723 (15)	0.98098 (13)	0.50220 (13)	0.0216 (3)
O1	0.7385 (4)	0.6577 (4)	0.6206 (4)	0.0200 (8)
H11	0.714 (7)	0.619 (5)	0.552 (2)	0.033 (19)*
H12	0.666 (5)	0.687 (6)	0.630 (6)	0.039 (19)*
N1	1.0249 (5)	1.1946 (4)	0.8540 (4)	0.0219 (11)
H1	1.077768	1.277490	0.863992	0.026*
N2	1.1604 (5)	1.1615 (4)	0.7142 (4)	0.0239 (11)
H21	1.210656	1.245035	0.725912	0.029*
H22	1.180074	1.109362	0.662307	0.029*
N3	0.9957 (5)	0.8895 (4)	0.6795 (4)	0.0207 (11)
H31	1.013412	0.926401	0.614533	0.031*
H32	0.910623	0.817732	0.658148	0.031*
H33	1.080894	0.866756	0.714239	0.031*
C1	1.0544 (6)	1.1142 (5)	0.7748 (5)	0.0163 (11)
C2	0.9672 (6)	0.9818 (5)	0.7621 (5)	0.0138 (10)
C3	0.8594 (6)	0.9399 (5)	0.8260 (5)	0.0166 (11)
H3	0.801713	0.850647	0.816354	0.020*
C4	0.8338 (7)	1.0302 (5)	0.9070 (5)	0.0237 (13)
H41	0.758216	1.002400	0.951731	0.028*
C5	0.9173 (6)	1.1551 (5)	0.9200 (5)	0.0227 (13)
H5	0.902074	1.216442	0.974894	0.027*

N4	0.6479 (5)	0.1627 (4)	0.6711 (4)	0.0182 (10)
H4	0.660330	0.111762	0.614219	0.022*
N5	0.8359 (5)	0.3288 (4)	0.6238 (4)	0.0236 (11)
H51	0.847672	0.273505	0.570243	0.028*
H52	0.892155	0.410810	0.634629	0.028*
N6	0.7879 (5)	0.5058 (4)	0.7981 (4)	0.0163 (10)
H61	0.764422	0.540181	0.730778	0.024*
H62	0.892872	0.518114	0.819174	0.024*
H63	0.758381	0.545460	0.856654	0.024*
C6	0.7327 (6)	0.2881 (5)	0.6888 (5)	0.0147 (11)
C7	0.7050 (6)	0.3677 (5)	0.7784 (5)	0.0139 (10)
C8	0.6028 (5)	0.3158 (5)	0.8446 (5)	0.0163 (11)
H8	0.585925	0.369955	0.904868	0.020*
C9	0.5238 (6)	0.1843 (5)	0.8239 (5)	0.0205 (12)
H9	0.455741	0.147067	0.871621	0.025*
C10	0.5452 (6)	0.1091 (5)	0.7341 (5)	0.0191 (12)
H10	0.488022	0.019523	0.716078	0.023*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Bi1	0.01174 (11)	0.01138 (11)	0.01661 (13)	0.00237 (7)	0.00483 (8)	0.00072 (8)
Cl1	0.0263 (7)	0.0161 (7)	0.0216 (8)	0.0048 (5)	0.0082 (6)	-0.0046 (6)
Cl2	0.0183 (6)	0.0211 (7)	0.0211 (8)	0.0060 (5)	0.0035 (6)	0.0002 (6)
Cl3	0.0194 (6)	0.0190 (7)	0.0191 (8)	0.0026 (5)	0.0055 (6)	0.0032 (6)
Cl4	0.0300 (7)	0.0165 (7)	0.0251 (8)	0.0083 (5)	0.0090 (6)	-0.0004 (6)
Cl5	0.0154 (6)	0.0157 (6)	0.0166 (7)	0.0032 (5)	0.0028 (5)	-0.0004 (5)
Cl6	0.0194 (6)	0.0180 (7)	0.0231 (8)	0.0070 (5)	0.0096 (6)	0.0057 (6)
Cl7	0.0239 (7)	0.0247 (7)	0.0199 (8)	0.0109 (5)	0.0088 (6)	0.0025 (6)
O1	0.0153 (19)	0.024 (2)	0.022 (3)	0.0085 (16)	0.0050 (18)	-0.0008 (19)
N1	0.023 (2)	0.012 (2)	0.030 (3)	0.0060 (18)	0.004 (2)	0.002 (2)
N2	0.028 (3)	0.011 (2)	0.030 (3)	-0.0012 (19)	0.014 (2)	-0.004 (2)
N3	0.027 (3)	0.010 (2)	0.026 (3)	0.0038 (18)	0.013 (2)	0.002 (2)
C1	0.014 (2)	0.016 (3)	0.021 (3)	0.006 (2)	0.004 (2)	0.004 (2)
C2	0.016 (2)	0.015 (3)	0.011 (3)	0.007 (2)	0.001 (2)	0.001 (2)
C3	0.015 (2)	0.019 (3)	0.013 (3)	0.002 (2)	0.002 (2)	0.000 (2)
C4	0.022 (3)	0.030 (3)	0.023 (4)	0.011 (2)	0.012 (3)	0.005 (3)
C5	0.023 (3)	0.031 (3)	0.017 (3)	0.013 (2)	0.006 (3)	-0.001 (3)
N4	0.019 (2)	0.015 (2)	0.017 (3)	0.0016 (18)	0.004 (2)	-0.003 (2)
N5	0.030 (3)	0.018 (2)	0.025 (3)	0.0024 (19)	0.016 (2)	0.001 (2)
N6	0.016 (2)	0.013 (2)	0.019 (3)	0.0041 (17)	0.005 (2)	-0.0023 (19)
C6	0.013 (2)	0.016 (3)	0.012 (3)	0.004 (2)	-0.001 (2)	-0.003 (2)
C7	0.013 (2)	0.013 (3)	0.014 (3)	0.0051 (19)	0.000 (2)	0.002 (2)
C8	0.013 (2)	0.019 (3)	0.016 (3)	0.004 (2)	0.002 (2)	0.000 (2)
C9	0.016 (3)	0.017 (3)	0.029 (4)	0.002 (2)	0.011 (3)	0.002 (3)
C10	0.016 (3)	0.016 (3)	0.023 (3)	0.000 (2)	0.005 (2)	0.005 (2)

Geometric parameters (Å, °)

Bi1—C11	2.6812 (12)	C3—H3	0.9500
Bi1—C12	2.7986 (14)	C4—C5	1.337 (8)
Bi1—C13	2.8899 (12)	C4—H41	0.9500
Bi1—C14	2.6970 (13)	C5—H5	0.9500
Bi1—C15	2.6312 (13)	N4—C6	1.342 (6)
Bi1—C16	2.5896 (12)	N4—C10	1.348 (6)
O1—H11	0.837 (10)	N4—H4	0.8800
O1—H12	0.836 (10)	N5—C6	1.335 (6)
N1—C1	1.346 (7)	N5—H51	0.8800
N1—C5	1.373 (7)	N5—H52	0.8800
N1—H1	0.8800	N6—C7	1.455 (6)
N2—C1	1.331 (6)	N6—H61	0.9100
N2—H21	0.8800	N6—H62	0.9100
N2—H22	0.8800	N6—H63	0.9100
N3—C2	1.454 (6)	C6—C7	1.418 (7)
N3—H31	0.9100	C7—C8	1.367 (6)
N3—H32	0.9100	C8—C9	1.385 (7)
N3—H33	0.9100	C8—H8	0.9500
C1—C2	1.415 (7)	C9—C10	1.364 (7)
C2—C3	1.360 (7)	C9—H9	0.9500
C3—C4	1.414 (7)	C10—H10	0.9500
C16—Bi1—C15	88.69 (4)	C2—C3—H3	120.3
C16—Bi1—C11	88.51 (4)	C4—C3—H3	120.3
C15—Bi1—C11	85.39 (4)	C5—C4—C3	119.3 (5)
C16—Bi1—C14	87.53 (4)	C5—C4—H41	120.4
C15—Bi1—C14	90.58 (4)	C3—C4—H41	120.4
C11—Bi1—C14	174.42 (4)	C4—C5—N1	120.0 (5)
C16—Bi1—C12	91.56 (4)	C4—C5—H5	120.0
C15—Bi1—C12	179.68 (4)	N1—C5—H5	120.0
C11—Bi1—C12	94.42 (4)	C6—N4—C10	124.7 (5)
C14—Bi1—C12	89.62 (4)	C6—N4—H4	117.6
C16—Bi1—C13	170.83 (4)	C10—N4—H4	117.6
C15—Bi1—C13	82.16 (4)	C6—N5—H51	120.0
C11—Bi1—C13	91.37 (4)	C6—N5—H52	120.0
C14—Bi1—C13	91.91 (4)	H51—N5—H52	120.0
C12—Bi1—C13	97.59 (4)	C7—N6—H61	109.5
H11—O1—H12	108 (6)	C7—N6—H62	109.5
C1—N1—C5	123.9 (5)	H61—N6—H62	109.5
C1—N1—H1	118.1	C7—N6—H63	109.5
C5—N1—H1	118.1	H61—N6—H63	109.5
C1—N2—H21	120.0	H62—N6—H63	109.5
C1—N2—H22	120.0	N5—C6—N4	119.2 (5)
H21—N2—H22	120.0	N5—C6—C7	125.0 (5)
C2—N3—H31	109.5	N4—C6—C7	115.8 (4)
C2—N3—H32	109.5	C8—C7—C6	120.7 (5)

H31—N3—H32	109.5	C8—C7—N6	120.8 (4)
C2—N3—H33	109.5	C6—C7—N6	118.4 (4)
H31—N3—H33	109.5	C7—C8—C9	120.0 (5)
H32—N3—H33	109.5	C7—C8—H8	120.0
N2—C1—N1	119.7 (5)	C9—C8—H8	120.0
N2—C1—C2	124.3 (5)	C10—C9—C8	119.1 (5)
N1—C1—C2	116.0 (4)	C10—C9—H9	120.5
C3—C2—C1	121.4 (5)	C8—C9—H9	120.5
C3—C2—N3	119.9 (5)	N4—C10—C9	119.5 (5)
C1—C2—N3	118.7 (4)	N4—C10—H10	120.3
C2—C3—C4	119.4 (5)	C9—C10—H10	120.3
C5—N1—C1—N2	179.5 (5)	C10—N4—C6—N5	177.1 (5)
C5—N1—C1—C2	-0.3 (8)	C10—N4—C6—C7	-2.2 (8)
N2—C1—C2—C3	-179.3 (5)	N5—C6—C7—C8	-176.4 (5)
N1—C1—C2—C3	0.5 (8)	N4—C6—C7—C8	2.8 (7)
N2—C1—C2—N3	1.3 (8)	N5—C6—C7—N6	3.6 (8)
N1—C1—C2—N3	-178.9 (5)	N4—C6—C7—N6	-177.2 (5)
C1—C2—C3—C4	-0.1 (8)	C6—C7—C8—C9	-0.6 (8)
N3—C2—C3—C4	179.3 (5)	N6—C7—C8—C9	179.4 (5)
C2—C3—C4—C5	-0.6 (8)	C7—C8—C9—C10	-2.5 (8)
C3—C4—C5—N1	0.8 (9)	C6—N4—C10—C9	-0.8 (8)
C1—N1—C5—C4	-0.4 (9)	C8—C9—C10—N4	3.2 (8)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...Cl3 ⁱ	0.88	2.31	3.154 (5)	160
N2—H21...Cl4 ⁱ	0.88	2.43	3.215 (4)	150
N2—H22...Cl7	0.88	2.35	3.223 (5)	171
N3—H31...Cl7 ⁱⁱ	0.91	2.68	3.202 (5)	118
N3—H32...O1	0.91	1.94	2.848 (6)	176
N3—H33...Cl1 ⁱⁱⁱ	0.91	2.37	3.228 (5)	157
N4—H4...Cl7 ^{iv}	0.88	2.35	3.181 (4)	158
N5—H51...Cl7 ^{iv}	0.88	2.70	3.453 (5)	144
N5—H52...Cl5 ⁱⁱⁱ	0.88	2.43	3.290 (5)	167
N6—H61...O1	0.91	1.91	2.794 (6)	163
N6—H62...Cl3 ⁱⁱⁱ	0.91	2.29	3.167 (4)	163
N6—H63...Cl2	0.91	2.38	3.218 (4)	153
O1—H11...Cl4 ^v	0.84 (1)	2.36 (2)	3.177 (5)	165 (6)
O1—H12...Cl6	0.84 (1)	2.26 (2)	3.083 (4)	170 (6)

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

Tetrakis(2-amino-3-methylpyridinium) di- μ -chlorido-bis[tetrachloridobismuth(III)] (2)

Crystal data

(C₆H₉N₂)₄[Bi₂Cl₁₀]
 $M_r = 1209.07$
 Triclinic, $P\bar{1}$
 $a = 8.8144$ (3) Å
 $b = 8.9982$ (3) Å
 $c = 12.3440$ (4) Å
 $\alpha = 76.784$ (3)°
 $\beta = 87.111$ (3)°
 $\gamma = 88.514$ (3)°
 $V = 951.80$ (6) Å³

$Z = 1$
 $F(000) = 572$
 $D_x = 2.109$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 6026 reflections
 $\theta = 3.2$ – 29.2 °
 $\mu = 9.96$ mm⁻¹
 $T = 160$ K
 Block, colourless
 0.25 × 0.15 × 0.07 mm

Data collection

Oxford Diffraction SuperNova dual radiation diffractometer
 Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray source
 Mirror monochromator
 Detector resolution: 10.3801 pixels mm⁻¹
 ω scans
 Absorption correction: gaussian (CrysAlis PRO; Rigaku OD, 2018)

$T_{\min} = 0.660$, $T_{\max} = 1.000$
 8469 measured reflections
 4463 independent reflections
 4137 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\max} = 29.5$ °, $\theta_{\min} = 2.8$ °
 $h = -11 \rightarrow 11$
 $k = -10 \rightarrow 11$
 $l = -11 \rightarrow 16$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.049$
 $S = 1.02$
 4463 reflections
 201 parameters
 54 restraints
 Primary atom site location: dual

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.015P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.89$ e Å⁻³
 $\Delta\rho_{\min} = -1.03$ e Å⁻³

Special details

Experimental. Data collection and full structure determination done by Prof. Anthony Linden: anthony.linden@chem.uzh.ch

Solvent used: 2M HCl Cooling Device: Oxford Instruments Cryojet XL Crystal mount: on a glass fibre Frames collected: 312 Seconds exposure per frame: 3.0 Degrees rotation per frame: 1.0 Crystal-detector distance (mm): 55.0 Client: Levi Senior Sample code: LS010

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Rigid body restraints were applied to the atoms of the cation containing atom N3.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Bi1	0.50769 (2)	0.39447 (2)	0.17732 (2)	0.01904 (5)
Cl1	0.50021 (11)	0.12800 (10)	0.30547 (8)	0.0342 (2)

Cl2	0.53940 (10)	0.53069 (11)	0.33900 (8)	0.0316 (2)
Cl3	0.80433 (10)	0.36762 (11)	0.14781 (9)	0.0311 (2)
Cl4	0.19902 (10)	0.42985 (10)	0.20710 (8)	0.0275 (2)
Cl5	0.47878 (12)	0.29835 (11)	-0.02343 (8)	0.0339 (2)
N1	0.1469 (3)	0.6424 (3)	0.3902 (2)	0.0236 (7)
H1	0.190004	0.588325	0.345739	0.028*
N2	-0.0854 (3)	0.5797 (3)	0.3363 (2)	0.0241 (7)
H21	-0.037783	0.526435	0.293025	0.029*
H22	-0.185334	0.584809	0.339472	0.029*
C1	-0.0069 (4)	0.6519 (4)	0.3964 (3)	0.0201 (7)
C2	-0.0762 (4)	0.7402 (4)	0.4683 (3)	0.0220 (8)
C3	0.0177 (4)	0.8060 (4)	0.5287 (3)	0.0270 (8)
H31	-0.026500	0.862991	0.578447	0.032*
C4	0.1757 (4)	0.7925 (4)	0.5199 (3)	0.0314 (9)
H4	0.238106	0.839019	0.562910	0.038*
C5	0.2381 (4)	0.7110 (4)	0.4482 (3)	0.0296 (9)
H5	0.345384	0.702426	0.438924	0.036*
C6	-0.2452 (4)	0.7578 (4)	0.4745 (3)	0.0290 (9)
H61	-0.280318	0.809261	0.401056	0.044*
H62	-0.274901	0.818780	0.528682	0.044*
H63	-0.291321	0.656853	0.497726	0.044*
N3	0.1583 (4)	0.8106 (4)	0.0943 (3)	0.0449 (10)
H3	0.207612	0.748010	0.059175	0.054*
N4	-0.0581 (4)	0.7233 (4)	0.0399 (3)	0.0435 (9)
H41	-0.002586	0.663843	0.005540	0.052*
H42	-0.157750	0.722971	0.038404	0.052*
C7	0.0078 (5)	0.8122 (4)	0.0933 (3)	0.0361 (9)
C8	-0.0776 (5)	0.9127 (4)	0.1492 (3)	0.0274 (8)
C9	0.0085 (5)	1.0004 (5)	0.1983 (4)	0.0380 (10)
H9	-0.043656	1.069626	0.235317	0.046*
C10	0.1659 (6)	0.9968 (5)	0.1985 (4)	0.0499 (12)
H10	0.218704	1.061239	0.234552	0.060*
C11	0.2436 (6)	0.8974 (5)	0.1452 (4)	0.0447 (11)
H11	0.351336	0.889422	0.143717	0.054*
C12	-0.2428 (5)	0.9150 (5)	0.1498 (4)	0.0398 (10)
H121	-0.275546	0.939059	0.072959	0.060*
H122	-0.282958	0.992859	0.188067	0.060*
H123	-0.281062	0.814759	0.188748	0.060*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Bi1	0.01407 (8)	0.02466 (8)	0.01962 (8)	-0.00037 (5)	-0.00009 (5)	-0.00777 (5)
Cl1	0.0329 (6)	0.0299 (5)	0.0370 (6)	0.0011 (4)	0.0011 (4)	-0.0027 (4)
Cl2	0.0246 (5)	0.0464 (6)	0.0298 (5)	-0.0023 (4)	-0.0013 (4)	-0.0209 (4)
Cl3	0.0145 (4)	0.0381 (5)	0.0427 (6)	0.0007 (4)	0.0013 (4)	-0.0142 (4)
Cl4	0.0141 (4)	0.0353 (5)	0.0360 (6)	0.0007 (4)	-0.0006 (4)	-0.0143 (4)
Cl5	0.0458 (6)	0.0310 (5)	0.0280 (5)	-0.0058 (4)	-0.0029 (4)	-0.0126 (4)

N1	0.0229 (17)	0.0233 (15)	0.0240 (17)	0.0039 (13)	0.0030 (13)	-0.0054 (12)
N2	0.0221 (16)	0.0282 (16)	0.0238 (17)	0.0011 (13)	0.0025 (13)	-0.0101 (13)
C1	0.0217 (19)	0.0178 (17)	0.0170 (18)	0.0010 (14)	0.0022 (14)	0.0032 (13)
C2	0.026 (2)	0.0184 (17)	0.0192 (19)	0.0037 (15)	0.0026 (15)	-0.0012 (13)
C3	0.034 (2)	0.0233 (19)	0.025 (2)	0.0027 (16)	-0.0008 (17)	-0.0080 (15)
C4	0.028 (2)	0.029 (2)	0.040 (3)	0.0005 (17)	-0.0092 (18)	-0.0118 (17)
C5	0.021 (2)	0.027 (2)	0.038 (2)	-0.0004 (16)	-0.0019 (17)	-0.0014 (17)
C6	0.025 (2)	0.031 (2)	0.032 (2)	0.0051 (16)	0.0019 (17)	-0.0095 (16)
N3	0.033 (2)	0.035 (2)	0.054 (3)	0.0113 (15)	0.0176 (18)	0.0107 (16)
N4	0.061 (3)	0.0355 (19)	0.036 (2)	-0.0048 (18)	0.0116 (18)	-0.0150 (16)
C7	0.047 (2)	0.024 (2)	0.032 (2)	-0.0013 (17)	0.0063 (19)	0.0032 (16)
C8	0.034 (2)	0.0230 (18)	0.023 (2)	0.0018 (16)	0.0053 (16)	-0.0009 (14)
C9	0.039 (2)	0.033 (2)	0.038 (3)	-0.0009 (18)	-0.003 (2)	0.0019 (18)
C10	0.052 (3)	0.049 (3)	0.045 (3)	-0.016 (2)	-0.015 (2)	0.002 (2)
C11	0.046 (3)	0.036 (2)	0.043 (3)	-0.002 (2)	0.004 (2)	0.0077 (19)
C12	0.037 (2)	0.043 (3)	0.039 (3)	-0.001 (2)	0.001 (2)	-0.010 (2)

Geometric parameters (Å, °)

Bi1—C11	2.5533 (10)	C6—H61	0.9800
Bi1—C12	2.5992 (9)	C6—H62	0.9800
Bi1—C13	2.6342 (9)	C6—H63	0.9800
Bi1—C14	2.7471 (8)	N3—C7	1.327 (5)
Bi1—C15	2.8300 (9)	N3—C11	1.368 (6)
Bi1—C15 ⁱ	2.9760 (10)	N3—H3	0.8800
N1—C5	1.351 (5)	N4—C7	1.310 (5)
N1—C1	1.356 (4)	N4—H41	0.8800
N1—H1	0.8800	N4—H42	0.8800
N2—C1	1.323 (4)	C7—C8	1.435 (5)
N2—H21	0.8800	C8—C9	1.364 (6)
N2—H22	0.8800	C8—C12	1.455 (6)
C1—C2	1.426 (5)	C9—C10	1.387 (6)
C2—C3	1.372 (5)	C9—H9	0.9500
C2—C6	1.494 (5)	C10—C11	1.377 (6)
C3—C4	1.396 (5)	C10—H10	0.9500
C3—H31	0.9500	C11—H11	0.9500
C4—C5	1.360 (5)	C12—H121	0.9800
C4—H4	0.9500	C12—H122	0.9800
C5—H5	0.9500	C12—H123	0.9800
C11—Bi1—C12	93.93 (3)	N1—C5—H5	120.1
C11—Bi1—C13	90.08 (3)	C4—C5—H5	120.1
C12—Bi1—C13	91.38 (3)	C2—C6—H61	109.5
C11—Bi1—C14	91.13 (3)	C2—C6—H62	109.5
C12—Bi1—C14	87.92 (3)	H61—C6—H62	109.5
C13—Bi1—C14	178.64 (3)	C2—C6—H63	109.5
C11—Bi1—C15	96.18 (3)	H61—C6—H63	109.5
C12—Bi1—C15	169.86 (3)	H62—C6—H63	109.5

C13—Bi1—C15	87.88 (3)	C7—N3—C11	125.8 (4)
C14—Bi1—C15	92.59 (3)	C7—N3—H3	117.1
C11—Bi1—C15 ⁱ	178.47 (3)	C11—N3—H3	117.1
C12—Bi1—C15 ⁱ	87.27 (3)	C7—N4—H41	120.0
C13—Bi1—C15 ⁱ	88.94 (3)	C7—N4—H42	120.0
C14—Bi1—C15 ⁱ	89.86 (3)	H41—N4—H42	120.0
C15—Bi1—C15 ⁱ	82.60 (3)	N4—C7—N3	118.8 (4)
Bi1—C15—Bi1 ⁱ	97.40 (3)	N4—C7—C8	122.1 (4)
C5—N1—C1	124.0 (3)	N3—C7—C8	119.1 (4)
C5—N1—H1	118.0	C9—C8—C7	114.6 (4)
C1—N1—H1	118.0	C9—C8—C12	125.5 (4)
C1—N2—H21	120.0	C7—C8—C12	119.8 (4)
C1—N2—H22	120.0	C8—C9—C10	125.4 (4)
H21—N2—H22	120.0	C8—C9—H9	117.3
N2—C1—N1	119.0 (3)	C10—C9—H9	117.3
N2—C1—C2	123.1 (3)	C11—C10—C9	118.2 (5)
N1—C1—C2	117.9 (3)	C11—C10—H10	120.9
C3—C2—C1	117.5 (3)	C9—C10—H10	120.9
C3—C2—C6	123.1 (3)	N3—C11—C10	116.8 (4)
C1—C2—C6	119.5 (3)	N3—C11—H11	121.6
C2—C3—C4	122.6 (3)	C10—C11—H11	121.6
C2—C3—H31	118.7	C8—C12—H121	109.5
C4—C3—H31	118.7	C8—C12—H122	109.5
C5—C4—C3	118.3 (4)	H121—C12—H122	109.5
C5—C4—H4	120.8	C8—C12—H123	109.5
C3—C4—H4	120.8	H121—C12—H123	109.5
N1—C5—C4	119.7 (3)	H122—C12—H123	109.5
C5—N1—C1—N2	-179.8 (3)	C11—N3—C7—N4	179.3 (4)
C5—N1—C1—C2	0.2 (5)	C11—N3—C7—C8	0.2 (6)
N2—C1—C2—C3	178.2 (3)	N4—C7—C8—C9	-178.4 (4)
N1—C1—C2—C3	-1.8 (5)	N3—C7—C8—C9	0.7 (6)
N2—C1—C2—C6	-2.1 (5)	N4—C7—C8—C12	1.5 (6)
N1—C1—C2—C6	177.9 (3)	N3—C7—C8—C12	-179.4 (4)
C1—C2—C3—C4	1.6 (5)	C7—C8—C9—C10	-0.9 (6)
C6—C2—C3—C4	-178.1 (3)	C12—C8—C9—C10	179.3 (4)
C2—C3—C4—C5	0.2 (6)	C8—C9—C10—C11	0.1 (7)
C1—N1—C5—C4	1.6 (6)	C7—N3—C11—C10	-1.0 (7)
C3—C4—C5—N1	-1.8 (6)	C9—C10—C11—N3	0.9 (6)

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

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots C14	0.88	2.46	3.287 (3)	156
N2—H21 \cdots C14	0.88	2.52	3.324 (3)	153
N2—H22 \cdots C12 ⁱⁱ	0.88	2.49	3.345 (3)	165

N3—H3...Cl5 ⁱ	0.88	2.81	3.451 (4)	131
N4—H41...Cl3 ⁱ	0.88	2.57	3.360 (3)	150
N4—H42...Cl5 ⁱⁱⁱ	0.88	2.86	3.737 (4)	175

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x-1, y, z$; (iii) $-x, -y+1, -z$.

Tetrakis(2-amino-3-methylpyridinium) di- μ -bromido-bis[tetrabromidobismuth(III)] (3)

Crystal data

(C₆H₉N₂)₄[Bi₂Br₁₀]

$M_r = 1653.67$

Triclinic, $P\bar{1}$

$a = 9.2145$ (3) Å

$b = 9.0678$ (2) Å

$c = 12.6314$ (4) Å

$\alpha = 75.476$ (3)°

$\beta = 86.926$ (3)°

$\gamma = 89.221$ (2)°

$V = 1020.22$ (5) Å³

$Z = 1$

$F(000) = 752$

$D_x = 2.692$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 11813 reflections

$\theta = 3.2$ – 29.1 °

$\mu = 18.43$ mm⁻¹

$T = 160$ K

Needle, yellow

$0.15 \times 0.14 \times 0.07$ mm

Data collection

Oxford Diffraction SuperNova dual radiation diffractometer

Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray source

Mirror monochromator

Detector resolution: 10.3801 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku OD, 2018)

$T_{\min} = 0.274$, $T_{\max} = 1.000$

22534 measured reflections

5122 independent reflections

4575 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$

$\theta_{\max} = 29.6$ °, $\theta_{\min} = 2.8$ °

$h = -12 \rightarrow 12$

$k = -12 \rightarrow 11$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.059$

$S = 1.06$

5122 reflections

202 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0239P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.52$ e Å⁻³

$\Delta\rho_{\min} = -1.77$ e Å⁻³

Extinction correction: SHELXL2018

(Sheldrick, 2015b),

$F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00191 (12)

Special details

Experimental. Data collection and full structure determination done by Prof. Anthony Linden:

anthony.linden@chem.uzh.ch

Solvent used: 2M HBr Cooling Device: Oxford Instruments Cryojet XL Crystal mount: on a glass fibre Frames collected:

779 Seconds exposure per frame: 4.0 Degrees rotation per frame: 1.0 Crystal-detector distance (mm): 55.0 Client: Levi

Senior Sample code: LS015

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Bi1	0.50924 (2)	0.39135 (2)	0.18009 (2)	0.01729 (6)
Br1	0.49907 (5)	0.10892 (4)	0.31794 (3)	0.03099 (11)
Br2	0.54101 (5)	0.53721 (5)	0.34378 (3)	0.03024 (11)
Br3	0.80913 (4)	0.36706 (5)	0.14958 (4)	0.02761 (10)
Br4	0.19658 (4)	0.42565 (5)	0.20682 (3)	0.02398 (10)
Br5	0.47475 (5)	0.28502 (5)	-0.02029 (3)	0.02953 (11)
N1	0.1423 (4)	0.6474 (4)	0.3917 (3)	0.0233 (7)
H1	0.182106	0.594938	0.347717	0.028*
N2	-0.0819 (4)	0.5842 (4)	0.3417 (3)	0.0236 (7)
H21	-0.038140	0.531909	0.299312	0.028*
H22	-0.177440	0.589217	0.346206	0.028*
C1	-0.0037 (4)	0.6559 (4)	0.3992 (3)	0.0186 (8)
C2	-0.0686 (4)	0.7419 (4)	0.4696 (3)	0.0203 (8)
C3	0.0223 (5)	0.8057 (4)	0.5276 (3)	0.0261 (9)
H31	-0.018820	0.860328	0.576999	0.031*
C4	0.1735 (5)	0.7937 (5)	0.5173 (4)	0.0307 (10)
H4	0.233970	0.840133	0.558282	0.037*
C5	0.2323 (5)	0.7145 (5)	0.4475 (4)	0.0302 (10)
H5	0.334778	0.706145	0.437882	0.036*
C6	-0.2303 (5)	0.7586 (5)	0.4778 (3)	0.0287 (10)
H61	-0.264979	0.808926	0.405592	0.043*
H62	-0.256672	0.820236	0.529537	0.043*
H63	-0.275192	0.657767	0.503642	0.043*
N3	0.1565 (5)	0.8165 (4)	0.0970 (3)	0.0442 (11)
H3	0.203006	0.755442	0.062552	0.053*
N4	-0.0543 (5)	0.7318 (4)	0.0450 (3)	0.0449 (11)
H41	-0.003796	0.673130	0.010658	0.054*
H42	-0.149760	0.732884	0.044756	0.054*
C7	0.0126 (6)	0.8173 (5)	0.0962 (4)	0.0335 (11)
C8	-0.0674 (5)	0.9164 (4)	0.1518 (3)	0.0259 (9)
C9	0.0146 (5)	1.0014 (5)	0.1998 (4)	0.0341 (11)
H9	-0.034406	1.068018	0.237036	0.041*
C10	0.1645 (6)	0.9982 (6)	0.1983 (4)	0.0490 (15)
H10	0.215978	1.061851	0.232809	0.059*
C11	0.2389 (6)	0.9005 (5)	0.1457 (4)	0.0445 (13)
H11	0.341889	0.892861	0.143944	0.053*
C12	-0.2276 (5)	0.9185 (5)	0.1540 (4)	0.0398 (12)
H121	-0.259677	0.944393	0.078855	0.060*
H122	-0.264395	0.994630	0.191737	0.060*
H123	-0.265109	0.817750	0.192919	0.060*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Bi1	0.01270 (9)	0.02202 (9)	0.01806 (9)	0.00003 (6)	-0.00008 (6)	-0.00686 (6)

Br1	0.0271 (3)	0.0268 (2)	0.0350 (3)	0.00156 (19)	0.0008 (2)	-0.00079 (19)
Br2	0.0243 (2)	0.0457 (3)	0.0272 (2)	-0.0019 (2)	-0.00147 (18)	-0.02122 (19)
Br3	0.0127 (2)	0.0323 (2)	0.0384 (2)	0.00028 (17)	0.00157 (18)	-0.01046 (19)
Br4	0.0124 (2)	0.0303 (2)	0.0308 (2)	0.00217 (16)	-0.00031 (17)	-0.01082 (17)
Br5	0.0410 (3)	0.0264 (2)	0.0239 (2)	-0.00511 (19)	-0.00182 (19)	-0.01101 (17)
N1	0.022 (2)	0.0224 (17)	0.0241 (17)	0.0033 (14)	0.0047 (15)	-0.0044 (14)
N2	0.023 (2)	0.0247 (17)	0.0255 (18)	0.0037 (14)	0.0000 (15)	-0.0101 (14)
C1	0.022 (2)	0.0142 (18)	0.0164 (18)	0.0039 (16)	-0.0002 (16)	0.0020 (14)
C2	0.022 (2)	0.0163 (18)	0.0195 (19)	0.0019 (16)	-0.0004 (17)	0.0000 (15)
C3	0.034 (3)	0.020 (2)	0.023 (2)	0.0015 (18)	-0.0022 (19)	-0.0051 (17)
C4	0.026 (3)	0.030 (2)	0.038 (3)	-0.0017 (19)	-0.011 (2)	-0.010 (2)
C5	0.022 (2)	0.030 (2)	0.035 (2)	-0.0020 (19)	-0.004 (2)	-0.0022 (19)
C6	0.026 (3)	0.034 (2)	0.029 (2)	0.0040 (19)	0.0025 (19)	-0.0127 (19)
N3	0.039 (3)	0.033 (2)	0.049 (3)	0.0100 (19)	0.018 (2)	0.0064 (19)
N4	0.064 (3)	0.037 (2)	0.036 (2)	-0.010 (2)	0.014 (2)	-0.0153 (19)
C7	0.044 (3)	0.023 (2)	0.027 (2)	-0.006 (2)	0.008 (2)	0.0039 (18)
C8	0.036 (3)	0.021 (2)	0.019 (2)	0.0014 (19)	-0.0012 (19)	-0.0025 (16)
C9	0.029 (3)	0.033 (2)	0.037 (3)	0.004 (2)	-0.006 (2)	0.001 (2)
C10	0.056 (4)	0.036 (3)	0.050 (3)	-0.012 (3)	-0.021 (3)	0.004 (2)
C11	0.044 (3)	0.032 (3)	0.048 (3)	-0.002 (2)	0.008 (3)	0.005 (2)
C12	0.033 (3)	0.044 (3)	0.041 (3)	-0.001 (2)	0.001 (2)	-0.009 (2)

Geometric parameters (Å, °)

Bi1—Br1	2.7114 (4)	C6—H61	0.9800
Bi1—Br2	2.7491 (4)	C6—H62	0.9800
Bi1—Br3	2.7830 (4)	C6—H63	0.9800
Bi1—Br4	2.9043 (4)	N3—C7	1.327 (6)
Bi1—Br5	2.9590 (4)	N3—C11	1.355 (7)
Bi1—Br5 ⁱ	3.1172 (4)	N3—H3	0.8800
N1—C1	1.347 (5)	N4—C7	1.306 (6)
N1—C5	1.360 (5)	N4—H41	0.8800
N1—H1	0.8800	N4—H42	0.8800
N2—C1	1.331 (5)	C7—C8	1.445 (6)
N2—H21	0.8800	C8—C9	1.354 (6)
N2—H22	0.8800	C8—C12	1.475 (6)
C1—C2	1.426 (5)	C9—C10	1.381 (7)
C2—C3	1.366 (6)	C9—H9	0.9500
C2—C6	1.497 (6)	C10—C11	1.388 (8)
C3—C4	1.397 (6)	C10—H10	0.9500
C3—H31	0.9500	C11—H11	0.9500
C4—C5	1.357 (6)	C12—H121	0.9800
C4—H4	0.9500	C12—H122	0.9800
C5—H5	0.9500	C12—H123	0.9800
Br1—Bi1—Br2	94.306 (14)	C4—C5—H5	120.5
Br1—Bi1—Br3	90.383 (13)	N1—C5—H5	120.5
Br2—Bi1—Br3	91.286 (13)	C2—C6—H61	109.5

Br1—Bi1—Br4	91.388 (13)	C2—C6—H62	109.5
Br2—Bi1—Br4	88.747 (13)	H61—C6—H62	109.5
Br3—Bi1—Br4	178.221 (12)	C2—C6—H63	109.5
Br1—Bi1—Br5	95.067 (13)	H61—C6—H63	109.5
Br2—Bi1—Br5	170.620 (13)	H62—C6—H63	109.5
Br3—Bi1—Br5	89.036 (13)	C7—N3—C11	126.4 (5)
Br4—Bi1—Br5	90.642 (13)	C7—N3—H3	116.8
Br1—Bi1—Br5 ⁱ	179.186 (13)	C11—N3—H3	116.8
Br2—Bi1—Br5 ⁱ	85.969 (13)	C7—N4—H41	120.0
Br3—Bi1—Br5 ⁱ	88.844 (13)	C7—N4—H42	120.0
Br4—Bi1—Br5 ⁱ	89.383 (13)	H41—N4—H42	120.0
Br5—Bi1—Br5 ⁱ	84.665 (12)	N4—C7—N3	120.5 (5)
Bi1—Br5—Bi1 ⁱ	95.335 (12)	N4—C7—C8	121.2 (5)
C1—N1—C5	124.3 (4)	N3—C7—C8	118.3 (4)
C1—N1—H1	117.9	C9—C8—C7	115.4 (4)
C5—N1—H1	117.9	C9—C8—C12	124.8 (4)
C1—N2—H21	120.0	C7—C8—C12	119.8 (4)
C1—N2—H22	120.0	C8—C9—C10	124.6 (5)
H21—N2—H22	120.0	C8—C9—H9	117.7
N2—C1—N1	119.4 (3)	C10—C9—H9	117.7
N2—C1—C2	122.5 (4)	C9—C10—C11	118.9 (5)
N1—C1—C2	118.0 (4)	C9—C10—H10	120.5
C3—C2—C1	117.4 (4)	C11—C10—H10	120.5
C3—C2—C6	122.7 (4)	N3—C11—C10	116.3 (5)
C1—C2—C6	119.9 (4)	N3—C11—H11	121.8
C2—C3—C4	122.6 (4)	C10—C11—H11	121.8
C2—C3—H31	118.7	C8—C12—H121	109.5
C4—C3—H31	118.7	C8—C12—H122	109.5
C5—C4—C3	118.7 (4)	H121—C12—H122	109.5
C5—C4—H4	120.6	C8—C12—H123	109.5
C3—C4—H4	120.6	H121—C12—H123	109.5
C4—C5—N1	119.0 (4)	H122—C12—H123	109.5
C5—N1—C1—N2	-179.2 (4)	C11—N3—C7—N4	179.2 (4)
C5—N1—C1—C2	0.6 (5)	C11—N3—C7—C8	0.1 (7)
N2—C1—C2—C3	177.6 (3)	N4—C7—C8—C9	-178.6 (4)
N1—C1—C2—C3	-2.2 (5)	N3—C7—C8—C9	0.4 (6)
N2—C1—C2—C6	-2.2 (6)	N4—C7—C8—C12	1.8 (6)
N1—C1—C2—C6	178.0 (3)	N3—C7—C8—C12	-179.1 (4)
C1—C2—C3—C4	2.2 (6)	C7—C8—C9—C10	-0.1 (7)
C6—C2—C3—C4	-178.0 (4)	C12—C8—C9—C10	179.4 (4)
C2—C3—C4—C5	-0.6 (6)	C8—C9—C10—C11	-0.8 (7)
C3—C4—C5—N1	-1.2 (6)	C7—N3—C11—C10	-1.0 (7)
C1—N1—C5—C4	1.2 (6)	C9—C10—C11—N3	1.3 (7)

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...Br4	0.88	2.62	3.456 (3)	158
N2—H21...Br4	0.88	2.68	3.496 (3)	154
N2—H22...Br2 ⁱⁱ	0.88	2.65	3.504 (4)	165
N3—H3...Br5 ⁱ	0.88	3.02	3.653 (4)	130
N4—H41...Br3 ⁱ	0.88	2.72	3.521 (4)	152
N4—H42...Br5 ⁱⁱⁱ	0.88	3.04	3.912 (5)	173

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x-1, y, z$; (iii) $-x, -y+1, -z$.

Bis(4-amino-3-ammoniopyridinium) di- μ -chlorido-bis[tetrachloridobismuth(III)] dihydrate (4)

Crystal data

(C₅H₉N₃)₂[Bi₂Cl₁₀]·2H₂O

M_r = 1030.79

Monoclinic, *C2/c*

a = 18.0583 (2) Å

b = 12.07450 (12) Å

c = 13.43800 (15) Å

β = 104.0805 (11)°

V = 2842.05 (5) Å³

Z = 4

F(000) = 1904

D_x = 2.409 Mg m⁻³

Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 20128 reflections

θ = 3.4–29.4°

μ = 13.33 mm⁻¹

T = 160 K

Block, colourless

0.20 × 0.18 × 0.08 mm

Data collection

Oxford Diffraction SuperNova dual radiation diffractometer

Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray source

Mirror monochromator

Detector resolution: 10.3801 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku OD, 2018)

T_{min} = 0.348, *T_{max}* = 1.000

30758 measured reflections

3742 independent reflections

3505 reflections with *I* > 2 σ (*I*)

R_{int} = 0.034

θ_{max} = 29.5°, θ_{min} = 2.7°

h = -24→24

k = -16→16

l = -18→17

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2 σ (*F*²)] = 0.016

wR(*F*²) = 0.030

S = 1.08

3742 reflections

182 parameters

12 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: geom & difmap

H atoms treated by a mixture of independent and constrained refinement

w = 1/[$\sigma^2(F_o^2) + (0.0104P)^2 + 2.6097P$]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.003

$\Delta\rho_{max}$ = 0.66 e Å⁻³

$\Delta\rho_{min}$ = -0.55 e Å⁻³

Extinction correction: SHELXL2018

(Sheldrick, 2015b),

*F_c** = *kF_c*[1 + 0.001*xF_c*² $\lambda^3/\sin(2\theta)$]^{-1/4}

Extinction coefficient: 0.000247 (12)

Special details

Experimental. Data collection and full structure determination done by Prof. Anthony Linden:
anthony.linden@chem.uzh.ch

Solvent used: 2M HCl Cooling Device: Oxford Instruments Cryojet XL Crystal mount: on a glass fibre Frames collected: 817 Seconds exposure per frame: 8.0 Degrees rotation per frame: 1.0 Crystal-detector distance (mm): 55.0 Client: Levi Senior Sample code: LS033

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Anion sites across a centre of inversion. Two sites for water molecules disordered about twofold axes. Distance and angle restraints applied to the water H atoms. Distance restraints applied to all N-H H atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Bi1	0.35117 (2)	0.72988 (2)	-0.05830 (2)	0.01728 (3)	
Cl1	0.46209 (3)	0.86237 (5)	-0.03702 (5)	0.03036 (13)	
Cl2	0.40227 (4)	0.59985 (5)	-0.18555 (4)	0.03157 (14)	
Cl3	0.27578 (3)	0.85878 (4)	-0.21265 (4)	0.02234 (11)	
Cl4	0.42774 (3)	0.60321 (4)	0.10076 (4)	0.02130 (11)	
Cl5	0.30319 (3)	0.86838 (5)	0.08236 (4)	0.02636 (12)	
N1	0.61203 (12)	0.66820 (18)	-0.07273 (15)	0.0298 (5)	
H1	0.6008 (16)	0.6206 (19)	-0.1237 (16)	0.048 (9)*	
N2	0.60265 (10)	0.68466 (17)	0.19552 (14)	0.0213 (4)	
H21	0.5785 (14)	0.6189 (13)	0.190 (2)	0.040 (8)*	
H22	0.5709 (13)	0.7352 (17)	0.213 (2)	0.033 (8)*	
H23	0.6480 (8)	0.679 (2)	0.2424 (15)	0.031 (7)*	
N3	0.66863 (13)	0.89037 (18)	0.16324 (18)	0.0349 (5)	
H31	0.6629 (16)	0.876 (2)	0.2255 (11)	0.046 (9)*	
H32	0.6898 (17)	0.9524 (15)	0.152 (2)	0.062 (10)*	
C1	0.59972 (12)	0.64156 (19)	0.01852 (16)	0.0230 (5)	
H11	0.577815	0.571984	0.027900	0.028*	
C2	0.61865 (12)	0.71426 (17)	0.09767 (16)	0.0186 (4)	
C3	0.65074 (12)	0.81845 (19)	0.08692 (17)	0.0227 (5)	
C4	0.66180 (13)	0.8418 (2)	-0.01215 (19)	0.0303 (5)	
H4	0.683158	0.910721	-0.024913	0.036*	
C5	0.64214 (15)	0.7667 (2)	-0.0878 (2)	0.0334 (6)	
H5	0.649733	0.783718	-0.153616	0.040*	
O1	0.5074 (3)	0.8331 (3)	0.2772 (2)	0.0267 (8)	0.5
H1A	0.532 (3)	0.846 (4)	0.3376 (15)	0.040*	0.5
H1B	0.503 (5)	0.889 (2)	0.239 (3)	0.040*	0.5
O2	0.4782 (2)	1.0460 (4)	0.2339 (6)	0.0560 (17)	0.5
H2A	0.4319 (12)	1.062 (6)	0.223 (6)	0.084*	0.5
H2B	0.502 (3)	1.089 (5)	0.204 (5)	0.084*	0.5

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Bi1	0.01610 (5)	0.01685 (5)	0.01932 (5)	0.00110 (3)	0.00514 (3)	0.00141 (3)
Cl1	0.0208 (3)	0.0294 (3)	0.0389 (3)	-0.0061 (2)	0.0032 (2)	0.0049 (3)
Cl2	0.0496 (4)	0.0243 (3)	0.0239 (3)	0.0113 (3)	0.0149 (3)	0.0031 (2)
Cl3	0.0222 (3)	0.0179 (2)	0.0242 (3)	-0.0008 (2)	0.0003 (2)	0.0013 (2)
Cl4	0.0250 (3)	0.0189 (3)	0.0195 (2)	0.0009 (2)	0.0044 (2)	-0.0004 (2)
Cl5	0.0290 (3)	0.0219 (3)	0.0299 (3)	-0.0061 (2)	0.0106 (2)	-0.0054 (2)
N1	0.0356 (11)	0.0328 (12)	0.0222 (10)	-0.0038 (9)	0.0092 (9)	-0.0067 (9)
N2	0.0210 (10)	0.0248 (10)	0.0177 (9)	-0.0010 (9)	0.0037 (8)	0.0018 (8)
N3	0.0453 (13)	0.0210 (11)	0.0346 (13)	-0.0111 (10)	0.0021 (11)	-0.0022 (9)
C1	0.0225 (11)	0.0235 (12)	0.0228 (11)	-0.0024 (9)	0.0054 (9)	-0.0002 (9)
C2	0.0170 (10)	0.0203 (11)	0.0182 (10)	0.0015 (8)	0.0038 (8)	0.0046 (8)
C3	0.0198 (11)	0.0205 (12)	0.0247 (11)	-0.0004 (9)	-0.0007 (9)	0.0024 (9)
C4	0.0276 (12)	0.0292 (13)	0.0331 (13)	-0.0053 (10)	0.0057 (10)	0.0121 (11)
C5	0.0315 (14)	0.0452 (16)	0.0261 (13)	-0.0016 (12)	0.0118 (11)	0.0083 (11)
O1	0.030 (2)	0.0257 (17)	0.023 (2)	0.0002 (16)	0.003 (2)	0.0021 (12)
O2	0.069 (5)	0.044 (2)	0.064 (5)	0.016 (2)	0.034 (4)	0.017 (3)

Geometric parameters (\AA , $^\circ$)

Bi1—Cl1	2.5247 (5)	N3—H31	0.885 (10)
Bi1—Cl2	2.6474 (5)	N3—H32	0.871 (10)
Bi1—Cl3	2.6840 (5)	C1—C2	1.357 (3)
Bi1—Cl4	2.7170 (5)	C1—H11	0.9500
Bi1—Cl5	2.8136 (5)	C2—C3	1.407 (3)
Bi1—Cl5 ⁱ	2.9738 (5)	C3—C4	1.422 (3)
N1—C1	1.338 (3)	C4—C5	1.344 (4)
N1—C5	1.344 (3)	C4—H4	0.9500
N1—H1	0.880 (10)	C5—H5	0.9500
N2—C2	1.458 (3)	O1—H1A	0.839 (10)
N2—H21	0.900 (10)	O1—H1B	0.840 (10)
N2—H22	0.907 (10)	O2—H2A	0.837 (10)
N2—H23	0.906 (10)	O2—H2B	0.842 (10)
N3—C3	1.323 (3)		
Cl1—Bi1—Cl2	93.29 (2)	H21—N2—H23	109 (2)
Cl1—Bi1—Cl3	87.673 (17)	H22—N2—H23	113 (2)
Cl2—Bi1—Cl3	92.048 (17)	C3—N3—H31	123 (2)
Cl1—Bi1—Cl4	91.700 (17)	C3—N3—H32	118 (2)
Cl2—Bi1—Cl4	89.060 (16)	H31—N3—H32	120 (3)
Cl3—Bi1—Cl4	178.756 (16)	N1—C1—C2	119.8 (2)
Cl1—Bi1—Cl5	84.998 (18)	N1—C1—H11	120.1
Cl2—Bi1—Cl5	177.559 (18)	C2—C1—H11	120.1
Cl3—Bi1—Cl5	89.619 (17)	C1—C2—C3	122.0 (2)
Cl4—Bi1—Cl5	89.256 (16)	C1—C2—N2	118.75 (19)
Cl1—Bi1—Cl5 ⁱ	164.142 (18)	C3—C2—N2	119.26 (19)

C12—Bi1—C15 ⁱ	99.089 (18)	N3—C3—C2	122.4 (2)
C13—Bi1—C15 ⁱ	82.042 (16)	N3—C3—C4	122.2 (2)
C14—Bi1—C15 ⁱ	98.344 (16)	C2—C3—C4	115.4 (2)
C15—Bi1—C15 ⁱ	82.905 (16)	C5—C4—C3	120.2 (2)
Bi1—C15—Bi1 ⁱ	97.096 (16)	C5—C4—H4	119.9
C1—N1—C5	121.0 (2)	C3—C4—H4	119.9
C1—N1—H1	119.9 (19)	N1—C5—C4	121.7 (2)
C5—N1—H1	119.1 (19)	N1—C5—H5	119.1
C2—N2—H21	110.3 (17)	C4—C5—H5	119.1
C2—N2—H22	110.1 (17)	H1A—O1—H1B	113.1 (19)
H21—N2—H22	107 (2)	H2A—O2—H2B	112.9 (19)
C2—N2—H23	107.5 (16)		
C5—N1—C1—C2	-0.8 (3)	N2—C2—C3—C4	-177.80 (19)
N1—C1—C2—C3	0.4 (3)	N3—C3—C4—C5	-179.4 (2)
N1—C1—C2—N2	178.2 (2)	C2—C3—C4—C5	-0.1 (3)
C1—C2—C3—N3	179.3 (2)	C1—N1—C5—C4	0.7 (4)
N2—C2—C3—N3	1.5 (3)	C3—C4—C5—N1	-0.2 (4)
C1—C2—C3—C4	0.0 (3)		

Symmetry code: (i) $-x+1/2, -y+3/2, -z$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...C12 ⁱⁱ	0.88 (1)	2.56 (2)	3.300 (2)	142 (2)
N1—H1...C14 ⁱⁱⁱ	0.88 (1)	2.78 (2)	3.356 (2)	124 (2)
N2—H21...C12 ⁱⁱⁱ	0.90 (1)	2.67 (2)	3.438 (2)	144 (2)
N2—H21...C14	0.90 (1)	2.70 (2)	3.2570 (19)	121 (2)
N2—H22...O1	0.91 (1)	1.98 (1)	2.879 (5)	169 (3)
N2—H22...O1 ^{iv}	0.91 (1)	1.87 (1)	2.766 (5)	168 (3)
N2—H23...C13 ^v	0.91 (1)	2.28 (1)	3.1137 (19)	152 (2)
N3—H31...C15 ^{iv}	0.89 (1)	2.51 (2)	3.342 (2)	158 (3)
N3—H32...C13 ^{vi}	0.87 (1)	2.45 (2)	3.209 (2)	146 (3)
O1—H1A...C11 ^{iv}	0.84 (1)	2.66 (3)	3.418 (3)	151 (5)
O1—H1B...O2	0.84 (1)	1.94 (4)	2.661 (5)	143 (6)
O2—H2B...C11 ^{vi}	0.84 (1)	2.55 (4)	3.282 (7)	147 (7)

Symmetry codes: (ii) $-x+1, y, -z-1/2$; (iii) $-x+1, -y+1, -z$; (iv) $-x+1, y, -z+1/2$; (v) $x+1/2, -y+3/2, z+1/2$; (vi) $-x+1, -y+2, -z$.

catena-Poly[2,6-diaminopyridinium [[*cis*-diiodidobismuth(III)]-di- μ -iodido]] (5)

Crystal data

(C₅H₈N₃)[BiI₄]
M_r = 826.72
 Monoclinic, *P*2₁/*n*
a = 12.02106 (15) Å
b = 7.80880 (9) Å
c = 15.3298 (2) Å
 β = 90.0530 (11)°

V = 1439.01 (3) Å³
Z = 4
F(000) = 1416
D_x = 3.816 Mg m⁻³
 Mo *K* α radiation, λ = 0.71073 Å
 Cell parameters from 19181 reflections
 θ = 3.1–30.3°

$\mu = 20.80 \text{ mm}^{-1}$
 $T = 160 \text{ K}$

Prism, red
 $0.16 \times 0.10 \times 0.04 \text{ mm}$

Data collection

Oxford Diffraction SuperNova dual radiation diffractometer
 Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray source
 Mirror monochromator
 Detector resolution: $10.3801 \text{ pixels mm}^{-1}$
 ω scans
 Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2018)

$T_{\min} = 0.259$, $T_{\max} = 1.000$
 35690 measured reflections
 4076 independent reflections
 3831 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$
 $\theta_{\max} = 30.4^\circ$, $\theta_{\min} = 2.9^\circ$
 $h = -15 \rightarrow 16$
 $k = -11 \rightarrow 11$
 $l = -21 \rightarrow 21$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.040$
 $S = 1.05$
 4076 reflections
 120 parameters
 0 restraints
 Primary atom site location: dual
 Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0158P)^2 + 1.0108P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 1.21 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.04 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL2018 (Sheldrick, 2015b),
 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.00085 (3)

Special details

Experimental. Data collection and full structure determination done by Prof. Anthony Linden: anthony.linden@chem.uzh.ch

Solvent used: 2M HI Cooling Device: Oxford Instruments Cryojet XL Crystal mount: on a glass fibre Frames collected: 843 Seconds exposure per frame: 4.0 Degrees rotation per frame: 1.0 Crystal-detector distance (mm): 55.0 Client: Levi Senior Sample code: LS014

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a pseudomerohedral twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Bi1	0.50460 (2)	0.74323 (2)	0.58217 (2)	0.01486 (5)
I1	0.34952 (2)	0.87654 (3)	0.71421 (2)	0.02166 (7)
I2	0.67606 (2)	0.60869 (3)	0.69839 (2)	0.02465 (7)
I3	0.64735 (2)	1.07351 (3)	0.57417 (2)	0.01894 (6)
I4	0.37076 (2)	0.40914 (3)	0.58707 (2)	0.01862 (6)
N1	0.9263 (3)	0.8116 (4)	0.5537 (2)	0.0208 (7)
H1	0.866088	0.859132	0.575544	0.025*
N2	0.8629 (3)	0.8991 (4)	0.4191 (3)	0.0284 (9)
H2A	0.806907	0.948964	0.445890	0.034*
H2B	0.868236	0.904688	0.361884	0.034*

N3	0.9804 (4)	0.7490 (5)	0.6951 (3)	0.0351 (10)
H3A	0.920276	0.801655	0.713883	0.042*
H3B	1.027092	0.703144	0.732718	0.042*
C1	0.9402 (3)	0.8146 (5)	0.4653 (3)	0.0210 (9)
C2	1.0331 (4)	0.7373 (5)	0.4300 (3)	0.0230 (9)
H2	1.045469	0.738032	0.368830	0.028*
C3	1.1076 (4)	0.6590 (5)	0.4857 (3)	0.0229 (9)
H3	1.170743	0.602856	0.461827	0.028*
C4	1.0934 (3)	0.6595 (5)	0.5748 (3)	0.0218 (9)
H4	1.146698	0.606093	0.611665	0.026*
C5	1.0007 (4)	0.7388 (5)	0.6103 (3)	0.0223 (9)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Bi1	0.01475 (8)	0.01618 (7)	0.01365 (8)	−0.00005 (5)	0.00050 (6)	−0.00046 (6)
I1	0.02187 (14)	0.02647 (13)	0.01666 (13)	0.00351 (10)	0.00292 (11)	−0.00414 (10)
I2	0.02031 (14)	0.02924 (14)	0.02440 (15)	0.00093 (11)	−0.00569 (12)	0.00617 (11)
I3	0.01781 (13)	0.01897 (12)	0.02003 (13)	−0.00332 (10)	−0.00335 (11)	0.00159 (10)
I4	0.01745 (13)	0.01773 (12)	0.02070 (14)	−0.00210 (9)	0.00599 (10)	−0.00229 (10)
N1	0.0154 (17)	0.0211 (16)	0.026 (2)	0.0028 (14)	0.0027 (14)	−0.0034 (15)
N2	0.025 (2)	0.0316 (19)	0.028 (2)	0.0045 (16)	−0.0034 (17)	0.0052 (17)
N3	0.035 (3)	0.049 (2)	0.021 (2)	0.0148 (19)	0.0009 (19)	0.0006 (18)
C1	0.020 (2)	0.0187 (19)	0.024 (2)	−0.0040 (16)	−0.0041 (17)	0.0000 (17)
C2	0.022 (2)	0.025 (2)	0.021 (2)	−0.0032 (16)	0.0051 (18)	−0.0031 (17)
C3	0.019 (2)	0.0167 (19)	0.033 (3)	−0.0024 (16)	0.0040 (18)	−0.0040 (18)
C4	0.018 (2)	0.0191 (19)	0.028 (2)	0.0007 (16)	−0.0001 (18)	0.0011 (18)
C5	0.018 (2)	0.022 (2)	0.026 (2)	−0.0007 (15)	−0.0005 (19)	0.0017 (17)

Geometric parameters (\AA , $^\circ$)

Bi1—I1	2.9432 (3)	N2—H2B	0.8800
Bi1—I2	2.9187 (3)	N3—C5	1.325 (6)
Bi1—I3	3.1003 (3)	N3—H3A	0.8800
Bi1—I3 ⁱ	3.3348 (3)	N3—H3B	0.8800
Bi1—I4	3.0660 (3)	C1—C2	1.381 (6)
Bi1—I4 ⁱⁱ	3.2248 (3)	C2—C3	1.380 (6)
N1—C1	1.365 (6)	C2—H2	0.9500
N1—C5	1.369 (5)	C3—C4	1.376 (6)
N1—H1	0.8800	C3—H3	0.9500
N2—C1	1.342 (5)	C4—C5	1.387 (6)
N2—H2A	0.8800	C4—H4	0.9500
I2—Bi1—I1	98.912 (9)	C1—N2—H2B	120.0
I2—Bi1—I4	92.810 (8)	H2A—N2—H2B	120.0
I1—Bi1—I4	87.214 (8)	C5—N3—H3A	120.0
I2—Bi1—I3	86.160 (8)	C5—N3—H3B	120.0
I1—Bi1—I3	94.815 (8)	H3A—N3—H3B	120.0

I4—Bi1—I3	177.843 (9)	N2—C1—N1	116.6 (4)
I2—Bi1—I4 ⁱⁱ	91.716 (9)	N2—C1—C2	124.6 (4)
I1—Bi1—I4 ⁱⁱ	168.189 (9)	N1—C1—C2	118.7 (4)
I4—Bi1—I4 ⁱⁱ	87.131 (8)	C3—C2—C1	118.4 (4)
I3—Bi1—I4 ⁱⁱ	91.004 (8)	C3—C2—H2	120.8
I2—Bi1—I3 ⁱ	168.288 (10)	C1—C2—H2	120.8
I1—Bi1—I3 ⁱ	89.748 (8)	C4—C3—C2	122.1 (4)
I4—Bi1—I3 ⁱ	95.489 (8)	C4—C3—H3	118.9
I3—Bi1—I3 ⁱ	85.263 (7)	C2—C3—H3	118.9
I4 ⁱⁱ —Bi1—I3 ⁱ	80.483 (8)	C3—C4—C5	119.4 (4)
Bi1—I3—Bi1 ⁱ	94.738 (7)	C3—C4—H4	120.3
Bi1—I4—Bi1 ⁱⁱ	92.869 (8)	C5—C4—H4	120.3
C1—N1—C5	123.8 (4)	N3—C5—N1	118.5 (4)
C1—N1—H1	118.1	N3—C5—C4	124.1 (4)
C5—N1—H1	118.1	N1—C5—C4	117.5 (4)
C1—N2—H2A	120.0		
C5—N1—C1—N2	-176.4 (4)	C2—C3—C4—C5	1.0 (6)
C5—N1—C1—C2	1.4 (6)	C1—N1—C5—N3	177.6 (4)
N2—C1—C2—C3	178.1 (4)	C1—N1—C5—C4	-2.0 (6)
N1—C1—C2—C3	0.5 (6)	C3—C4—C5—N3	-178.8 (4)
C1—C2—C3—C4	-1.7 (6)	C3—C4—C5—N1	0.8 (6)

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots I3	0.88	3.12	3.941 (3)	157
N2—H2A \cdots I3	0.88	2.92	3.773 (4)	165
N2—H2B \cdots I1 ⁱⁱⁱ	0.88	3.16	3.811 (4)	132
N3—H3A \cdots I2 ^{iv}	0.88	2.98	3.754 (4)	147
N3—H3B \cdots I1 ^v	0.88	3.06	3.816 (4)	145

Symmetry codes: (iii) $x+1/2, -y+3/2, z-1/2$; (iv) $-x+3/2, y+1/2, -z+3/2$; (v) $-x+3/2, y-1/2, -z+3/2$.

catena-Poly[2,6-diaminopyridinium [[*cis*-dibromidobismuth(III)]-di- μ -bromido]] (6)

Crystal data

(C₅H₇N₂)[BiBr₄]
 $M_r = 623.75$
 Monoclinic, $P2_1/c$
 $a = 11.66220$ (15) \AA
 $b = 14.08143$ (19) \AA
 $c = 7.35193$ (9) \AA
 $\beta = 94.7149$ (13) $^\circ$
 $V = 1203.25$ (3) \AA^3
 $Z = 4$

$F(000) = 1096$
 $D_x = 3.443$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA
 Cell parameters from 13232 reflections
 $\theta = 3.5\text{--}29.3^\circ$
 $\mu = 27.89$ mm⁻¹
 $T = 160$ K
 Block, colourless
 0.21 \times 0.08 \times 0.06 mm

Data collection

Oxford Diffraction SuperNova dual radiation diffractometer	$T_{\min} = 0.735$, $T_{\max} = 1.000$
Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray source	26081 measured reflections
Mirror monochromator	3128 independent reflections
Detector resolution: 10.3801 pixels mm ⁻¹	2794 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.040$
Absorption correction: gaussian (CrysAlis PRO; Rigaku OD, 2018)	$\theta_{\max} = 29.5^\circ$, $\theta_{\min} = 2.9^\circ$
	$h = -16 \rightarrow 15$
	$k = -19 \rightarrow 19$
	$l = -10 \rightarrow 9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: geom & difmap
$R[F^2 > 2\sigma(F^2)] = 0.023$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.050$	$w = 1/[\sigma^2(F_o^2) + (0.0231P)^2 + 0.9774P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
3127 reflections	$(\Delta/\sigma)_{\max} = 0.001$
121 parameters	$\Delta\rho_{\max} = 1.26 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\min} = -2.21 \text{ e } \text{\AA}^{-3}$
Primary atom site location: dual	

Special details

Experimental. Data collection and full structure determination done by Prof. Anthony Linden: anthony.linden@chem.uzh.ch

Solvent used: 2M HBr Cooling Device: Oxford Instruments Cryojet XL Crystal mount: on a glass fibre Frames collected: 813 Seconds exposure per frame: 8.0 Degrees rotation per frame: 1.0 Crystal-detector distance (mm): 55.0 Client: Levi Senior Sample code: LS036

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Bi1	0.26448 (2)	0.33482 (2)	0.52386 (2)	0.01425 (5)
Br1	0.13501 (3)	0.47782 (3)	0.37005 (5)	0.02171 (10)
Br2	0.41622 (3)	0.45100 (3)	0.69260 (5)	0.01968 (9)
Br3	0.11987 (3)	0.33214 (3)	0.82384 (5)	0.01866 (9)
Br4	0.40032 (3)	0.32819 (3)	0.21440 (5)	0.01834 (9)
N1	0.1705 (4)	0.5749 (3)	0.9120 (6)	0.0401 (11)
H1	0.144 (5)	0.523 (5)	0.881 (8)	0.06 (2)*
N2	0.3249 (4)	0.8303 (3)	1.0181 (6)	0.0306 (9)
H21	0.285 (5)	0.878 (5)	0.978 (8)	0.059 (19)*
H22	0.389 (5)	0.830 (4)	1.079 (8)	0.056 (19)*
C1	0.2767 (5)	0.5783 (4)	1.0033 (6)	0.0393 (13)
H11	0.314405	0.520835	1.040512	0.047*
C2	0.3290 (4)	0.6616 (3)	1.0414 (6)	0.0274 (10)
H2	0.402901	0.662979	1.106108	0.033*
C3	0.2741 (3)	0.7471 (3)	0.9855 (5)	0.0191 (8)

C4	0.1635 (3)	0.7410 (3)	0.8953 (5)	0.0237 (9)
H4	0.122560	0.797233	0.859612	0.028*
C5	0.1155 (4)	0.6550 (3)	0.8594 (6)	0.0307 (11)
H5	0.041453	0.651245	0.795595	0.037*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Bi1	0.01459 (8)	0.01259 (9)	0.01554 (8)	-0.00020 (5)	0.00109 (6)	0.00034 (5)
Br1	0.01822 (19)	0.0174 (2)	0.0288 (2)	0.00216 (16)	-0.00217 (16)	0.00382 (16)
Br2	0.01819 (18)	0.0172 (2)	0.0231 (2)	-0.00246 (15)	-0.00186 (15)	-0.00160 (15)
Br3	0.01692 (19)	0.0173 (2)	0.0222 (2)	0.00106 (15)	0.00430 (15)	0.00167 (14)
Br4	0.01725 (19)	0.0181 (2)	0.01999 (19)	-0.00329 (15)	0.00321 (15)	-0.00210 (14)
N1	0.062 (3)	0.020 (2)	0.042 (2)	-0.017 (2)	0.025 (2)	-0.0098 (19)
N2	0.025 (2)	0.027 (2)	0.038 (2)	-0.0059 (18)	-0.0059 (19)	0.0008 (18)
C1	0.063 (4)	0.025 (3)	0.034 (3)	0.019 (3)	0.026 (3)	0.010 (2)
C2	0.029 (2)	0.032 (3)	0.021 (2)	0.012 (2)	0.0059 (18)	0.0051 (18)
C3	0.0204 (19)	0.021 (2)	0.0162 (19)	-0.0004 (17)	0.0027 (15)	0.0018 (16)
C4	0.022 (2)	0.023 (2)	0.026 (2)	0.0014 (18)	0.0000 (17)	-0.0011 (17)
C5	0.028 (2)	0.033 (3)	0.032 (2)	-0.012 (2)	0.007 (2)	-0.006 (2)

Geometric parameters (\AA , $^\circ$)

Bi1—Br1	2.7079 (4)	N2—H21	0.85 (6)
Bi1—Br2	2.6431 (4)	N2—H22	0.84 (6)
Bi1—Br3	2.8846 (4)	C1—C2	1.341 (7)
Bi1—Br3 ⁱ	3.1822 (4)	C1—H11	0.9500
Bi1—Br4	2.8787 (4)	C2—C3	1.408 (6)
Bi1—Br4 ⁱⁱ	3.0620 (4)	C2—H2	0.9500
N1—C5	1.338 (7)	C3—C4	1.403 (5)
N1—C1	1.361 (7)	C4—C5	1.352 (6)
N1—H1	0.81 (6)	C4—H4	0.9500
N2—C3	1.326 (6)	C5—H5	0.9500
Br2—Bi1—Br1	93.702 (13)	C1—N1—H1	118 (4)
Br2—Bi1—Br4	90.017 (12)	C3—N2—H21	114 (4)
Br1—Bi1—Br4	91.046 (12)	C3—N2—H22	117 (4)
Br2—Bi1—Br3	93.452 (12)	H21—N2—H22	128 (6)
Br1—Bi1—Br3	89.314 (12)	C2—C1—N1	120.9 (5)
Br4—Bi1—Br3	176.482 (12)	C2—C1—H11	119.6
Br2—Bi1—Br4 ⁱⁱ	87.020 (12)	N1—C1—H11	119.6
Br1—Bi1—Br4 ⁱⁱ	176.605 (12)	C1—C2—C3	119.9 (5)
Br4—Bi1—Br4 ⁱⁱ	92.272 (11)	C1—C2—H2	120.0
Br3—Bi1—Br4 ⁱⁱ	87.331 (11)	C3—C2—H2	120.0
Br2—Bi1—Br3 ⁱ	169.462 (12)	N2—C3—C4	121.2 (4)
Br1—Bi1—Br3 ⁱ	95.756 (12)	N2—C3—C2	121.1 (4)
Br4—Bi1—Br3 ⁱ	85.182 (11)	C4—C3—C2	117.7 (4)
Br3—Bi1—Br3 ⁱ	91.301 (11)	C5—C4—C3	119.7 (4)

Br4 ⁱⁱ —Bi1—Br3 ⁱ	83.810 (12)	C5—C4—H4	120.1
Bi1—Br3—Bi1 ⁱⁱ	92.407 (11)	C3—C4—H4	120.1
Bi1—Br4—Bi1 ⁱ	95.064 (11)	N1—C5—C4	121.2 (5)
C5—N1—C1	120.6 (4)	N1—C5—H5	119.4
C5—N1—H1	121 (4)	C4—C5—H5	119.4
C5—N1—C1—C2	-0.5 (7)	N2—C3—C4—C5	178.1 (4)
N1—C1—C2—C3	-0.5 (7)	C2—C3—C4—C5	-2.4 (6)
C1—C2—C3—N2	-178.6 (4)	C1—N1—C5—C4	-0.1 (7)
C1—C2—C3—C4	1.9 (6)	C3—C4—C5—N1	1.5 (7)

Symmetry codes: (i) $x, -y+1/2, z-1/2$; (ii) $x, -y+1/2, z+1/2$.

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 ⁱⁱⁱ ⋯Br3	0.81 (6)	2.74 (6)	3.521 (4)	163 (6)
N2—H21 ⁱⁱⁱ ⋯Br1 ⁱⁱⁱ	0.85 (6)	2.76 (7)	3.605 (5)	173 (5)
N2—H22 ^{iv} ⋯Br4 ^{iv}	0.84 (6)	2.78 (6)	3.620 (4)	179 (5)

Symmetry codes: (iii) $x, -y+3/2, z+1/2$; (iv) $-x+1, y+1/2, -z+3/2$.