Salts of two pentahalo(*N*-donor)-bismuthate(III) anions: [BiX₅L]²⁻ (X = Cl, Br; L = pyridine, 4-picoline)

Siân C. James, Yvonne G. Lawson, Nicholas C. Norman, A. Guy Orpen and Michael J. Quayle*

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, England
Correspondence e-mail: michael.j.quayle@umist.ac.uk

Two pentahalo(*N*-donor)bismuthate(III) salts, bis[hydrogen bis(4-picoline)(1+)] pentabromo(4-picoline-*N*)bismuthate(III), $(C_{12}H_{15}N_2)_2[BiBr_5(C_6H_7N)]$, (I), and bis(pyridinium) pentachloro(pyridine-*N*)bismuthate(III), $(C_5H_6N)_2[BiCl_5(C_5H_5N)]$, (II), are described which show modest deviations from octahedral geometry at bismuth. In (I), the cations comprise two 4-picoline molecules sharing a proton and in (II), pyridinium cations are present. The anion in (I) has twofold and that in (II) has mirror crystallographic symmetry. Both structures show a layered packing formed by the anions with the cations between the layers. Ring–ring interactions seem important in (I), whilst in (II), N/C—H···Cl—Bi hydrogen bonding is abundant.

Comment

The crystal structure of [(4-pic)₂H]₂[BiBr₅(4-pic)] (4-pic = 4-picoline), (I), contains the pentabromo(4-pic)bismuthate(III) dianion lying at a twofold axis of symmetry (along Br1—Bi1—N1—C4). The cations are hydrogen bonded containing two molecules of 4-picoline sharing a proton (Fig. 1).
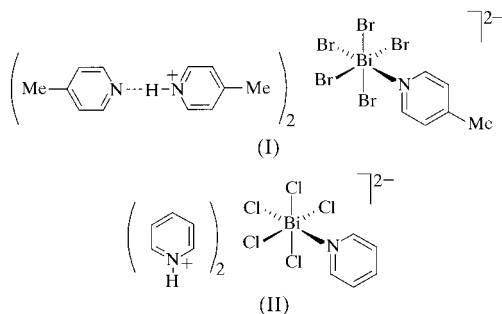
In the compound [(pyH)]₂[BiCl₅(py)] (py = pyridine), (II) (Fig. 2), the cations are simple pyridinium ions. In the anion of (I), the Br1—Bi1—N1 angle is exactly 180° and the symmetry-independent *trans* bond angles are 169.74 (2) [Br3—Bi1—Br3ⁱ; symmetry code: (i) −x, y, ½ − z] and 173.59 (2)° (Br2—Bi1—Br2ⁱ). The *cis* angles range from 84.872 (11) to 95.129 (12)°. Notably, the Bi—Br bond distance *trans* to the 4-

picoline is shorter [Bi1—Br1 2.772 (2) Å] than the others [Bi1—Br2 2.869 (3) Å and Bi1—Br3 2.850 (2) Å] presumably due to the lower *trans* influence of the *N*-donor ligand.

In the anion of (II), which has mirror symmetry, the Bi—Cl bond distances range from 2.6950 (12) to 2.728 (2) Å, but in this case, the bond *trans* to the pyridine ligand is the longest of the Bi–halide bonds. The Bi—N distances in both anions [2.618 (5) Å in (I) and 2.536 (5) Å in (II)] are significantly shorter than the two Bi—N distances in *cis*-[BiI₄(py)₂]⁻ [2.703 (2) and 2.751 (3) Å; Carmalt *et al.*, 1996] in which there are no discernible differences in Bi—I distances.

Two other salts containing the [BiCl₅(py)]²⁻ anion have been structurally characterized as *N′,N′*-diethylthiocarbamoylpyridinium (Raston *et al.*, 1981), (III), and *N*-(*N′,N′*-diethylcarbamoyl)pyridine (Bharadwaj *et al.*, 1994), (IV), salts. In both cases, the anion lies over a twofold axis. The symmetry independent Bi—Cl bond distances in (III) are 2.638 (2) Å (*trans* to N), and 2.699 (2) and 2.691 (3) Å (*trans* to Cl). Similarly, for (IV), the bond lengths are 2.626 (2) Å (*trans* to N) and 2.694 (2) Å (*trans* to Cl, for two bonds). Thus, the Bi—Cl distance in (III) and (IV) *trans* to N is shorter than those *trans* to Cl, the opposite of that in (II). That it is difficult to assess the relative *trans* influences of nitrogen and chlorine in these complexes is probably due to the relatively soft intramolecular parameters. These are prone to distortion by so-called packing effects such as hydrogen bonding.

The geometry about the Bi centre in (II) is close to regular octahedral, with *cis* angles of 90±3°. The *trans* angle deviating most from 180° is Cl1—Bi1—Cl1ⁱᵛ [174.21 (5)°, see Table 2]. Slightly larger distortions are found in the anions of (III) and (IV), with *cis* angles deviating by up to 6° and *trans* angles by up to 10° from ideal geometries.
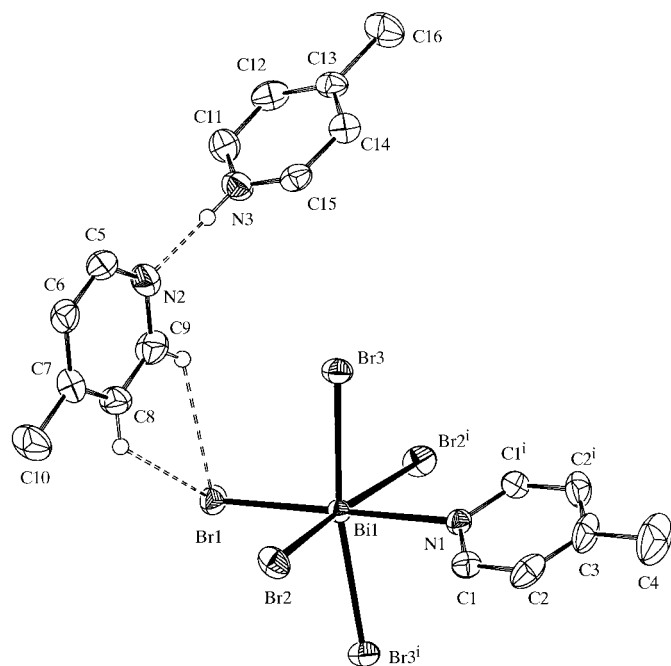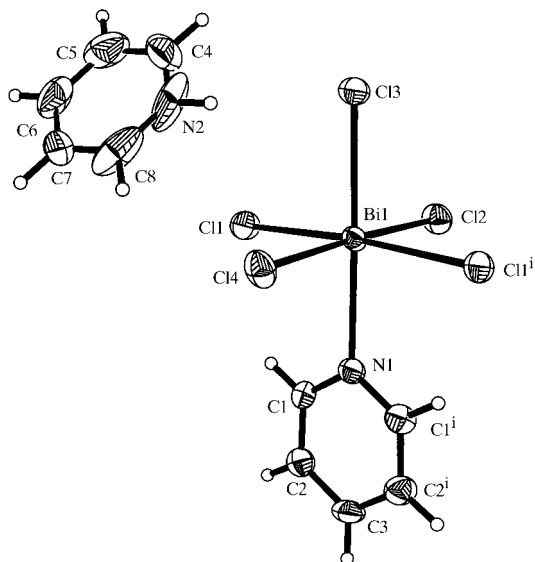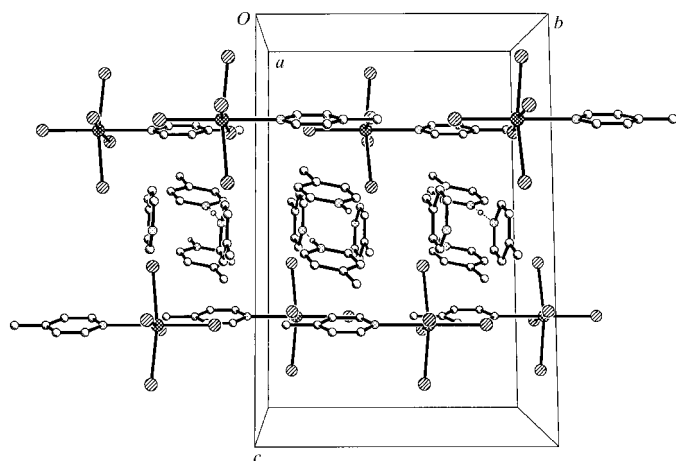

Figure 1
The hydrogen bonding in (I), showing one image of the disordered methyl group in the picoline ligand. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) −x, y, ½ − z.]

metal-organic compounds

Figure 2
The molecular structure of (II) with ellipsoids at the 50% probability level. [Symmetry code: (i) $x, -\frac{1}{2} - y, z$.]

In (I), Br1 is involved in two weak hydrogen bonds with the $[(4\text{-pic})_2\text{H}]^+$ cations in a bifurcated mode (Br1$\cdots$H9 = 2.98, Br1$\cdots$H8 = 3.00 Å; C8—H8$\cdots$Br1 = 127, C9—H9$\cdots$Br1 = 129°). The cations contain a short hydrogen bond [N3—H3 = 0.92, H3$\cdots$N2 = 1.76, N$\cdots$N = 2.667 (6) Å and N3—H3$\cdots$N2 = 167°], consistent with the formulation of the cations as $[(4\text{-pic})_2\text{H}]^+$ rather than as separate $[4\text{-picH}]^+$ cations and 4-pic solvent molecules.

The crystal structure of (I) is shown in Fig. 3. The packing can be best described as layers in an *ABBA* arrangement along the crystallographic *c* direction, with two $[(4\text{-pic})_2\text{H}]^+$ cations encased by *A* layers of the anion. The driving force behind this packing arrangement appears to be ring–ring interactions affording a close-packed structure. As shown in Fig. 3, there are ring–ring interactions between the 4-pic ligand of the anion and a cation with a 3.31 Å separation. The interplane separation between the cations is 3.63 Å. In the *b* direction, the separation between the cation rings is 4.19 Å.

Figure 3
The crystal structure of (I) viewed along the *b* axis.

The crystal structure of (II) is made up of chains of anions running approximately parallel to the crystallographic *b* axis that are hydrogen bonded to cations which occupy the space between adjacent layers (Fig. 4). There are two different orientations of chains, tilted at an angle of 65.9° to each other (Bi1/Cl1/Cl1'/Cl2/Cl4 plane), one of which is shown in detail in Fig. 4. There is a plethora of Bi—Cl$\cdots$H—C/N hydrogen bonds (H$\cdots$Cl distances = 2.633–2.865 Å, see Table 2 for details), whilst ring–ring interactions that were important in the structure of (I) are absent. Anions in chains are held together by C—H$\cdots$Cl hydrogen bonds related by a centre of symmetry. The anion hydrogen bonds to a cation (Cl1$\cdots$H7) and Cl4, which is perpendicular to the anion chains, hydrogen bonds to two separate cations. A tetrameric motif is formed between two chlorines in separate chains and the NH protons of two separate cations. The pyridinium cation is inclined at an angle of 45.3° to the pyridine ligand.
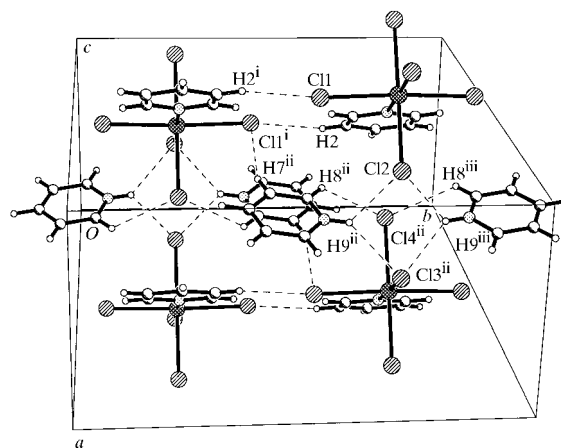
Figure 4
The crystal structure of (II) viewed along the *b* axis. [Symmetry codes: (i) $1 - x, 1 - y, 2 - z$; (ii) $x, y, 1 - z$; (iii) $x, \frac{3}{2} - y, 1 - z$.]

Experimental

The reaction of 4-picoline (0.030 ml, 0.30 mmol) and Bi(1,2-S$_2$-4-MeC$_6$H$_3$)Br (0.30 mmol) in tetrahydrofuran (15 ml) afforded an orange precipitate and an orange mother liquor. Yellow crystals of (I) were obtained by cooling the orange mother liquor. For the preparation of compound (II), a solution of BiCl$_3$ in pyridine (1.5 ml) was layered with more pyridine (1.5 ml) and then hexane (10 ml), and colourless block-like crystals of (II) were grown over several days at room temperature. (pyH)$_2$[BiCl$_5$(py)] requires C 28.80, N 6.70, H 2.75, Cl 28.4%; obtained C 25.30, N 5.55, H 2.35, Cl 22.50%.

Compound (I)

Crystal data

$(C_{12}H_{15}N_2)_2[BiBr_5(C_6H_7N)]$	$D_x = 1.948$ Mg m^{-3}
$M_r = 1076.18$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 272
$a = 14.789\,(13)$ Å	reflections
$b = 13.140\,(8)$ Å	$\theta = 5$–25°
$c = 19.064\,(16)$ Å	$\mu = 10.276$ mm^{-1}
$\beta = 97.94\,(3)°$	$T = 173\,(2)$ K
$V = 3669\,(5)$ Å^3	Block, yellow
$Z = 4$	$0.25 \times 0.25 \times 0.20$ mm

Data collection

Siemens SMART area-detector diffractometer	4188 independent reflections

ω rotation scans with narrow frames — 3306 reflections with $I > 2\sigma(I)$

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) — $\theta_{max} = 27.49°$

$T_{min} = 0.124$, $T_{max} = 0.128$

$h = -19 \rightarrow 18$

$k = 0 \rightarrow 17$

$l = 0 \rightarrow 24$

4188 measured reflections

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.055$

$S = 0.919$

4188 reflections

191 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0238P)^2]$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$

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

$\Delta\rho_{max} = 1.22$ e Å^{-3}

$\Delta\rho_{min} = -0.89$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Bi1—N1	2.618 (5)	Bi1—Br3	2.850 (2)
Bi1—Br1	2.772 (2)	Bi1—Br2	2.869 (3)

N1—Bi1—Br1	180	Br1—Bi1—Br2	93.203 (12)
N1—Bi1—Br3	84.872 (11)	Br3—Bi1—Br2	90.68 (3)
Br1—Bi1—Br3	95.128 (11)	C1—N1—Bi1	121.6 (3)

Compound (II)

Crystal data

$(C_5H_6N)_2[BiCl_5(C_5H_5N)]$

$M_r = 625.55$

Orthorhombic, *Pnma*

$a = 18.699 (2)$ Å

$b = 14.889 (3)$ Å

$c = 7.408 (3)$ Å

$V = 2062.4 (9)$ Å^3

$Z = 4$

$D_x = 2.015$ Mg m^{-3}

Mo $K\alpha$ radiation

Cell parameters from 158 reflections

$\theta = 5–25°$

$\mu = 9.199$ mm^{-1}

$T = 173 (2)$ K

Block, yellow

$0.2 \times 0.2 \times 0.2$ mm

Data collection

Siemens SMART area-detector diffractometer

ω rotation scans with narrow frames

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)

$T_{min} = 0.137$, $T_{max} = 0.158$

12 283 measured reflections

2459 independent reflections

1956 reflections with $I > 2\sigma(I)$

$R_{int} = 0.057$

$\theta_{max} = 27.48°$

$h = -24 \rightarrow 24$

$k = -18 \rightarrow 19$

$l = -9 \rightarrow 6$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.052$

$S = 1.068$

2459 reflections

119 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0240P)^2]$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$

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

$\Delta\rho_{max} = 0.77$ e Å^{-3}

$\Delta\rho_{min} = -1.00$ e Å^{-3}

Extinction correction: *SHELXTL* (Siemens, 1995)

Extinction coefficient: 0.00194 (10)

Table 2
Selected geometric parameters (Å, °) for (II).

Bi1—N1	2.536 (5)	Cl1···H2^i	2.80
Bi1—Cl2	2.675 (2)	Cl1···H7^{ii}	2.86
Bi1—Cl1	2.6950 (12)	Cl2···H9^{iii}	2.64
Bi1—Cl4	2.702 (2)	Cl3···H9	2.63
Bi1—Cl3	2.728 (2)	Cl4···H8	2.87

N1—Bi1—Cl2	89.57 (13)	Cl1—Bi1—Cl3	92.73 (3)
N1—Bi1—Cl1	87.30 (3)	Cl4—Bi1—Cl3	90.82 (6)
Cl2—Bi1—Cl1	88.95 (3)	C1—N1—Bi1	121.5 (3)
Cl1^{iv}—Bi1—Cl1	174.21 (5)	Bi1—Cl1···H2^i	164
N1—Bi1—Cl4	87.59 (13)	Bi1—Cl1···H7^{ii}	92
Cl2—Bi1—Cl4	177.16 (5)	H9^v···Cl2—Bi1	125
Cl1—Bi1—Cl4	90.91 (3)	H9···Cl3—Bi1	88
N1—Bi1—Cl3	178.42 (13)	Bi1—Cl4···H8	107
Cl2—Bi1—Cl3	92.01 (6)		

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

H atoms were constrained to idealized geometries and assigned isotropic displacement parameters $1.2U_{iso}$ of their attached carbon for aromatic H atoms and $1.5U_{iso}$ for methyl-H atoms, with the exception of H3 in (I) which was located in the electron-density difference map and the coordinates refined. In (I), the methyl-H atoms on C4 are disordered over the twofold axis.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Siemens, 1995); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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