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Bis(4,4′-bipyridinium) di-μ-bromo-bis[tetrabromobismuthate(III)]

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The crystal structure of the title complex, $(C_{10}H_{10}N_2)_2[BiBr_{10}]$ or $(bipyH_2)_2[Bi_2Br_{10}]$, where $bipyH_2$ is 4,4′-bipyridinium, is built of $bipyH_2$ dications and decabromodibismuthate tetraanions; the latter occupy special positions at inversion centres. The Bi atom in the anion has a distorted octahedral environment. N—H···Br hydrogen bonds link the ions into infinite chains running along the $[1\overline{1}\overline{1}]$ direction.

Key indicators

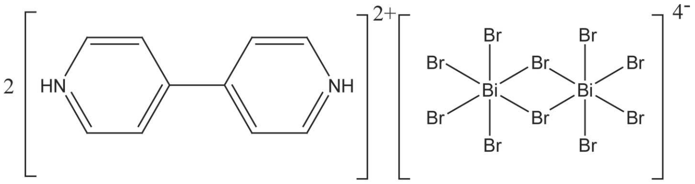
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.015 Å
R factor = 0.038
wR factor = 0.099
Data-to-parameter ratio = 18.3

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

Comment

A number of adducts formed by nitrogen-containing ligands with bismuth(III) salts have been reported (Summers *et al.*, 1994). Recently, however, bismuth(III) coordination chemistry has gained more prominence, particularly in the light of the role of bismuth compounds in ^{212}Bi isotope therapy in cancer research (Sun *et al.*, 1997) and the use of bismuth complexes in the treatment of peptic ulcers (Sun *et al.*, 1997; Baxter, 1992).

In continuation of our studies of metal complexes with nitrogen-containing ligands, as well as of salts of protonated nitrogen ligands with metal-containing anions, we report here the synthesis and structure of the title compound, $(bipyH_2)_2[Bi_2Br_{10}]$, (I) [$bipyH_2$ is 4,4′-bipyridinium].



(I)

The crystal structure of complex (I) is built up of bipyridinium dications and decabromodibismuthate tetraanions; the latter have two octahedra sharing a common edge and occupy special positions with a centre of symmetry at the centre of the Bi_2Br_2 ring. A view of the formula unit, made up of two cations and an anion, is shown in Fig. 1.

The Bi1 coordination environment has the geometry of a substantially distorted octahedron, with the *cis* and *trans* angles in the ranges 84.96 (3)–95.10 (4)° and 174.45 (3)–177.58 (3)°, respectively. The differences in the Bi—Br bond lengths can be attributed to the different environments of the halogen atoms, which may be either bridging (Br5) or terminal (Br1–Br4). The Bi—Br distances are also affected by the function of the halogen atom in the *trans*-position, and may be influenced by the involvement of a Br atom in the N—H···Br

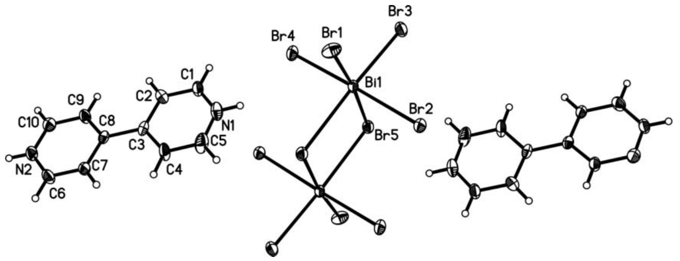


Figure 1
The structure of complex (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Unlabelled atoms are related to the corresponding labelled atoms by inversion [symmetry code $(1 - x, 2 - y, 1 - z)$].

hydrogen bonds (see below). Accordingly, the Bi1—Br5 and Bi1—Br5^{i} bonds [symmetry code: (i) $-x + 1, -y + 2, -z + 1$] are the longest [2.9897 (11) and 3.0912 (11) Å, respectively], while the corresponding *trans* distances Bi1—Br1 and Bi1—Br3 are the shortest in the Bi1 coordination environment [2.7140 (12) and 2.7512 (11) Å, respectively].

The two pyridinium rings in the cation of (I) are nearly coplanar, the angle formed by their mean planes being only 4.6 (3)°.

The crystal packing of (I) is characterized by N—H···Br hydrogen bonding, as shown in Fig. 2. The geometry of the hydrogen bonds is summarized in Table 2. The N—H···Br bonds link the ions into infinite chains running along the $[1\overline{1}\overline{1}]$ direction.

Experimental

Bismuth tribromide (0.5 mmol) was dissolved in dichloromethane (20 ml) and 4,4′-bipyridine (0.5 mmol) was added with stirring at room temperature. The pale-yellow crystals which precipitated after a few days were filtered off, washed with acetone and dried under a vacuum (yield 79%; m.p. 408 K). Analysis, calculated for $C_{20}H_{20}Bi_2Br_{10}N_4$ (M_r = 1533.4): C 15.67, H 1.31, N 3.65%; found: C 15.89, H 1.44, N 3.30%.

Crystal data

$(C_{10}H_{10}N_2)_2[Bi_2Br_{10}]$
$M_r = 1533.4$
Triclinic, $P\overline{1}$
$a = 8.5435$ (18) Å
$b = 10.191$ (2) Å
$c = 11.344$ (2) Å
$\alpha = 113.609$ (3)°
$\beta = 100.661$ (3)°
$\gamma = 99.411$ (3)°
$V = 857.9$ (3) Å^3
$Z = 1$
$D_x = 2.968$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 21.91$ mm^{-1}
$T = 298$ (2) K
Block, yellow
0.13 × 0.13 × 0.12 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.163$, $T_{max} = 0.178$ (expected range = 0.066–0.072)
4547 measured reflections
2991 independent reflections
2364 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 25.0$°

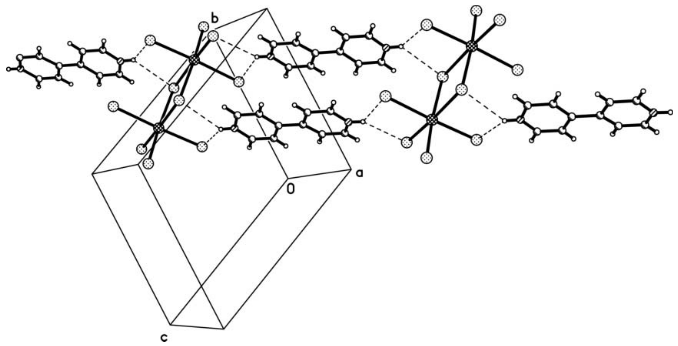


Figure 2
Ionic chains in the crystal structure of (I). Intermolecular hydrogen bonds are shown as dashed lines.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.099$
$S = 1.00$
2991 reflections
163 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 2.56$ e Å^{-3}
$\Delta\rho_{min} = -1.96$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Bi1—Br1	2.7140 (12)	Bi1—Br4	2.7856 (12)
Bi1—Br2	2.9149 (12)	Bi1—Br5	2.9897 (11)
Bi1—Br3	2.7512 (11)	Bi1—Br5^{i}	3.0912 (11)
Br1—Bi1—Br3	95.10 (4)	Br4—Bi1—Br5	88.15 (3)
Br1—Bi1—Br4	90.04 (4)	Br2—Bi1—Br5	90.82 (3)
Br3—Bi1—Br4	92.08 (3)	Br1—Bi1—Br5^{i}	174.45 (3)
Br1—Bi1—Br2	92.16 (4)	Br3—Bi1—Br5^{i}	89.80 (3)
Br3—Bi1—Br2	88.75 (3)	Br4—Bi1—Br5^{i}	87.18 (3)
Br4—Bi1—Br2	177.58 (3)	Br2—Bi1—Br5^{i}	90.54 (3)
Br1—Bi1—Br5	90.16 (4)	Br5—Bi1—Br5^{i}	84.96 (3)
Br3—Bi1—Br5	174.73 (3)	Bi1—Br5—Bi1^{i}	95.04 (3)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Br4	0.86	2.77	3.449 (9)	137
N1—H1···Br5	0.86	2.91	3.519 (9)	130
N2—H2···Br2^{ii}	0.86	2.77	3.418 (8)	134
N2—H2···Br3^{ii}	0.86	2.78	3.444 (9)	135

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

All H atoms were positioned geometrically (C—H = 0.93 Å and N—H = 0.88 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}$(carrier). The highest peak and deepest hole in the final difference map are at distances of 1.00 and 1.02 Å from Bi1, respectively.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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References

Baxter, G. F. (1992). *Chem. Br.* **28**, 445–458.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*a*). *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Summers, S. P., Abboud, K. A., Farrah, S. R. & Palenik, G. J. (1994). *Inorg. Chem.* **33**, 88–92.
Sun, H., Li, H. & Sadler, P. J. (1997). *Chem. Ber.* **130**, 669–702.

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