

Jonathan P. H. Charmant,*
Nicholas C. Norman and
Jonathan StarbuckSchool of Chemistry, University of Bristol, Bristol
BS8 1TS, EnglandCorrespondence e-mail:
jon.charmant@bris.ac.uk

Key indicators

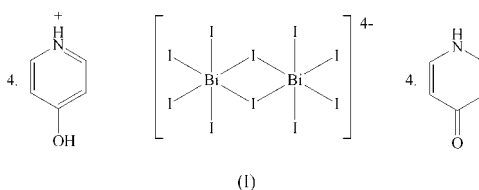
Single-crystal X-ray study
 $T = 173\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.018\text{ \AA}$
 R factor = 0.046
 wR factor = 0.102
Data-to-parameter ratio = 22.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.A bis[pentaiodobismuthate(III)] salt of
4-hydroxypyridinium

The crystal structure of tetra(4-hydroxypyridinium) di- μ -iodo-bis[tetraiodobismuthate(III)] 4-pyridone tetrasolvate, $(\text{C}_5\text{H}_6\text{NO})_4[\text{Bi}_2\text{I}_{10}]\cdot 4\text{C}_5\text{H}_5\text{NO}$, has been determined. The structure contains discrete centrosymmetric $[\text{Bi}_2\text{I}_{10}]^{4-}$ anions enclosed in a hydrogen-bonded array of 4-hydroxypyridinium cations and 4-pyridone molecules.

Received 1 February 2002
Accepted 15 February 2002
Online 15 March 2002

Comment

The chemistry of iodoantimonate and iodobismuthate anions has been an area of some interest (Fisher & Norman, 1994). Iodobismuthate anions exhibit considerable structural variety and examples of both polymeric (Carmalt *et al.*, 1995; Geiser *et al.*, 1990; Krautscheid, 1995; Rogers *et al.*, 1992) and oligomeric (Clegg *et al.*, 1991; Eickmeier *et al.*, 1999; Krautscheid, 1994; Kubiak & Ejsmont, 1999) forms are known. Of the numerous counter-cations present, we note, in relation to this study, a dinuclear iodobismuthate with a hydrogen-bonded cation, namely $[2,2'\text{-Hbipy}]_4[\text{Bi}_2\text{I}_{10}]$ (Bowmaker *et al.*, 1998). Herein we report the structure of a dinuclear iodobismuthate, (I), in which the 4-hydroxypyridinium cations form a hydrogen-bonded network with neutral 4-pyridone molecules.



One of the products of the reaction of 4-pyridone and diiodophenylbismuth(III) in tetrahydrofuran (THF) is the title compound, a salt containing a dimeric periodobismuth tetra-anion and a 1:1 mixture of hydroxypyridinium counterions and 4-pyridone starting material (Fig. 1). The hydrogen bonding shown in Fig. 1, combined with interactions between $\text{H}2\text{A}$ and $\text{O}4(1-x, 2-y, 2-z)$, gives rise to a hydrogen-bonded set of close-packed ribbons of 4-hydroxypyridinium cations and 4-pyridone molecules (Fig. 2) into which the anions are incorporated. Hydrogen-bond $\text{N}\cdots\text{O}$ and $\text{O}\cdots\text{O}$ distances within the ribbons range from 2.518 (11) to 2.715 (12) Å. Much weaker interactions are seen between the ribbons and the iodo ligands of the bismuthate anions; the shortest $\text{N}\cdots\text{I}$ hydrogen-bonding contact is 3.627 (9) Å (Table 2).

Experimental

Crystals of the title compound were obtained as a minor product from the reaction between BiI_2Ph (0.100 g, 0.185 mmol) and 4-pyridone (0.020 g, 0.21 mmol), both dissolved in THF, to which an overlay of

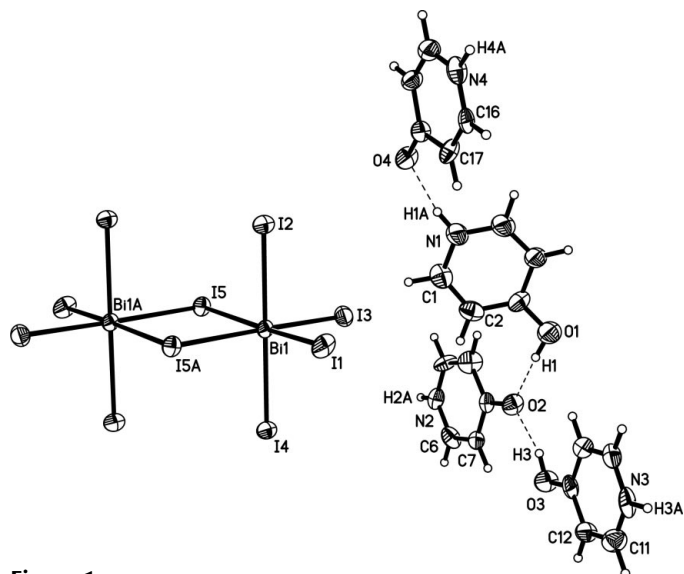


Figure 1
The molecular structure of the title compound, showing 50% probability displacement ellipsoids. Hydrogen bonds are shown as dashed lines.

hexane was added. Solvent diffusion over a period of some days at room temperature afforded a small quantity of red crystals.

Crystal data

$(C_5H_6NO)_4[Bi_2I_{10}] \cdot 4C_5H_5NO$
 $M_r = 2451.80$
 Triclinic, $P\bar{1}$
 $a = 10.366$ (3) Å
 $b = 12.362$ (3) Å
 $c = 13.504$ (5) Å
 $\alpha = 116.212$ (13)°
 $\beta = 95.05$ (2)°
 $\gamma = 92.914$ (16)°
 $V = 1538.6$ (8) Å³

$Z = 1$
 $D_x = 2.646$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5958 reflections
 $\theta = 2-25^\circ$
 $\mu = 10.78$ mm⁻¹
 $T = 173$ (2) K
 Lath, red
 $0.15 \times 0.05 \times 0.02$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans with 0.3° frames
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.440$, $T_{\max} = 0.810$
 15998 measured reflections

6960 independent reflections
 4015 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.061$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -13 \rightarrow 12$
 $k = -16 \rightarrow 16$
 $l = -17 \rightarrow 17$

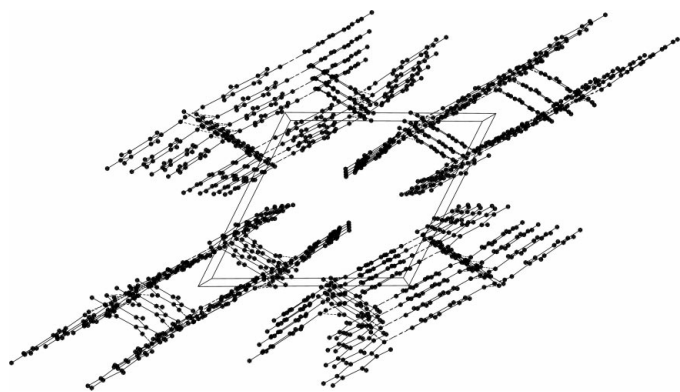


Figure 2
Packing diagram, viewed down the a axis, showing hydrogen-bonded ribbons of 4-pyridone and 4-hydroxypyridinium. The bismuth-containing anions have been omitted for clarity.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.102$
 $S = 0.90$
 6960 reflections
 307 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0377P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.87$ e Å⁻³
 $\Delta\rho_{\text{min}} = -2.67$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Bi1—I1	2.9657 (12)	O4—C18	1.279 (13)
Bi1—I3	3.0082 (12)	C1—C2	1.379 (17)
Bi1—I4	3.0502 (13)	C2—C3	1.391 (16)
Bi1—I2	3.1056 (13)	C3—C4	1.390 (17)
Bi1—I5	3.2099 (12)	C4—C5	1.355 (17)
Bi1—I5 ⁱ	3.2197 (12)	C6—C7	1.355 (15)
I5—Bi1 ⁱ	3.2197 (12)	C7—C8	1.408 (16)
N1—C1	1.324 (15)	C8—C9	1.416 (16)
N1—C5	1.329 (15)	C9—C10	1.341 (16)
N2—C10	1.343 (14)	C11—C12	1.356 (16)
N2—C6	1.374 (15)	C12—C13	1.377 (16)
N3—C11	1.335 (16)	C13—C14	1.427 (16)
N3—C15	1.345 (15)	C14—C15	1.355 (16)
N4—C20	1.340 (14)	C16—C17	1.357 (16)
N4—C16	1.341 (15)	C17—C18	1.439 (15)
O1—C3	1.329 (14)	C18—C19	1.424 (16)
O2—C8	1.311 (13)	C19—C20	1.359 (16)
O3—C13	1.317 (13)		
I1—Bi1—I3	95.43 (4)	I4—Bi1—I5	92.67 (3)
I1—Bi1—I4	91.10 (3)	I2—Bi1—I5	90.28 (3)
I3—Bi1—I4	88.77 (4)	I1—Bi1—I5 ⁱ	86.95 (4)
I1—Bi1—I2	85.81 (3)	I3—Bi1—I5 ⁱ	177.04 (3)
I3—Bi1—I2	93.51 (4)	I4—Bi1—I5 ⁱ	89.43 (4)
I4—Bi1—I2	176.31 (3)	I2—Bi1—I5 ⁱ	88.40 (4)
I1—Bi1—I5	174.51 (3)	I5—Bi1—I5 ⁱ	89.09 (4)
I3—Bi1—I5	88.65 (4)	Bi1—I5—Bi1 ⁱ	90.91 (4)

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1A \cdots O4	0.88	1.78	2.646 (14)	168
N2—H2A \cdots O4 ⁱ	0.88	1.87	2.715 (12)	160
N3—H3A \cdots I2 ⁱⁱ	0.88	3.29	3.870 (11)	126
N3—H3A \cdots I4 ⁱⁱⁱ	0.88	2.87	3.633 (10)	147
N4—H4A \cdots I1 ^{iv}	0.88	3.25	3.898 (11)	133
N4—H4A \cdots I2 ^{iv}	0.88	2.89	3.627 (9)	144
O1—H1 \cdots O2	0.84	1.75	2.567 (12)	164
O3—H3 \cdots O2	0.84	1.70	2.518 (11)	163

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

The hydroxyl H atoms were assigned to the rings in which the bond lengths show the least deviation from aromaticity (Table 1). These H atoms could not be located in a difference map and were assigned fixed positions in the plane of the pyridinium ring appropriate for hydrogen bonding to nearby acceptors, using the AFIX 83 instruction in *SHELXTL* (Bruker, 1998); $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. All other H atoms were constrained to ideal geometries and assigned isotropic displacement parameters 1.2 times those of their parent C atoms. The highest residual electron-density peak is found 0.92 Å from Bi1. Other residual electron-density peaks with values in the range $1.17-1.58$ e Å⁻³ are also found near the Bi1 atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SHELXTL* (Bruker, 1998);

program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We would like to thank the Cambridge Crystallographic Data Centre for project studentship funding (JS).

References

- Bowmaker, G. A., Junk, P. C., Lee, A. M., Skelton, B. W. & White, A. H. (1998). *Aust. J. Chem.* **51**, 293–309.
- Bruker (1998). *SMART*, *SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Carmalt, C. J., Farrugia, L. J. & Norman, N. C. (1995). *Z. Naturforsch. Teil B*, **50**, 1591–1596.
- Clegg, W., Errington, R. J., Fisher, G. A., Green, M. E., Hockless, D. C. R. & Norman, N. C. (1991). *Chem. Ber.* **124**, 2457–2459.
- Eickmeier, H., Jaschinski, B., Hepp, A., Nuss, J., Reuter, H. & Blachnik, R. (1999). *Z. Naturforsch. Teil B*, **54**, 305–313.
- Fisher, G. A. & Norman, N. C. (1994). *Adv. Inorg. Chem.* **41**, 233–271.
- Geiser, U., Wang, H. H., Budz, S. M., Lowry, M. J., Williams, J. M. Ren, J. & Whangbo, M.-H. (1990). *Inorg. Chem.* **29**, 1611–1614.
- Krautscheid, H. (1994). *Z. Anorg. Allg. Chem.* **620**, 1559–1564.
- Krautscheid, H. (1995). *Z. Anorg. Allg. Chem.* **621**, 2049–2054.
- Kubiak, R. & Ejsmont, K. (1999). *J. Mol. Struct.* **474**, 275–281.
- Rogers, R. D., Bond, A. H., Aguinaga, S. & Reyes, A. (1992). *J. Am. Chem. Soc.* **114**, 2967–2977.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.