



Synthesis and structural studies of a new complex of *catena*-poly[*p*-anisidinium [[diiodidobismuthate(III)]-di- μ -iodido] dihydrate]

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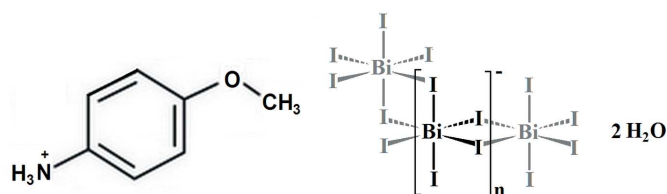
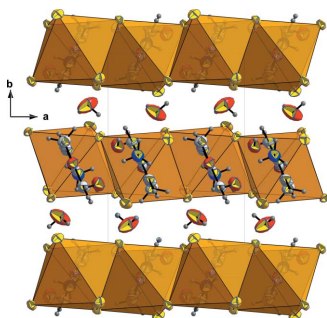
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A new organic–inorganic hybrid material, $\{(C_7H_{10}NO)[BiI_4] \cdot 2H_2O\}_n$, has been synthesized by slow evaporation of an aqueous solution at room temperature. The anionic sublattice of the crystal is built up by [BiI₆] octahedra sharing edges. The resulting zigzag chains extend along the *a*-axis direction and are arranged in a distorted hexagonal rod packing. The *p*-anisidinium cations and the water molecules are located in the voids of the anionic sublattice. The cations are linked to each other through N–H···O hydrogen bonds with the water molecules, and also through weaker N–H···I interactions to the anionic inorganic layers.

1. Chemical context

Previous X-ray structural studies showed that halogenido-bismuthate(III) complexes may contain an array of variously self-organized halobismuthate anions since different polynuclear species can be formed through oligomerization by halide bridging (Bowmaker *et al.*, 1998; Benetollo *et al.*, 1998; Alonzo *et al.*, 1999).

In general, the coordination sphere of bismuth appears to be dominated by an hexacoordination tendency with polybismuthate species arising from corner-, edge- or face-sharing [BiX₆] distorted octahedra. If the anionic sublattice dimensionality is clearly determined by the counter-cations, the effects of their most evident properties such as charge, size and shape are not predictable. Organic cations resulting from protonated nitrogen functionalities may provide a rich family of salts where the factors cited above could be varied rationally. In addition, since the important contribution to the lattice stabilization in the crystalline state is due to hydrogen-bonding interactions, it should be possible to influence the bismuth coordination geometry by changing the number and orientation of the hydrogen-bond donor sites of the cations. In an effort to increase the size of the [BiX₆] octahedra, iodine was used in the chemical synthesis.



2. Structural commentary

The principal building blocks of the title compound are octahedral iodidobismuthate [BiI₆] units, *p*-anisidinium

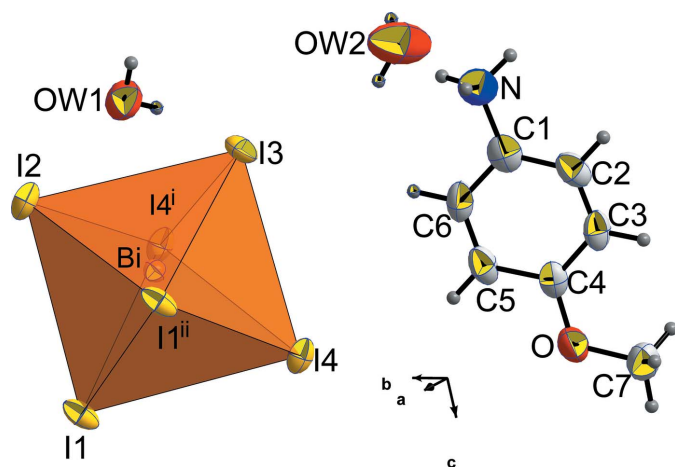


Figure 1
Representation of the structural units of $(C_7H_{10}NO)[BiI_4] \cdot 2H_2O$, with 50% probability displacement ellipsoids. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $2-x, 1-y, 1-z$.]

cations and two water molecules (Fig. 1). The anionic sublattice of the crystal is built of one-dimensional zigzag chains extending along the a -axis direction and composed of $[BiI_6]$ octahedra sharing edges as shown in Fig. 2. The one-dimensional secondary building unit (SBU) topology observed in the described structure is one of the most common and stable ones (Billing & Lemmerer, 2006) in bismuth halide hybrids. The shortest Bi–Bi distance [4.590 (1) Å] observed is in agreement with homologous structures having the same one-dimensional topology. The octahedral bismuth coordination is almost regular, proving the stereochemical inactivity of the $Bi^{3+} 6s^2$ electron lone pair. Furthermore, among the six octa-

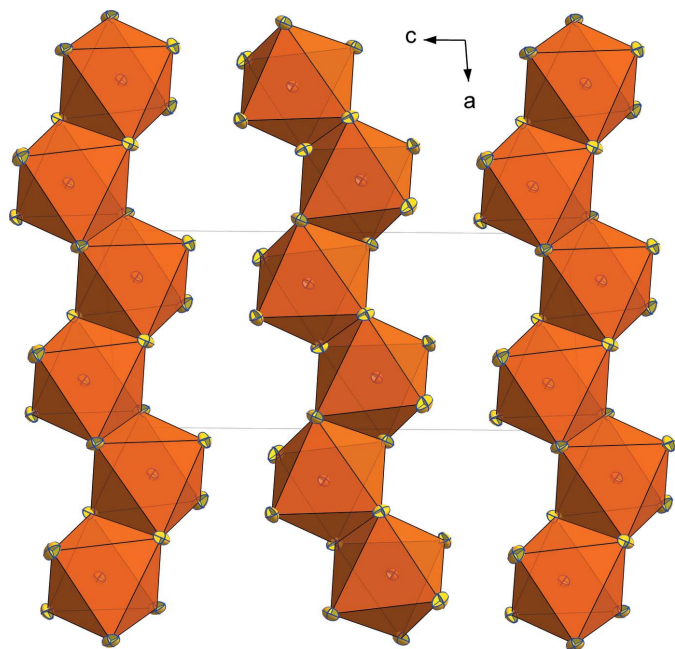


Figure 2
View of the anionic framework in the structure of $(C_7H_{10}NO)[BiI_4] \cdot 2H_2O$, showing the zigzag chains running along the a -axis direction.

Table 1
Selected bond lengths (Å).

| | | | |
|--------------------|------------|---------------------|------------|
| Bi–I2 | 2.8938 (7) | Bi–I1 ⁱⁱ | 3.1390 (8) |
| Bi–I3 | 2.9850 (7) | Bi–I1 | 3.1842 (8) |
| Bi–I4 ⁱ | 3.0184 (8) | Bi–I4 | 3.3238 (7) |

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

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

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|------------------------------------|-------|--------------|--------------|----------------|
| N–HA \cdots I3 ⁱⁱⁱ | 0.89 | 2.77 | 3.658 (10) | 176 |
| N–HB \cdots OW1 ^{iv} | 0.89 | 1.97 | 2.762 (12) | 147 |
| N–HC \cdots OW2 | 0.89 | 1.88 | 2.704 (14) | 154 |
| OW1–HW1A \cdots I3 | 0.85 | 2.77 | 3.604 (7) | 167 |
| OW2–HW2A \cdots I1 ⁱ | 0.85 | 3.23 | 3.817 (10) | 129 |
| OW2–HW2A \cdots I3 | 0.85 | 3.20 | 3.850 (12) | 135 |
| OW2–HW2B \cdots OW1 ^v | 0.85 | 2.32 | 2.925 (13) | 129 |

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

hedral vertices, two are monocoordinated with short bond lengths (I2 and I3), while the four others (I4, I1 and symmetry-related atoms) are bicoordinated exhibiting long bond lengths (Table 1).

In Fig. 3, it can be seen that each $[BiI_6]$ octahedron is linked to one p -anisidinium cation and a water molecule OW1 *via* $I3 \cdots HA-N$ and $I3 \cdots HW1A-OW1$ hydrogen bonds.

The p -anisidinium cation is adopting a quite planar configuration characterized by a slight r.m.s. deviation of 0.020 (9) Å. Each p -anisidinium cation interacts with one $[BiI_6]$ octahedron *via* $N-HA \cdots I3^i$ ($\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$), with two water molecules by $N-HB \cdots OW1^{ii}$ ($\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$) and $N-HC \cdots OW2$ hydrogen bonds (Table 2), as shown in Fig. 4.

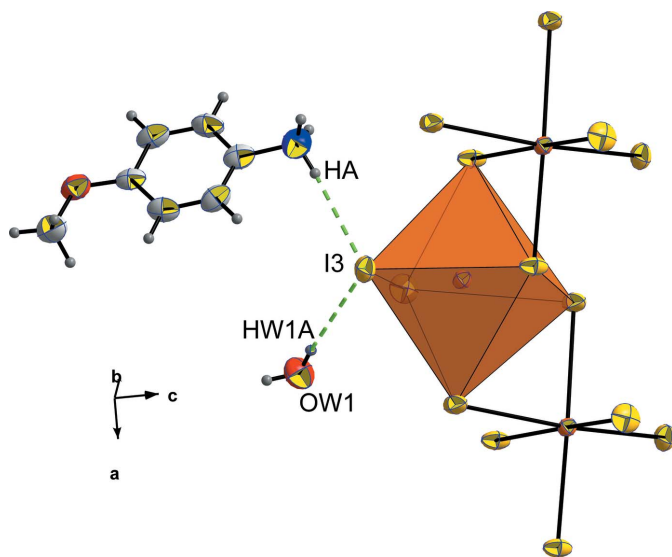


Figure 3
The environment of the $[BiI_6]$ octahedron in the structure of $(C_7H_{10}NO)[BiI_4] \cdot 2H_2O$. [Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.]

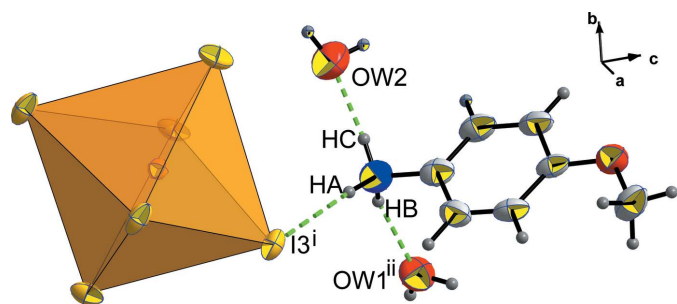


Figure 4
The environment of the *p*-anisidinium cation in the structure of $(C_7H_{10}NO)[BiI_4] \cdot 2H_2O$. [Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$.]

3. Supramolecular features

The role of the water molecules is crucial in the crystal cohesion. In fact, OW1 is engaged in three hydrogen bonds to one organic cation, one $[BiI_6]$ octahedra and one water molecule *via* $OW1 \cdots HB^i - N^i$, $OW1 - HW1A \cdots I3$ and $OW1 \cdots HW2B^{ii} - OW2^{ii}$, respectively, as shown in Fig. 5 [symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $x + 1, y, z$]. The second water molecule OW2 is linked to OW1 by $OW2 - HW2B \cdots OW1(-1 + x, y, z)$ and to the *p*-anisidinium cation by $N - HC \cdots OW2$ hydrogen bonds as shown in Fig. 6. The role of this water molecule can be seen better in Fig. 7 where molecular stacking along the *b* axis is observed, leaving an empty interlayer space where OW2 molecules are located, ensuring a strong link between organic and inorganic sheets.

There are two types of hydrogen bonds, the first one has nitrogen as the donor with iodine as an acceptor to form $N - H \cdots I$ bonds. The second type has nitrogen as the donor with oxygen as an acceptor to form $N - H \cdots O$ bonds. All these bonds are listed in Table 2. We have to note that HW2A is not involved in hydrogen bonding.

4. Database survey

A systematic search procedure in the Cambridge Structural Database (Version 5.36; Groom & Allen, 2014) based on the *p*-anisidinium cation scheme gives a total of 25 hits. Only two are hybrid compounds: $(C_7H_{10}NO)_4^+ [BiCl_6]_4^{3-} \cdot Cl^- \cdot H_2O$ (Liu,

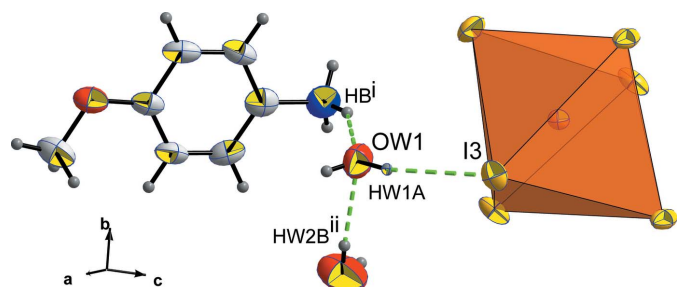


Figure 5
The environment of the OW1 water molecule. [Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $x + 1, y, z$.]

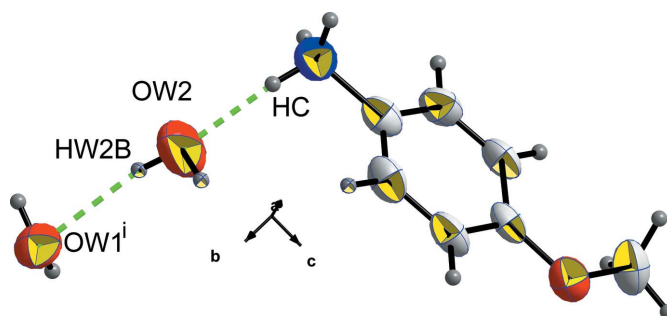


Figure 6
The environment of the OW2 water molecule. [Symmetry code: (i) $-1 + x, y, z$.]

2012) and $(C_7H_{10}NO)_{2n}^+ [Pb_3I_8]_n^{2-} \cdot 2nH_2O$ (Prakash *et al.*, 2009).

5. Synthesis and crystallization

The title compound was synthesized by dissolving stoichiometric amounts of bismuth(III) iodide in *p*-anisidine in a mixture of water and HI. The resulting solution was stirred well and kept at room temperature. Bright-red prismatic crystals were grown by slow evaporation in a couple of weeks. The purity of the synthesized compound was improved by successive recrystallization processes.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The hydrogen atoms were located

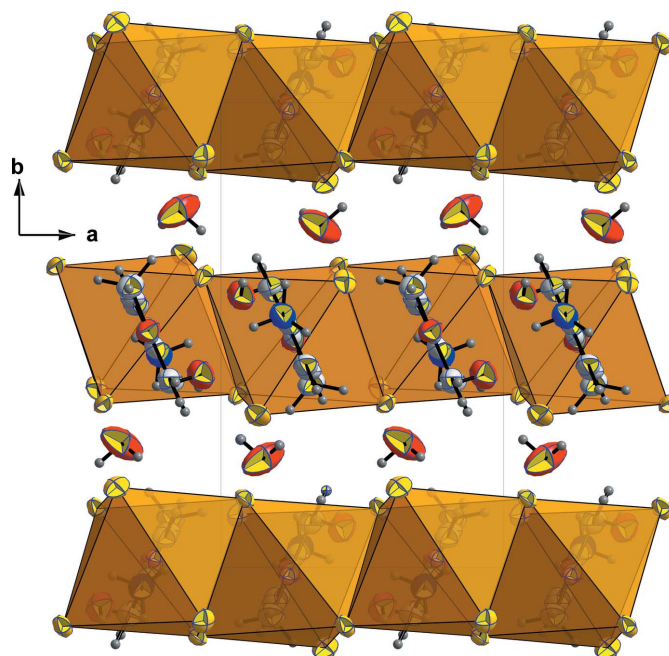


Figure 7
The molecular stacking along the *b* axis, showing the empty interlayer space where the OW2 water molecules are located.

Table 3
Experimental details.

| | |
|---|--|
| Crystal data | |
| Chemical formula | (C ₇ H ₁₀ NO)[BiI ₄] \cdot 2H ₂ O |
| <i>M_r</i> | 876.77 |
| Crystal system, space group | Monoclinic, <i>P</i> 2 ₁ / <i>n</i> |
| Temperature (K) | 293 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 7.779 (2), 12.747 (2), 18.252 (3) |
| β (°) | 94.97 (1) |
| <i>V</i> (Å ³) | 1803.0 (6) |
| <i>Z</i> | 4 |
| Radiation type | Mo <i>K</i> α |
| μ (mm ⁻¹) | 16.62 |
| Crystal size (mm) | 0.6 \times 0.2 \times 0.1 |
| Data collection | |
| Diffractometer | Enraf–Nonius CAD-4 |
| Absorption correction | ψ scan (North <i>et al.</i> , 1968) |
| <i>T</i> _{min} , <i>T</i> _{max} | 0.014, 0.036 |
| No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections | 5050, 3923, 3064 |
| <i>R</i> _{int} | 0.035 |
| (<i>sin</i> θ / λ) _{max} (Å ⁻¹) | 0.639 |
| Refinement | |
| <i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.035, 0.080, 1.05 |
| No. of reflections | 3923 |
| No. of parameters | 147 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³) | 1.68, -2.01 |

Computer programs: *CAD-4 EXPRESS* (Enraf–Nonius, 1994), *XCAD4* (Harms & Wocadlo, 1995), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2008) and *pubCIF* (Westrip, 2010).

in difference Fourier maps. Those attached to carbon were placed in calculated positions (C–H = 0.90–1.00 Å) while those attached to nitrogen were placed in experimental positions and their coordinates adjusted to give N–H = 0.89 Å. All were included as riding on their parent atoms with isotropic displacement parameters 1.2–1.5 times those of the parent atoms. Hydrogen positions for the water molecules

were partly located from a Fourier difference map and partly placed based on geometrical considerations. They are not of sufficient precision to refine the hydrogen-atom positions for the water molecules with angle and distance restraints and they were therefore treated as riding on their parent oxygen atoms.

Acknowledgements

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Acta Cryst. (2015). E71, 1352-1355 [https://doi.org/10.1107/S2056989015019489]

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Computing details

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

catena-Poly[*p*-anisidinium [[diiodidobismuthate(III)]-di- μ -iodido] dihydrate]

Crystal data

(C₇H₁₀NO)[BiI₄]·2H₂O

$M_r = 876.77$

Monoclinic, $P2_1/n$

$a = 7.779$ (2) Å

$b = 12.747$ (2) Å

$c = 18.252$ (3) Å

$\beta = 94.97$ (1)°

$V = 1803.0$ (6) Å³

$Z = 4$

$F(000) = 1528$

$D_x = 3.230$ Mg m⁻³

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

Cell parameters from 25 reflections

$\theta = 10$ – 15°

$\mu = 16.62$ mm⁻¹

$T = 293$ K

Prism, red

$0.6 \times 0.2 \times 0.1$ mm

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega/2\theta$ scans

Absorption correction: ψ scan
(North *et al.*, 1968)

$T_{\min} = 0.014$, $T_{\max} = 0.036$

5050 measured reflections

3923 independent reflections

3064 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

$\theta_{\max} = 27.0^\circ$, $\theta_{\min} = 2.2^\circ$

$h = -9 \rightarrow 1$

$k = -1 \rightarrow 16$

$l = -23 \rightarrow 23$

2 standard reflections every 120 min

intensity decay: 1%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.080$

$S = 1.05$

3923 reflections

147 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0317P)^2 + 8.0053P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 1.68 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -2.01 \text{ e } \text{Å}^{-3}$$

Special details

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 (Å²)

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{iso} [*] / <i>U</i> _{eq} |
|------|-------------|-------------|-------------|---|
| Bi | 0.73731 (4) | 0.51922 (2) | 0.43418 (2) | 0.02320 (9) |
| I1 | 0.93941 (7) | 0.62637 (5) | 0.57383 (3) | 0.03934 (16) |
| I2 | 0.86930 (9) | 0.67240 (5) | 0.33633 (4) | 0.04831 (18) |
| I3 | 0.56183 (8) | 0.38519 (5) | 0.31619 (3) | 0.04102 (16) |
| I4 | 0.58407 (7) | 0.35207 (5) | 0.55223 (3) | 0.03656 (15) |
| N | 0.2818 (12) | 0.0413 (8) | 0.2801 (5) | 0.059 (2) |
| HA | 0.1983 | 0.0059 | 0.2544 | 0.071* |
| HB | 0.3839 | 0.0176 | 0.2689 | 0.071* |
| HC | 0.2726 | 0.1092 | 0.2690 | 0.071* |
| C1 | 0.2662 (13) | 0.0267 (9) | 0.3590 (6) | 0.048 (3) |
| C2 | 0.1996 (13) | -0.0648 (9) | 0.3862 (6) | 0.051 (3) |
| H2 | 0.1622 | -0.1179 | 0.3536 | 0.061* |
| C3 | 0.1880 (13) | -0.0783 (8) | 0.4581 (6) | 0.047 (2) |
| H3 | 0.1400 | -0.1396 | 0.4750 | 0.056* |
| C4 | 0.2466 (12) | -0.0020 (7) | 0.5077 (6) | 0.040 (2) |
| C5 | 0.3162 (13) | 0.0920 (8) | 0.4821 (6) | 0.050 (3) |
| H5 | 0.3546 | 0.1446 | 0.5148 | 0.060* |
| C6 | 0.3261 (13) | 0.1043 (8) | 0.4071 (6) | 0.051 (3) |
| H6 | 0.3734 | 0.1651 | 0.3892 | 0.061* |
| C7 | 0.1791 (15) | -0.1049 (9) | 0.6110 (6) | 0.062 (3) |
| H7A | 0.0657 | -0.1186 | 0.5879 | 0.093* |
| H7B | 0.1738 | -0.0991 | 0.6632 | 0.093* |
| H7C | 0.2550 | -0.1613 | 0.6006 | 0.093* |
| O | 0.2425 (9) | -0.0092 (6) | 0.5833 (4) | 0.0522 (18) |
| OW1 | 0.9289 (10) | 0.4148 (6) | 0.2103 (4) | 0.063 (2) |
| HW1A | 0.8384 | 0.3981 | 0.2307 | 0.095* |
| HW1B | 0.9222 | 0.3883 | 0.1675 | 0.095* |
| OW2 | 0.1501 (15) | 0.2339 (8) | 0.2484 (5) | 0.110 (4) |
| HW2A | 0.1889 | 0.2855 | 0.2745 | 0.166* |
| HW2B | 0.0502 | 0.2499 | 0.2291 | 0.166* |

Atomic displacement parameters (Å²)

| | <i>U</i> ¹¹ | <i>U</i> ²² | <i>U</i> ³³ | <i>U</i> ¹² | <i>U</i> ¹³ | <i>U</i> ²³ |
|----|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Bi | 0.02239 (16) | 0.02297 (16) | 0.02394 (14) | -0.00093 (13) | 0.00020 (11) | -0.00034 (12) |
| I1 | 0.0305 (3) | 0.0385 (3) | 0.0470 (3) | 0.0095 (3) | -0.0082 (2) | -0.0207 (3) |

| | | | | | | |
|-----|------------|------------|------------|-------------|-------------|-------------|
| I2 | 0.0548 (4) | 0.0413 (4) | 0.0509 (4) | -0.0060 (3) | 0.0163 (3) | 0.0164 (3) |
| I3 | 0.0403 (3) | 0.0472 (4) | 0.0342 (3) | -0.0063 (3) | -0.0044 (2) | -0.0136 (3) |
| I4 | 0.0313 (3) | 0.0287 (3) | 0.0509 (3) | 0.0086 (2) | 0.0110 (3) | 0.0120 (3) |
| N | 0.056 (6) | 0.059 (6) | 0.061 (6) | 0.007 (5) | 0.001 (5) | 0.001 (5) |
| C1 | 0.034 (5) | 0.045 (6) | 0.066 (7) | 0.008 (5) | 0.001 (5) | -0.001 (5) |
| C2 | 0.050 (6) | 0.040 (6) | 0.060 (7) | 0.002 (5) | -0.007 (5) | -0.012 (5) |
| C3 | 0.046 (6) | 0.025 (5) | 0.069 (7) | 0.000 (4) | 0.005 (5) | 0.002 (5) |
| C4 | 0.027 (5) | 0.030 (5) | 0.063 (6) | 0.005 (4) | -0.001 (4) | 0.005 (4) |
| C5 | 0.045 (6) | 0.028 (5) | 0.073 (7) | -0.001 (5) | -0.010 (5) | -0.002 (5) |
| C6 | 0.045 (6) | 0.034 (6) | 0.073 (7) | -0.006 (5) | 0.005 (5) | 0.010 (5) |
| C7 | 0.060 (7) | 0.052 (7) | 0.071 (8) | -0.008 (6) | -0.010 (6) | 0.018 (6) |
| O | 0.051 (4) | 0.042 (4) | 0.062 (5) | -0.007 (3) | -0.006 (4) | 0.000 (4) |
| OW1 | 0.063 (5) | 0.068 (5) | 0.061 (5) | -0.007 (4) | 0.019 (4) | 0.004 (4) |
| OW2 | 0.135 (9) | 0.091 (8) | 0.098 (8) | 0.041 (7) | -0.029 (7) | -0.005 (6) |

Geometric parameters (Å, °)

| | | | |
|--------------------------------------|------------|----------|------------|
| Bi—I2 | 2.8938 (7) | C3—C4 | 1.379 (14) |
| Bi—I3 | 2.9850 (7) | C3—H3 | 0.9300 |
| Bi—I4 ⁱ | 3.0184 (8) | C4—O | 1.386 (13) |
| Bi—I1 ⁱⁱ | 3.1390 (8) | C4—C5 | 1.410 (14) |
| Bi—I1 | 3.1842 (8) | C5—C6 | 1.387 (15) |
| Bi—I4 | 3.3238 (7) | C5—H5 | 0.9300 |
| I1—Bi ⁱⁱ | 3.1390 (8) | C6—H6 | 0.9300 |
| I4—Bi ⁱ | 3.0184 (8) | C7—O | 1.425 (12) |
| N—C1 | 1.468 (14) | C7—H7A | 0.9600 |
| N—HA | 0.8900 | C7—H7B | 0.9600 |
| N—HB | 0.8900 | C7—H7C | 0.9600 |
| N—HC | 0.8900 | OW1—HW1A | 0.8518 |
| C1—C6 | 1.376 (15) | OW1—HW1B | 0.8479 |
| C1—C2 | 1.386 (15) | OW2—HW2A | 0.8511 |
| C2—C3 | 1.336 (14) | OW2—HW2B | 0.8499 |
| C2—H2 | 0.9300 | | |
| I2—Bi—I3 | 96.05 (2) | C2—C1—N | 121.5 (10) |
| I2—Bi—I4 ⁱ | 91.41 (2) | C3—C2—C1 | 121.3 (10) |
| I3—Bi—I4 ⁱ | 92.30 (2) | C3—C2—H2 | 119.4 |
| I2—Bi—I1 ⁱⁱ | 92.39 (2) | C1—C2—H2 | 119.4 |
| I3—Bi—I1 ⁱⁱ | 86.92 (2) | C2—C3—C4 | 120.5 (10) |
| I4 ⁱ —Bi—I1 ⁱⁱ | 176.18 (2) | C2—C3—H3 | 119.8 |
| I2—Bi—I1 | 91.58 (2) | C4—C3—H3 | 119.8 |
| I3—Bi—I1 | 170.46 (2) | C3—C4—O | 124.8 (9) |
| I4 ⁱ —Bi—I1 | 93.21 (2) | C3—C4—C5 | 119.8 (10) |
| I1 ⁱⁱ —Bi—I1 | 87.07 (2) | O—C4—C5 | 115.4 (9) |
| I2—Bi—I4 | 177.35 (2) | C6—C5—C4 | 118.6 (10) |
| I3—Bi—I4 | 86.19 (2) | C6—C5—H5 | 120.7 |
| I4 ⁱ —Bi—I4 | 87.08 (2) | C4—C5—H5 | 120.7 |
| I1 ⁱⁱ —Bi—I4 | 89.14 (2) | C1—C6—C5 | 120.3 (10) |

| | | | |
|-------------------------|------------|---------------|-----------|
| I1—Bi—I4 | 86.33 (2) | C1—C6—H6 | 119.9 |
| Bi ⁱⁱ —I1—Bi | 92.93 (2) | C5—C6—H6 | 119.9 |
| Bi ⁱ —I4—Bi | 92.92 (2) | O—C7—H7A | 109.5 |
| C1—N—HA | 109.5 | O—C7—H7B | 109.5 |
| C1—N—HB | 109.5 | H7A—C7—H7B | 109.5 |
| HA—N—HB | 109.5 | O—C7—H7C | 109.5 |
| C1—N—HC | 109.5 | H7A—C7—H7C | 109.5 |
| HA—N—HC | 109.5 | H7B—C7—H7C | 109.5 |
| HB—N—HC | 109.5 | C4—O—C7 | 116.7 (8) |
| C6—C1—C2 | 119.6 (11) | HW1A—OW1—HW1B | 108.5 |
| C6—C1—N | 118.9 (10) | HW2A—OW2—HW2B | 108.4 |

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

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> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| N—HA...I3 ⁱⁱⁱ | 0.89 | 2.77 | 3.658 (10) | 176 |
| N—HB...OW1 ^{iv} | 0.89 | 1.97 | 2.762 (12) | 147 |
| N—HC...OW2 | 0.89 | 1.88 | 2.704 (14) | 154 |
| OW1—HW1A...I3 | 0.85 | 2.77 | 3.604 (7) | 167 |
| OW2—HW2A...I1 ⁱ | 0.85 | 3.23 | 3.817 (10) | 129 |
| OW2—HW2A...I3 | 0.85 | 3.20 | 3.850 (12) | 135 |
| OW2—HW2B...OW1 ^v | 0.85 | 2.32 | 2.925 (13) | 129 |

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