



Crystal structure and Hirshfeld surface analysis of the organic–inorganic hybrid compound tris(2-iodoethylammonium) hexaiodidobismuthate(III)

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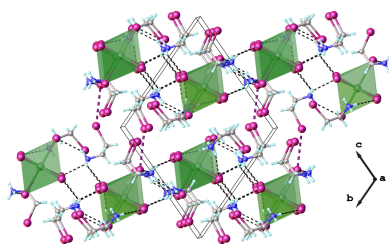
The asymmetric unit of the title organic–inorganic salt, $(\text{IC}_2\text{H}_4\text{NH}_3)_3[\text{BiI}_6]$, consists of a $[\text{BiI}_6]^{3-}$ octahedron and three 2-iodoethylammonium cations. The octahedra do not interact with each other, and the supramolecular arrangement is ensured by an intricate network of $\text{N}-\text{H}\cdots\text{I}$ hydrogen bonds between cations and anions. In addition, a weak $\text{I}\cdots\text{I}$ interaction between an organic cation and the coordination octahedron is present in the crystal structure. Hirshfeld surface analysis revealed that the most important contributions to the crystal packing are from $\text{H}\cdots\text{I}$ (72.3%) and $\text{I}\cdots\text{I}$ (11.3%) interactions.

1. Chemical context

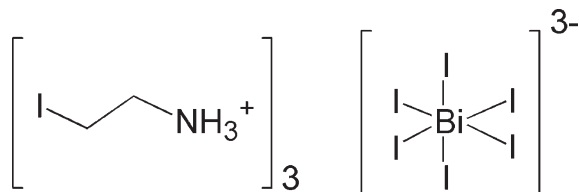
Organic–inorganic halidobismuthates(III) represent a promising class of hybrid compounds that attract attention due to their structural versatility in combination with interesting physical properties. For example, these bismuth-based compounds are currently used as a less toxic alternative to lead-based perovskites for applications as light-emitting diodes (Zhou *et al.*, 2018), for X-ray detection (Wang *et al.*, 2023) or for photovoltaics (Zhang *et al.*, 2020).

Hybrid halidobismuthates(III) contain the $[\text{BiX}_6]^{3-}$ ($X = \text{Cl}$, Br or I) coordination octahedron as a fundamental building block, which can assemble into very different topologies in the crystal structure, starting from those containing discrete anionic halidometallic units up to structures with anionic chains or layers (alternatively named as 0-D, 1-D and 2-D halidometallic building blocks). For instance, hybrid bismuthates with general formula $A_3[\text{Bi}_2X_9]$ tend to crystallize with two structural set-ups: one forms inorganic layers, exemplified by methylammonium (MA) bismuth bromide $(\text{MA})_3[\text{Bi}_2\text{Br}_9]$ (Li *et al.*, 2019), while the other one is characterized by a formation of isolated face-sharing $[\text{Bi}_2X_9]^{3-}$ bi-octahedra, exemplified by $(\text{MA})_3\text{Bi}_2\text{I}_9$ (Hoye *et al.*, 2016).

Interestingly, the decrease of dimensionality in the anion leads to an increased localization of electronic states and decreased valence and conduction bands, which results in the occurrence of self-trapped excitons and strong excitonic emission. Hence, highly effective luminescence with different emission wavelengths have been observed for 0-D halidobismuthates. For example, highly efficient blue (480 nm) emission with a quantum yield of 58% was achieved for 0-D hybrid tetraphenylphosphonium (TPP) bismuth chloride $(\text{TPP})_2[\text{BiCl}_5]$ (Lai *et al.*, 2024). At the same time, 4-(chloromethyl)pyridinium bismuth chloride $(4\text{-cmpyH})_2[\text{BiCl}_5]$ was



shown to display yellow luminescence with an emission wavelength of 597 nm and a quantum yield of 5.56% (Qi *et al.*, 2022).



In this context, we report here on the crystal structure and Hirshfeld surface analysis of a new organic-inorganic compound, (2-iodoethylammonium)₃[BiI₆], which is composed of discrete [BiI₆]³⁻ anions.

2. Structural commentary

The coordination octahedron [BiI₆]³⁻ is slightly distorted (Fig. 1), with Bi–I bond lengths ranging from 3.0287 (3) to 3.1333 (3) Å (Table 1). Such a small variation in bond length leads to a relatively small bond length distortion parameter, $\Delta d = 1/6 \Sigma(d_i - d)^2/d^2 = 1.1 \cdot 10^{-4}$ (where d_i is one of six individual bond lengths in the octahedron and d is the mean Bi–I bond length). The *cis*-(I–Bi–I) angles (α) lie in the interval 88.529 (9)–91.561 (9)°, which also indicates the occurrence of octahedral distortion, and can be described by the following parameter, $\Sigma = \Sigma|90^\circ - \alpha| = 19.674^\circ$. The formed coordination octahedra are isolated, providing a 0-D topology in the crystal structure (Fig. 2); these octahedra are aligned parallel to (003). The charge of the [BiI₆]³⁻ anions is balanced by three crystallographically unique 2-iodoethylammonium cations, the I–C, C–C and C–N bond lengths of which are within the expected range. All three 2-iodoethylammonium cations adopt a synclinal conformation with torsion angles of

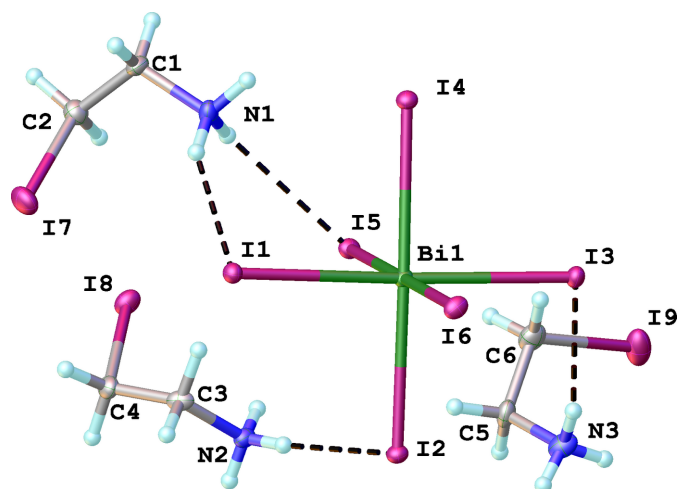


Figure 1
The molecular structures of the entities in the asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level; dashed lines represent N–H···I hydrogen bonds.

Table 1
Selected bond lengths (Å).

Bi1–I6	3.0287 (3)	Bi1–I4	3.0786 (3)
Bi1–I3	3.0698 (3)	Bi1–I1	3.1068 (4)
Bi1–I2	3.0733 (3)	Bi1–I5	3.1333 (3)

Table 2
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–H1A···I1	0.94	2.77	3.639 (4)	154
N1–H1B···I5 ⁱ	0.94	3.04	3.735 (4)	132
N1–H1C···I5	0.94	2.97	3.726 (4)	138
N1–H1C···I4 ⁱ	0.94	3.08	3.751 (4)	130
N2–H2A···I2	0.84	2.83	3.660 (4)	170
N2–H2B···I4 ⁱⁱ	0.84	2.98	3.716 (4)	148
N2–H2C···I1 ⁱⁱ	0.84	3.00	3.730 (4)	146
N3–H3C···I3	0.85	2.89	3.712 (4)	167
N3–H3D···I6 ⁱⁱⁱ	0.85	2.91	3.659 (4)	148
N3–H3E···I3 ⁱⁱⁱ	0.85	2.90	3.614 (4)	144

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

68.6 (5)° (for the N1-containing cation), –66.2 (4)° (N2) and 64.1 (5)° (N3).

3. Supramolecular features

In the crystal structure, the supramolecular arrangement is mainly provided by numerous N–H···I hydrogen bonds between the ammonium groups of the cations and the I[–] ligand atoms of the anions (Fig. 2). All of the I[–] ligand atoms of the anion, and all of the H atoms of the ammonium NH₃ groups are involved in these interactions, one (N1–H1C) in a bifurcated manner (Table 2). In addition, the distances

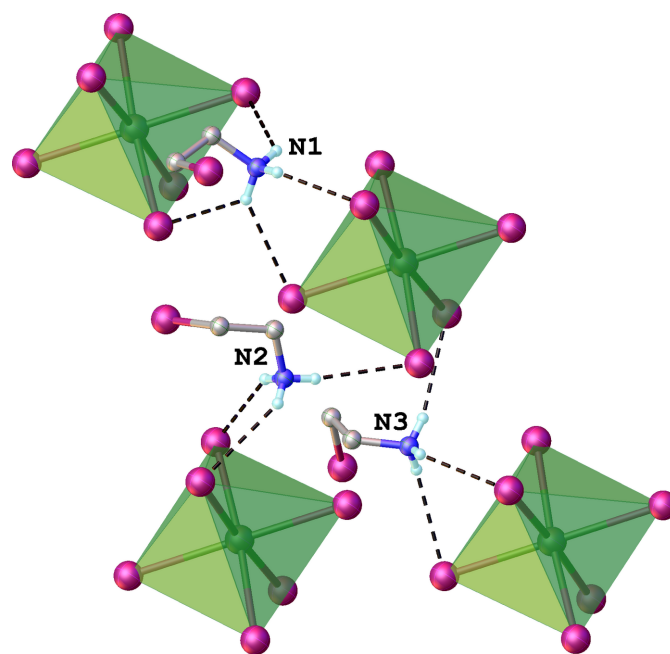


Figure 2
Details of the N–H···I hydrogen-bonding network (dashed lines) between organic cations and inorganic anions (represented as polyhedra). Only H atoms involved in these interactions are shown.

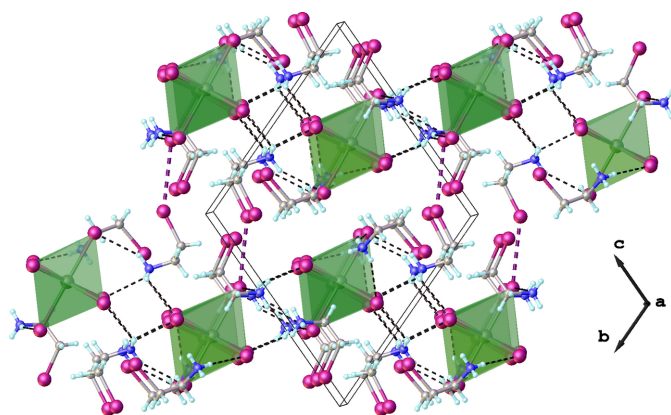


Figure 3
Crystal packing of the title compound plotted along the *a* axis. N—H...I hydrogen bonds are drawn as black dashed lines, and weak I...I contacts as pink dashed lines.

between the carbon atoms of CH₂ groups in organic cations and I atoms of coordination octahedra range from 3.801 to 3.963 Å suggesting the presence of weak C—H...I interactions. In addition, a weak I7...I3 contact [3.9663 (4) Å] is formed between one iodine atom of 2-iodoethylammonium and another iodine atom of the coordination octahedron (Fig. 3). The length of this contact is in the order of the sum of the van der Waals radius of two iodine atoms.

4. Hirshfeld surface analysis

Weak interactions in the structure were additionally analysed by means of a Hirshfeld surface analysis using *CrystalExplorer* (Spackman *et al.*, 2021). According to the colour code of the calculated Hirshfeld surface (Fig. 4*a,b*), the contacts between atoms with lengths approximately equal to the sum of their van der Waals radii are shown in white, and contacts that are shorter are shown in red, while those that are longer are shown in blue. On the 3-D colour map only N—H...I contacts

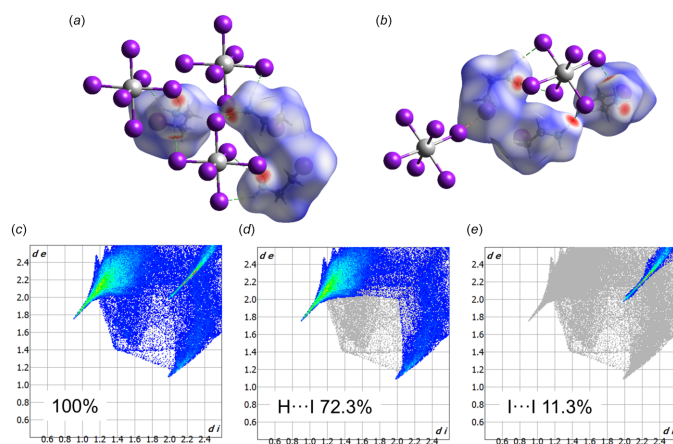


Figure 4
(*a*), (*b*) Hirshfeld surface plotted over a fixed colour scale, which shows the strongest intermolecular interactions in red; (*c*), (*d*), (*e*) two-dimensional fingerprint plots and their percentage contributions.

are marked in red, suggesting that these are the strongest interactions. The weak I...I contact is shown in white, which supports the statement given in the previous section. Two-dimensional fingerprint plots (Fig. 4*c–e*) display the presence of two types of relevant contacts in the structure: H...I with 72.3% contribution and I...I with 11.3% contribution. The remaining contacts are represented by H...H interactions.

5. Database survey

A search of the Cambridge Structure Database (CSD, version 5.45, updated September 2024; Groom *et al.*, 2016) revealed that the formation of [Bi₂I₉]^{3−} dimers is more common than of isolated [BiI₆]^{3−} octahedra. Some selected examples of crystal structures with discrete [BiI₆]^{3−} moieties are HUFBAO, which is (MA)₃[BiI₆]·3MACl (MA = methylammonium; Zhang *et al.*, 2020), MAMNEX02, which is (PBA)₄[BiI₆]I·H₂O [(PBA) = C₆H₅(CH₂)₄NH₃] (Chen *et al.*, 2021) and MIJVEK, which is (DPA)₂[BiI₆]I₃ (DPA = C₃H₁₆N₂; Wang *et al.*, 2023). The main difference between these structures and the title compound is a mutual arrangement of isolated [BiI₆]^{3−} inorganic octahedra. In the case of HUFBAO, [BiI₆]^{3−} octahedra are stacked along the *ac* plane, in MIJVEK these octahedra are located along the *ab* plane and in MAMNEX02 along the *bc* plane. Thus, three examples from the literature can generally be described as structures containing ‘layers’ of inorganic octahedra (although these octahedra are not bonded to each other), which alternate with an organic component. In the title compound, the inorganic octahedra are arranged relative to each other like the vertices of a honeycomb (when viewed along the *a* axis). This arrangement allows for more significant interaction between the organic and inorganic parts of the structure, resulting in the formation of multiple hydrogen bonds, as described.

6. Synthesis and crystallization

Crystals of the title compound have been obtained serendipitously during an intended synthesis of aziridinium (AzrH) bismuth iodide. (AzrH)₃[Bi₂I₉]·Bi₂O₃ (0.1 mmol) was dissolved in 0.5 ml of concentrated HI (57%_wt). Aziridine (0.1 mol) was dissolved in 1 ml of water and added dropwise to the former solution. Orange crystals formed within 30 minutes, were collected and stored under Paratone(R) oil prior to the diffraction measurement. The formation of (2-IC₂H₄NH₃)₃[BiI₆] instead of the target perovskite was established only in the single-crystal X-ray diffraction experiment.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were placed at calculated positions and refined isotropically with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. H atoms of secondary CH₂ groups were refined as riding, while H atoms of NH₃⁺ groups were refined as rotating.

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Table 3

Experimental details.

Crystal data	
Chemical formula	(C ₂ H ₇ IN) ₃ [BiI ₆]
<i>M_r</i>	1486.34
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.5014 (2), 12.8233 (3), 13.6364 (3)
α , β , γ (°)	107.689 (2), 107.067 (2), 92.749 (2)
<i>V</i> (Å ³)	1338.49 (6)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	16.96
Crystal size (mm)	0.19 × 0.1 × 0.05
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix Analytical (<i>CrysAlis PRO</i> ; Rigaku OD, 2023)
Absorption correction	
<i>T_{min}</i> , <i>T_{max}</i>	0.137, 0.506
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	19499, 6651, 5947
<i>R_{int}</i>	0.028
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.712
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.025, 0.049, 1.04
No. of reflections	6651
No. of parameters	179
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	2.38, -1.94

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *OLEX2* (Dolomanov *et al.*, 2009) and *pubCIF* (Westrip, 2010).

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Computing details

Tris(2-iodoethylammonium) hexaiodidobismuthate(III)

Crystal data

(C₂H₇IN)₃·[BiI₆]

$M_r = 1486.34$

Triclinic, $P\bar{1}$

$a = 8.5014$ (2) Å

$b = 12.8233$ (3) Å

$c = 13.6364$ (3) Å

$\alpha = 107.689$ (2)°

$\beta = 107.067$ (2)°

$\gamma = 92.749$ (2)°

$V = 1338.49$ (6) Å³

$Z = 2$

$F(000) = 1276$

$D_x = 3.688$ Mg m⁻³

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

Cell parameters from 12539 reflections

$\theta = 2.5$ – 30.2 °

$\mu = 16.96$ mm⁻¹

$T = 100$ K

Prism, clear intense orange

$0.19 \times 0.1 \times 0.05$ mm

Data collection

XtaLAB Synergy, Dualflex, HyPix
diffractometer

Detector resolution: 10.0000 pixels mm⁻¹

ω scans

Absorption correction: analytical
(CrysAlisPro; Rigaku OD, 2023)

$T_{\min} = 0.137$, $T_{\max} = 0.506$

19499 measured reflections

6651 independent reflections

5947 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 30.4$ °, $\theta_{\min} = 2.5$ °

$h = -11 \rightarrow 10$

$k = -16 \rightarrow 17$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.049$

$S = 1.04$

6651 reflections

179 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0173P)^2 + 0.4063P]$

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

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

$\Delta\rho_{\max} = 2.38$ e Å⁻³

$\Delta\rho_{\min} = -1.94$ e Å⁻³

Extinction correction: SHELXL (Sheldrick,
2015b), $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00014 (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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Bi1	0.16816 (2)	0.69742 (2)	0.33843 (2)	0.01111 (5)
I5	0.33222 (3)	0.60094 (2)	0.15861 (2)	0.01361 (7)
I4	−0.16844 (3)	0.62750 (2)	0.15397 (2)	0.01349 (7)
I1	0.11528 (3)	0.46673 (2)	0.36362 (2)	0.01363 (7)
I3	0.19810 (4)	0.92705 (2)	0.31390 (2)	0.01440 (7)
I2	0.51762 (3)	0.76130 (2)	0.50855 (2)	0.01362 (7)
I6	0.01073 (3)	0.79056 (3)	0.51288 (2)	0.01571 (7)
I8	0.58571 (4)	0.31642 (3)	0.11272 (3)	0.01952 (8)
I7	0.17041 (4)	0.14625 (3)	0.15984 (3)	0.02642 (9)
I9	0.66397 (5)	1.02469 (3)	0.16011 (3)	0.03205 (9)
N2	0.6922 (4)	0.5384 (3)	0.3540 (3)	0.0149 (8)
H2A	0.663 (3)	0.5957 (17)	0.390 (2)	0.018*
H2B	0.684 (3)	0.5409 (14)	0.2918 (18)	0.018*
H2C	0.791 (3)	0.5349 (12)	0.386 (2)	0.018*
N3	0.6590 (5)	0.9734 (4)	0.3921 (3)	0.0219 (10)
H3C	0.556 (3)	0.9749 (17)	0.3818 (15)	0.026*
H3D	0.704 (4)	1.034 (2)	0.3922 (16)	0.026*
H3E	0.704 (4)	0.9647 (14)	0.453 (2)	0.026*
N1	0.0028 (5)	0.3580 (3)	0.0687 (3)	0.0183 (9)
H1A	0.031 (4)	0.3599 (4)	0.141 (2)	0.022*
H1B	−0.086 (3)	0.3978 (13)	0.0535 (17)	0.022*
H1C	0.095 (3)	0.3901 (12)	0.0579 (18)	0.022*
C5	0.6821 (6)	0.8794 (4)	0.3028 (4)	0.0204 (11)
H5A	0.801517	0.884170	0.309359	0.025*
H5B	0.647553	0.808515	0.310931	0.025*
C4	0.6282 (6)	0.3321 (4)	0.2813 (4)	0.0180 (10)
H4A	0.562064	0.268387	0.284755	0.022*
H4B	0.747215	0.329848	0.316224	0.022*
C1	−0.0476 (6)	0.2402 (4)	−0.0057 (4)	0.0177 (10)
H1D	−0.089761	0.239060	−0.081909	0.021*
H1E	−0.139406	0.205092	0.009941	0.021*
C3	0.5814 (5)	0.4380 (4)	0.3433 (4)	0.0167 (10)
H3A	0.464643	0.442694	0.305470	0.020*
H3B	0.588874	0.436813	0.416807	0.020*
C2	0.0940 (6)	0.1740 (4)	0.0064 (4)	0.0207 (11)
H2D	0.190098	0.213498	−0.001433	0.025*
H2E	0.059806	0.101576	−0.052859	0.025*
C6	0.5834 (6)	0.8803 (4)	0.1924 (4)	0.0244 (12)
H6A	0.464389	0.877912	0.186693	0.029*

H6B 0.594239 0.813096 0.136611 0.029*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Bi1	0.01029 (9)	0.01076 (9)	0.01174 (9)	0.00051 (6)	0.00391 (7)	0.00285 (7)
I5	0.01205 (14)	0.01543 (16)	0.01372 (15)	0.00326 (11)	0.00523 (12)	0.00415 (12)
I4	0.01107 (14)	0.01490 (15)	0.01383 (15)	0.00077 (11)	0.00348 (11)	0.00456 (12)
I1	0.01375 (14)	0.01310 (15)	0.01452 (15)	0.00132 (11)	0.00420 (12)	0.00576 (12)
I3	0.01689 (15)	0.01120 (15)	0.01465 (15)	0.00080 (11)	0.00440 (12)	0.00454 (12)
I2	0.01114 (14)	0.01473 (15)	0.01353 (15)	0.00037 (11)	0.00297 (11)	0.00390 (12)
I6	0.01468 (15)	0.01651 (16)	0.01551 (16)	0.00063 (11)	0.00765 (12)	0.00232 (12)
I8	0.02162 (16)	0.01834 (17)	0.01683 (16)	-0.00061 (12)	0.00818 (13)	0.00205 (13)
I7	0.02723 (18)	0.0288 (2)	0.0284 (2)	0.00564 (14)	0.00640 (15)	0.01908 (16)
I9	0.0554 (2)	0.0230 (2)	0.02364 (19)	0.00998 (17)	0.01751 (17)	0.01078 (15)
N2	0.0132 (19)	0.014 (2)	0.015 (2)	0.0011 (15)	0.0032 (16)	0.0023 (16)
N3	0.021 (2)	0.024 (2)	0.019 (2)	-0.0036 (17)	0.0082 (18)	0.0047 (18)
N1	0.025 (2)	0.013 (2)	0.018 (2)	0.0042 (16)	0.0068 (17)	0.0050 (17)
C5	0.030 (3)	0.011 (2)	0.020 (3)	0.003 (2)	0.009 (2)	0.004 (2)
C4	0.018 (2)	0.015 (3)	0.021 (3)	-0.0007 (19)	0.004 (2)	0.008 (2)
C1	0.015 (2)	0.014 (2)	0.018 (3)	-0.0010 (18)	0.0014 (19)	0.0018 (19)
C3	0.013 (2)	0.024 (3)	0.013 (2)	-0.0011 (19)	0.0048 (19)	0.007 (2)
C2	0.019 (2)	0.021 (3)	0.022 (3)	0.004 (2)	0.007 (2)	0.008 (2)
C6	0.031 (3)	0.021 (3)	0.018 (3)	0.000 (2)	0.008 (2)	0.002 (2)

Geometric parameters (Å, °)

Bi1—I6	3.0287 (3)	N1—H1B	0.94 (3)
Bi1—I3	3.0698 (3)	N1—H1C	0.94 (3)
Bi1—I2	3.0733 (3)	N1—C1	1.498 (6)
Bi1—I4	3.0786 (3)	C5—H5A	0.9900
Bi1—I1	3.1068 (4)	C5—H5B	0.9900
Bi1—I5	3.1333 (3)	C5—C6	1.496 (7)
I8—C4	2.163 (5)	C4—H4A	0.9900
I7—C2	2.145 (5)	C4—H4B	0.9900
I9—C6	2.155 (5)	C4—C3	1.506 (7)
N2—H2A	0.84 (2)	C1—H1D	0.9900
N2—H2B	0.84 (2)	C1—H1E	0.9900
N2—H2C	0.84 (2)	C1—C2	1.505 (6)
N2—C3	1.502 (6)	C3—H3A	0.9900
N3—H3C	0.85 (3)	C3—H3B	0.9900
N3—H3D	0.85 (3)	C2—H2D	0.9900
N3—H3E	0.85 (3)	C2—H2E	0.9900
N3—C5	1.499 (6)	C6—H6A	0.9900
N1—H1A	0.94 (3)	C6—H6B	0.9900
I4—Bi1—I5	86.834 (9)	H5A—C5—H5B	107.9
I4—Bi1—I1	87.370 (9)	C6—C5—N3	112.2 (4)

I1—Bi1—I5	91.043 (9)	C6—C5—H5A	109.2
I3—Bi1—I5	91.561 (9)	C6—C5—H5B	109.2
I3—Bi1—I4	90.279 (9)	I8—C4—H4A	109.2
I3—Bi1—I1	176.391 (9)	I8—C4—H4B	109.2
I3—Bi1—I2	89.461 (9)	H4A—C4—H4B	107.9
I2—Bi1—I5	88.607 (9)	C3—C4—I8	112.2 (3)
I2—Bi1—I4	175.425 (10)	C3—C4—H4A	109.2
I2—Bi1—I1	93.101 (9)	C3—C4—H4B	109.2
I6—Bi1—I5	179.779 (10)	N1—C1—H1D	109.1
I6—Bi1—I4	93.367 (9)	N1—C1—H1E	109.1
I6—Bi1—I1	88.876 (9)	N1—C1—C2	112.5 (4)
I6—Bi1—I3	88.529 (9)	H1D—C1—H1E	107.8
I6—Bi1—I2	91.192 (9)	C2—C1—H1D	109.1
H2A—N2—H2B	109.5	C2—C1—H1E	109.1
H2A—N2—H2C	109.5	N2—C3—C4	112.2 (4)
H2B—N2—H2C	109.5	N2—C3—H3A	109.2
C3—N2—H2A	109.5	N2—C3—H3B	109.2
C3—N2—H2B	109.5	C4—C3—H3A	109.2
C3—N2—H2C	109.5	C4—C3—H3B	109.2
H3C—N3—H3D	109.5	H3A—C3—H3B	107.9
H3C—N3—H3E	109.5	I7—C2—H2D	109.0
H3D—N3—H3E	109.5	I7—C2—H2E	109.0
C5—N3—H3C	109.5	C1—C2—I7	113.0 (3)
C5—N3—H3D	109.5	C1—C2—H2D	109.0
C5—N3—H3E	109.5	C1—C2—H2E	109.0
H1A—N1—H1B	109.5	H2D—C2—H2E	107.8
H1A—N1—H1C	109.5	I9—C6—H6A	109.1
H1B—N1—H1C	109.5	I9—C6—H6B	109.1
C1—N1—H1A	109.5	C5—C6—I9	112.3 (3)
C1—N1—H1B	109.5	C5—C6—H6A	109.1
C1—N1—H1C	109.5	C5—C6—H6B	109.1
N3—C5—H5A	109.2	H6A—C6—H6B	107.9
N3—C5—H5B	109.2		
I8—C4—C3—N2	-66.2 (4)	N1—C1—C2—I7	68.6 (5)
N3—C5—C6—I9	64.1 (5)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots I1	0.94	2.77	3.639 (4)	154
N1—H1B \cdots I5 ⁱ	0.94	3.04	3.735 (4)	132
N1—H1C \cdots I5	0.94	2.97	3.726 (4)	138
N1—H1C \cdots I4 ⁱ	0.94	3.08	3.751 (4)	130
N2—H2A \cdots I2	0.84	2.83	3.660 (4)	170
N2—H2B \cdots I4 ⁱⁱ	0.84	2.98	3.716 (4)	148
N2—H2C \cdots I1 ⁱⁱ	0.84	3.00	3.730 (4)	146
N3—H3C \cdots I3	0.85	2.89	3.712 (4)	167

N3—H3D···I6 ⁱⁱⁱ	0.85	2.91	3.659 (4)	148
N3—H3E···I3 ⁱⁱⁱ	0.85	2.90	3.614 (4)	144

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