



ISSN 2414-3146

# Tris(*N,N,N',N',N'',N''*-hexaethylguanidinium) dodecaiodidotribismuthate(III)

Ioannis Tiritiris, Georg Knobloch, Stefan Saur and Willi Kantlehner\*

Fakultät Chemie/Organische Chemie, Hochschule Aalen, Beethovenstrasse 1, D-73430 Aalen, Germany. \*Correspondence e-mail: willi.kantlehner@hs-aalen.de

Received 16 February 2016

Accepted 8 March 2016

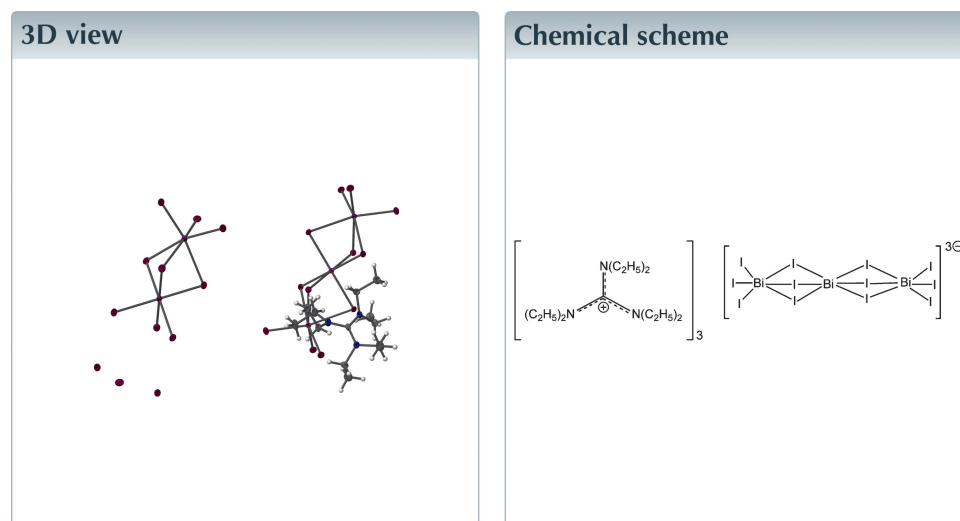
Edited by S. Parkin, University of Kentucky, USA

Keywords: crystal structure; hexaethylguanidinium salt; iodidobismuthate.

CCDC reference: 1459096

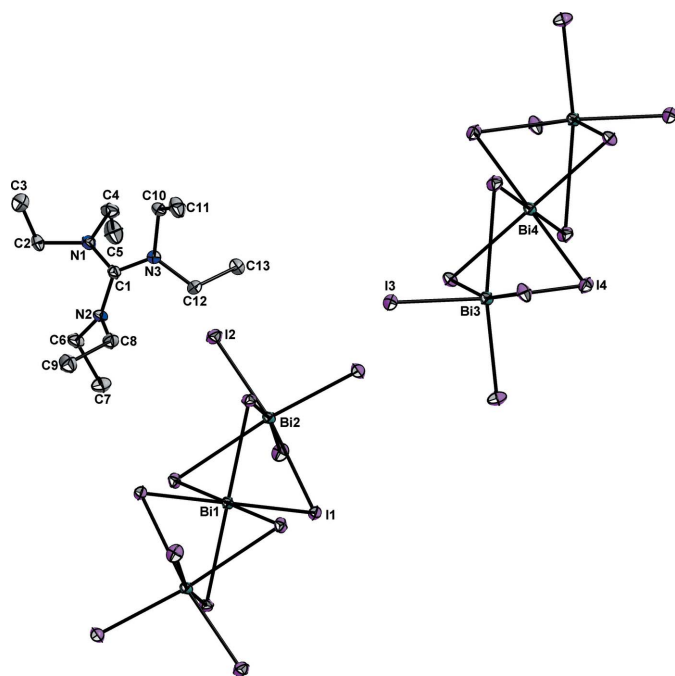
Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

The asymmetric unit of title compound,  $(C_{13}H_{30}N_3)[Bi_3I_{12}]$ , comprises one cation and two independent (1/6) fragments of the  $[Bi_3I_{12}]^{3-}$  ions. The C–N bond lengths in the guanidinium ion range from 1.340 (4) to 1.345 (4) Å, indicating partial double-bond character pointing towards charge delocalization within the NCN planes. The  $Bi^{III}$  ions are distorted octahedrally coordinated by six iodide ions, with Bi–I bond lengths ranging from 2.9206 (3) to 3.3507 (3) Å. Three  $[BiI_6]^{3-}$  octahedra are fused together through face-sharing, forming a trinuclear  $[Bi_3I_{12}]^{3-}$  unit.



## Structure description

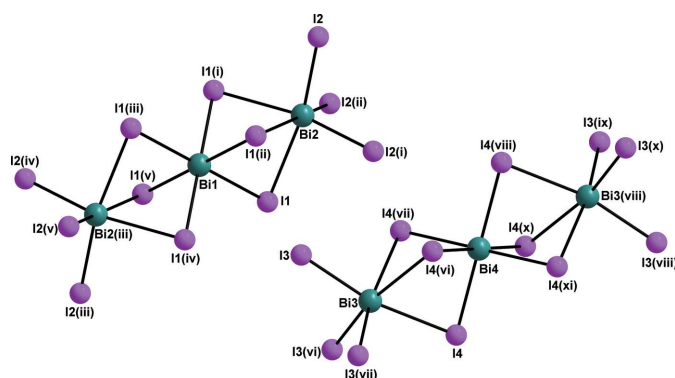
Peralkylated guanidinium ions with complex inorganic anions are considered to be organic–inorganic hybrid compounds. Their physical properties make them interesting for application in scanning electron microscopy (SEM), where the contrast and the brightness of the obtained pictures depend on the heaviest atom present in the anions. By testing various guanidinium salts with different inorganic complex anions, we found that guanidinium iodidobismuthates are very suitable candidates for this purpose (Knobloch *et al.*, 2016). One of them is the here presented title compound. The asymmetric unit comprises one *N,N,N',N',N'',N''*-hexaethylguanidinium ion and two independent (1/6) fragments of the  $[Bi_3I_{12}]^{3-}$  ions (Fig. 1). Both entire anions are constructed by the symmetry operators required to generate all equivalent positions, leading to two molecules with point group symmetry  $\bar{3}$  (Fig. 2). Prominent bond parameters in the guanidinium ion are: C1–N1 = 1.342 (4) Å, C1–N2 = 1.340 (4) Å and C1–N3 = 1.345 (4) Å, indicating partial double-bond character. The N–C1–N angles are: 120.5 (3)° (N1–C1–N2), 120.5 (3)° (N2–C1–N3) and 119.0 (3)° (N1–C1–N3), indicating a nearly ideal trigonal–planar surrounding of the carbon centre by the nitrogen atoms (r.m.s.



**Figure 1**  
An ellipsoid plot (50% probability level) of the title compound with atom labels for the asymmetric unit. H atoms have been omitted to enhance clarity.

deviation from the mean plane: 0.0009 Å). The positive charge is completely delocalized on the CN<sub>3</sub> plane.

The C–N and C–C bond lengths in the cation are in very good agreement with the data from the crystal structure analysis of known *N,N,N',N',N'',N''*-hexaethylguanidinium salts (Salchner *et al.*, 2014). The Bi<sup>III</sup> ions are distorted octahedrally coordinated by six iodide ions with Bi–I bond lengths ranging from 2.9206 (3) to 3.3507 (3) Å. Three [BiI<sub>6</sub>]<sup>3–</sup> octahedra are fused together through face-sharing, forming trinuclear [Bi<sub>3</sub>I<sub>12</sub>]<sup>3–</sup> units (Fig. 2). The bond lengths of bismuth to the terminal iodides [2.9206 (3)–2.9208 (3) Å] are shorter than the bridging ones [3.0504 (2)–3.3507 (3) Å]. The



**Figure 2**  
Two independent [Bi<sub>3</sub>I<sub>12</sub>]<sup>3–</sup> ions in the crystal structure of the title compound [symmetry operators: (i)  $-y, x - y, z$ ; (ii)  $-x + y, -x, z$ ; (iii)  $-x, -y, -z$ ; (iv)  $y, -x + y, -z$ ; (v)  $x - y, x, -z$ ; (vi)  $-x + y, -x + 1, z$ ; (vii)  $-y + 1, x - y + 1, z$ ; (viii)  $-x + \frac{2}{3}, -y + \frac{4}{3}, -z + \frac{1}{3}$ ; (ix)  $y - \frac{1}{3}, -x + y + \frac{1}{3}, -z + \frac{1}{3}$ ; (x)  $x - y + \frac{2}{3}, x + \frac{1}{3}, -z + \frac{1}{3}$ ].

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	(C <sub>13</sub> H <sub>30</sub> N <sub>3</sub> ) <sub>3</sub> [Bi <sub>3</sub> I <sub>12</sub> ]
<i>M<sub>r</sub></i>	2834.94
Crystal system, space group	Trigonal, <i>R</i> $\bar{3}$
Temperature (K)	100
<i>a</i> , <i>c</i> (Å)	18.7962 (11), 36.666 (2)
<i>V</i> (Å <sup>3</sup> )	11218.5 (17)
<i>Z</i>	6
Radiation type	Mo <i>K</i> α
$\mu$ (mm <sup>-1</sup> )	12.03
Crystal size (mm)	0.22 × 0.15 × 0.09
Data collection	
Diffractometer	Bruker Kappa APEXII DUO
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.110, 0.288
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	67733, 7602, 6037
<i>R</i> <sub>int</sub>	0.051
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.715
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.024, 0.042, 1.05
No. of reflections	7602
No. of parameters	197
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.82, -1.22

Computer programs: *APEX2* (Bruker, 2008), *SAINT* (Bruker, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg & Putz, 2005).

same anionic arrangement was observed in the crystal structure of the complex [Co(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>][CoI(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(-H<sub>2</sub>O)][Bi<sub>3</sub>I<sub>12</sub>] where the Bi–I bond lengths range from 2.853 (1) to 3.419 (1) Å (Chen *et al.*, 2011). Since no significant hydrogen bonding in the title compound exists, crystal packing is caused by electrostatic interactions between cations and anions.

### Synthesis and crystallization

The title compound was obtained by mixing an ethanolic solution of *N,N,N',N',N'',N''*-hexaethylguanidinium iodide with BiI<sub>3</sub>/KI dissolved in aqueous ethanol at room temperature. The orange-colored precipitate was removed by filtration and washed with water and ethanol. The product was recrystallized from an acetonitrile solution. After evaporation of the solvent at ambient temperature, red single crystals suitable for X-ray analysis emerged.

### Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

### Acknowledgements

The authors thank Dr W. Frey (Institut für Organische Chemie, Universität Stuttgart) for measuring the diffraction data.

## References

- Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Crystal Impact GbR, D-53002 Bonn, Germany.
- Bruker (2008). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chen, J., Chai, W., Song, L., Yang, Y. & Niu, F. (2011). *Acta Cryst.* **E67**, m1284–m1285.
- Knobloch, G., Saur, S., Gentner, A. R., Tussetschläger, S., Stein, T., Hader, B. & Kantlehner, W. (2016). *Z. Naturforsch. Teil B*, **71**. Accepted.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Salchner, R., Kahlenberg, V., Gelbrich, T., Wurst, K., Rauch, M., Laus, G. & Schottenberger, H. (2014). *Crystals*, **4**, 404–416.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.

## full crystallographic data

*IUCrData* (2016). **1**, x160391 [doi:10.1107/S2414314616003916]

**Tris(*N,N,N',N',N'',N''*-hexaethylguanidinium) dodecaiodotribismuthate(III)**

Ioannis Tiritiris, Georg Knobloch, Stefan Saur and Willi Kantlehner

Tris(*N,N,N',N',N'',N''*-hexaethylguanidinium) dodecaiodotribismuthate(III)

*Crystal data*

(C<sub>13</sub>H<sub>30</sub>N<sub>3</sub>)<sub>3</sub>[Bi<sub>3</sub>I<sub>12</sub>]

*M<sub>r</sub>* = 2834.94

Trigonal,  $R\bar{3}$

*a* = 18.7962 (11) Å

*c* = 36.666 (2) Å

*V* = 11218.5 (17) Å<sup>3</sup>

*Z* = 6

*F*(000) = 7632

*D<sub>x</sub>* = 2.518 Mg m<sup>-3</sup>

Mo *Kα* radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 67733 reflections

$\theta$  = 1.4–30.5°

$\mu$  = 12.03 mm<sup>-1</sup>

*T* = 100 K

Block, red

0.22 × 0.15 × 0.09 mm

*Data collection*

Bruker Kappa APEXII DUO

diffractometer

Radiation source: fine-focus sealed tube

Triumph monochromator

$\varphi$  scans, and  $\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Krause *et al.*, 2015)

*T<sub>min</sub>* = 0.110, *T<sub>max</sub>* = 0.288

67733 measured reflections

7602 independent reflections

6037 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.051

$\theta_{\max}$  = 30.5°,  $\theta_{\min}$  = 1.4°

*h* = -26→26

*k* = -22→26

*l* = -52→52

*Refinement*

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.024

*wR*(*F*<sup>2</sup>) = 0.042

*S* = 1.05

7602 reflections

197 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/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0142*P*)<sup>2</sup> + 2.3873*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 0.82 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -1.22 e Å<sup>-3</sup>

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Bi1	0.0000	0.0000	0.0000	0.01335 (6)
Bi2	0.0000	0.0000	0.10942 (2)	0.01406 (5)
I1	-0.11584 (2)	0.02617 (2)	0.04918 (2)	0.01666 (5)
I2	0.11983 (2)	-0.02533 (2)	0.14950 (2)	0.02233 (5)
Bi3	0.3333	0.6667	0.05163 (2)	0.01649 (5)
Bi4	0.3333	0.6667	0.1667	0.01538 (6)
I3	0.40727 (2)	0.58833 (2)	0.00951 (2)	0.02337 (5)
I4	0.24421 (2)	0.72553 (2)	0.11467 (2)	0.02108 (5)
C1	0.38631 (18)	0.05544 (18)	0.08341 (9)	0.0173 (7)
N1	0.41659 (15)	0.02118 (15)	0.10615 (8)	0.0197 (6)
C2	0.44533 (19)	-0.03422 (18)	0.09284 (10)	0.0230 (8)
H2A	0.4232	-0.0538	0.0681	0.028*
H2B	0.4244	-0.0827	0.1091	0.028*
N2	0.33831 (15)	0.01246 (15)	0.05538 (7)	0.0174 (6)
C3	0.5380 (2)	0.0089 (2)	0.09172 (11)	0.0335 (9)
H3A	0.5587	0.0555	0.0748	0.050*
H3B	0.5554	-0.0296	0.0834	0.050*
H3C	0.5600	0.0289	0.1162	0.050*
N3	0.40455 (15)	0.13338 (15)	0.08929 (8)	0.0193 (6)
C4	0.4176 (2)	0.0326 (2)	0.14611 (10)	0.0256 (8)
H4A	0.4237	0.0870	0.1514	0.031*
H4B	0.4655	0.0315	0.1567	0.031*
C5	0.3401 (2)	-0.0333 (2)	0.16385 (11)	0.0373 (10)
H5A	0.2931	-0.0288	0.1554	0.056*
H5B	0.3449	-0.0266	0.1904	0.056*
H5C	0.3319	-0.0875	0.1573	0.056*
C6	0.28081 (18)	-0.07622 (18)	0.05865 (10)	0.0219 (7)
H6A	0.2850	-0.0946	0.0835	0.026*
H6B	0.2964	-0.1059	0.0410	0.026*
C7	0.19188 (19)	-0.0981 (2)	0.05155 (11)	0.0305 (9)
H7A	0.1783	-0.0640	0.0670	0.046*
H7B	0.1549	-0.1561	0.0573	0.046*
H7C	0.1855	-0.0881	0.0258	0.046*
C8	0.3391 (2)	0.0528 (2)	0.02067 (9)	0.0224 (7)
H8A	0.3847	0.1104	0.0211	0.027*
H8B	0.2870	0.0535	0.0182	0.027*
C9	0.3494 (2)	0.0093 (2)	-0.01206 (10)	0.0295 (8)
H9A	0.3984	0.0041	-0.0087	0.044*
H9B	0.3556	0.0412	-0.0342	0.044*
H9C	0.3009	-0.0455	-0.0144	0.044*

C10	0.48544 (18)	0.19572 (18)	0.10388 (10)	0.0213 (7)
H10A	0.5220	0.1719	0.1050	0.026*
H10B	0.4783	0.2103	0.1290	0.026*
C11	0.5259 (2)	0.2729 (2)	0.08076 (11)	0.0307 (9)
H11A	0.5345	0.2590	0.0560	0.046*
H11B	0.5789	0.3124	0.0915	0.046*
H11C	0.4903	0.2972	0.0798	0.046*
C12	0.3444 (2)	0.1600 (2)	0.08205 (10)	0.0266 (8)
H12A	0.2920	0.1121	0.0740	0.032*
H12B	0.3649	0.2007	0.0620	0.032*
C13	0.3285 (2)	0.1980 (2)	0.11561 (11)	0.0320 (9)
H13A	0.3080	0.1578	0.1355	0.048*
H13B	0.2874	0.2138	0.1097	0.048*
H13C	0.3797	0.2467	0.1231	0.048*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Bi1	0.01312 (8)	0.01312 (8)	0.01381 (15)	0.00656 (4)	0.000	0.000
Bi2	0.01439 (6)	0.01439 (6)	0.01338 (11)	0.00720 (3)	0.000	0.000
I1	0.01568 (9)	0.01750 (10)	0.01937 (12)	0.01022 (8)	0.00063 (8)	-0.00090 (9)
I2	0.02293 (11)	0.02274 (11)	0.02346 (13)	0.01303 (9)	-0.00595 (9)	0.00027 (9)
Bi3	0.01604 (6)	0.01604 (6)	0.01740 (12)	0.00802 (3)	0.000	0.000
Bi4	0.01445 (8)	0.01445 (8)	0.01723 (16)	0.00723 (4)	0.000	0.000
I3	0.02558 (11)	0.02681 (11)	0.02443 (13)	0.01812 (10)	-0.00357 (10)	-0.00410 (10)
I4	0.02045 (10)	0.02005 (10)	0.02619 (13)	0.01272 (9)	-0.00040 (9)	0.00197 (9)
C1	0.0141 (14)	0.0174 (15)	0.0196 (18)	0.0072 (12)	0.0007 (13)	-0.0056 (14)
N1	0.0217 (14)	0.0149 (13)	0.0213 (17)	0.0083 (11)	-0.0047 (12)	-0.0033 (12)
C2	0.0259 (17)	0.0153 (15)	0.029 (2)	0.0116 (14)	-0.0049 (16)	-0.0060 (15)
N2	0.0145 (12)	0.0143 (12)	0.0208 (16)	0.0051 (10)	-0.0032 (11)	-0.0048 (11)
C3	0.029 (2)	0.039 (2)	0.038 (3)	0.0208 (17)	-0.0048 (18)	-0.0092 (19)
N3	0.0184 (13)	0.0186 (13)	0.0229 (16)	0.0107 (11)	-0.0063 (12)	-0.0057 (12)
C4	0.0302 (19)	0.0288 (18)	0.018 (2)	0.0149 (16)	-0.0057 (16)	-0.0037 (16)
C5	0.042 (2)	0.035 (2)	0.033 (3)	0.0183 (19)	0.009 (2)	0.0017 (19)
C6	0.0176 (15)	0.0164 (15)	0.026 (2)	0.0044 (13)	-0.0021 (15)	-0.0044 (14)
C7	0.0187 (17)	0.0304 (19)	0.038 (3)	0.0087 (15)	-0.0030 (16)	-0.0046 (18)
C8	0.0260 (17)	0.0268 (17)	0.0191 (19)	0.0166 (15)	-0.0024 (15)	-0.0007 (15)
C9	0.032 (2)	0.0320 (19)	0.026 (2)	0.0178 (17)	0.0009 (17)	-0.0028 (17)
C10	0.0186 (16)	0.0162 (15)	0.028 (2)	0.0080 (13)	-0.0070 (15)	-0.0067 (15)
C11	0.032 (2)	0.0207 (17)	0.036 (2)	0.0109 (15)	0.0021 (18)	-0.0031 (17)
C12	0.0247 (17)	0.0298 (18)	0.033 (2)	0.0196 (15)	-0.0132 (16)	-0.0129 (17)
C13	0.0287 (19)	0.033 (2)	0.040 (3)	0.0195 (17)	-0.0111 (18)	-0.0190 (18)

*Geometric parameters (Å, °)*

Bi1—I1 <sup>i</sup>	3.0504 (2)	C3—H3B	0.9800
Bi1—I1 <sup>ii</sup>	3.0504 (2)	C3—H3C	0.9800
Bi1—I1 <sup>iii</sup>	3.0504 (2)	N3—C12	1.471 (4)

Bi1—I1 <sup>iv</sup>	3.0504 (2)	N3—C10	1.480 (4)
Bi1—I1 <sup>v</sup>	3.0504 (2)	C4—C5	1.508 (5)
Bi1—I1	3.0504 (2)	C4—H4A	0.9900
Bi2—I2 <sup>i</sup>	2.9208 (3)	C4—H4B	0.9900
Bi2—I2 <sup>ii</sup>	2.9208 (3)	C5—H5A	0.9800
Bi2—I2	2.9208 (3)	C5—H5B	0.9800
Bi2—I1	3.3065 (3)	C5—H5C	0.9800
Bi2—I1 <sup>i</sup>	3.3065 (3)	C6—C7	1.531 (4)
Bi2—I1 <sup>ii</sup>	3.3065 (3)	C6—H6A	0.9900
Bi3—I3 <sup>vi</sup>	2.9206 (3)	C6—H6B	0.9900
Bi3—I3 <sup>vii</sup>	2.9206 (3)	C7—H7A	0.9800
Bi3—I3	2.9206 (3)	C7—H7B	0.9800
Bi3—I4	3.3507 (3)	C7—H7C	0.9800
Bi3—I4 <sup>vi</sup>	3.3507 (3)	C8—C9	1.518 (5)
Bi3—I4 <sup>vii</sup>	3.3507 (3)	C8—H8A	0.9900
Bi4—I4 <sup>vii</sup>	3.0853 (2)	C8—H8B	0.9900
Bi4—I4 <sup>vi</sup>	3.0853 (2)	C9—H9A	0.9800
Bi4—I4	3.0853 (2)	C9—H9B	0.9800
Bi4—I4 <sup>viii</sup>	3.0853 (2)	C9—H9C	0.9800
Bi4—I4 <sup>ix</sup>	3.0853 (2)	C10—C11	1.516 (5)
Bi4—I4 <sup>x</sup>	3.0853 (2)	C10—H10A	0.9900
C1—N2	1.340 (4)	C10—H10B	0.9900
C1—N1	1.342 (4)	C11—H11A	0.9800
C1—N3	1.345 (4)	C11—H11B	0.9800
N1—C2	1.476 (4)	C11—H11C	0.9800
N1—C4	1.480 (4)	C12—C13	1.526 (5)
C2—C3	1.511 (4)	C12—H12A	0.9900
C2—H2A	0.9900	C12—H12B	0.9900
C2—H2B	0.9900	C13—H13A	0.9800
N2—C6	1.470 (4)	C13—H13B	0.9800
N2—C8	1.477 (4)	C13—H13C	0.9800
C3—H3A	0.9800		
I1 <sup>i</sup> —Bi1—I1 <sup>iv</sup>	180.000 (14)	H2A—C2—H2B	108.0
I1—Bi1—I1 <sup>iii</sup>	180.0	C1—N2—C6	120.9 (3)
I1 <sup>ii</sup> —Bi1—I1 <sup>v</sup>	180.0	C1—N2—C8	121.4 (3)
I1 <sup>i</sup> —Bi1—I1 <sup>iii</sup>	91.384 (7)	C6—N2—C8	117.7 (3)
I1 <sup>ii</sup> —Bi1—I1 <sup>iv</sup>	91.384 (7)	C2—C3—H3A	109.5
I1—Bi1—I1 <sup>iv</sup>	91.384 (7)	C2—C3—H3B	109.5
I1—Bi1—I1 <sup>v</sup>	91.384 (7)	H3A—C3—H3B	109.5
I1 <sup>ii</sup> —Bi1—I1 <sup>iii</sup>	91.384 (7)	C2—C3—H3C	109.5
I1 <sup>i</sup> —Bi1—I1 <sup>v</sup>	91.384 (7)	H3A—C3—H3C	109.5
I1 <sup>iii</sup> —Bi1—I1 <sup>iv</sup>	88.616 (7)	H3B—C3—H3C	109.5
I1 <sup>iii</sup> —Bi1—I1 <sup>v</sup>	88.616 (7)	C1—N3—C12	121.4 (3)
I1 <sup>iv</sup> —Bi1—I1 <sup>v</sup>	88.616 (7)	C1—N3—C10	121.5 (3)
I1—Bi1—I1 <sup>i</sup>	88.616 (7)	C12—N3—C10	117.2 (2)
I1—Bi1—I1 <sup>ii</sup>	88.616 (7)	N1—C4—C5	111.8 (3)
I1 <sup>i</sup> —Bi1—I1 <sup>ii</sup>	88.616 (7)	N1—C4—H4A	109.3

I2—Bi2—I1	168.28 (3)	C5—C4—H4A	109.3
I2 <sup>i</sup> —Bi2—I1 <sup>i</sup>	168.28 (3)	N1—C4—H4B	109.3
I2 <sup>ii</sup> —Bi2—I1 <sup>ii</sup>	168.28 (3)	C5—C4—H4B	109.3
I2 <sup>i</sup> —Bi2—I2 <sup>ii</sup>	96.914 (8)	H4A—C4—H4B	107.9
I2—Bi2—I2 <sup>i</sup>	96.914 (8)	C4—C5—H5A	109.5
I2—Bi2—I2 <sup>ii</sup>	96.914 (8)	C4—C5—H5B	109.5
I2 <sup>i</sup> —Bi2—I1 <sup>ii</sup>	91.151 (6)	H5A—C5—H5B	109.5
I2 <sup>ii</sup> —Bi2—I1	91.151 (6)	C4—C5—H5C	109.5
I2—Bi2—I1 <sup>i</sup>	91.151 (6)	H5A—C5—H5C	109.5
I2—Bi2—I1 <sup>ii</sup>	90.517 (7)	H5B—C5—H5C	109.5
I2 <sup>i</sup> —Bi2—I1	90.517 (7)	N2—C6—C7	112.0 (3)
I2 <sup>ii</sup> —Bi2—I1 <sup>i</sup>	90.517 (7)	N2—C6—H6A	109.2
I1—Bi2—I1 <sup>i</sup>	80.243 (8)	C7—C6—H6A	109.2
I1—Bi2—I1 <sup>ii</sup>	80.243 (8)	N2—C6—H6B	109.2
I1 <sup>i</sup> —Bi2—I1 <sup>ii</sup>	80.243 (8)	C7—C6—H6B	109.2
Bi1—I1—Bi2	78.156 (7)	H6A—C6—H6B	107.9
I3—Bi3—I4	166.83 (2)	C6—C7—H7A	109.5
I3 <sup>vii</sup> —Bi3—I4 <sup>vii</sup>	166.83 (2)	C6—C7—H7B	109.5
I3 <sup>vi</sup> —Bi3—I4 <sup>vi</sup>	166.83 (2)	H7A—C7—H7B	109.5
I3 <sup>vii</sup> —Bi3—I4	97.553 (7)	C6—C7—H7C	109.5
I3—Bi3—I4 <sup>vi</sup>	97.553 (7)	H7A—C7—H7C	109.5
I3 <sup>vi</sup> —Bi3—I4 <sup>vii</sup>	97.553 (7)	H7B—C7—H7C	109.5
I3 <sup>vi</sup> —Bi3—I3 <sup>vii</sup>	94.628 (9)	N2—C8—C9	112.1 (3)
I3 <sup>vi</sup> —Bi3—I3	94.628 (9)	N2—C8—H8A	109.2
I3 <sup>vii</sup> —Bi3—I3	94.628 (9)	C9—C8—H8A	109.2
I3 <sup>vi</sup> —Bi3—I4	89.373 (7)	N2—C8—H8B	109.2
I3 <sup>vii</sup> —Bi3—I4 <sup>vi</sup>	89.373 (7)	C9—C8—H8B	109.2
I3—Bi3—I4 <sup>vii</sup>	89.373 (7)	H8A—C8—H8B	107.9
I4—Bi3—I4 <sup>vi</sup>	77.653 (8)	C8—C9—H9A	109.5
I4—Bi3—I4 <sup>vii</sup>	77.653 (8)	C8—C9—H9B	109.5
I4 <sup>vi</sup> —Bi3—I4 <sup>vii</sup>	77.653 (8)	H9A—C9—H9B	109.5
I4 <sup>vii</sup> —Bi4—I4 <sup>ix</sup>	180.0	C8—C9—H9C	109.5
I4—Bi4—I4 <sup>viii</sup>	180.0	H9A—C9—H9C	109.5
I4 <sup>vi</sup> —Bi4—I4 <sup>x</sup>	180.0	H9B—C9—H9C	109.5
I4 <sup>vii</sup> —Bi4—I4 <sup>x</sup>	94.178 (7)	N3—C10—C11	112.4 (3)
I4 <sup>vi</sup> —Bi4—I4 <sup>viii</sup>	94.178 (7)	N3—C10—H10A	109.1
I4—Bi4—I4 <sup>ix</sup>	94.178 (7)	C11—C10—H10A	109.1
I4—Bi4—I4 <sup>x</sup>	94.178 (7)	N3—C10—H10B	109.1
I4 <sup>vii</sup> —Bi4—I4 <sup>viii</sup>	94.178 (7)	C11—C10—H10B	109.1
I4 <sup>vi</sup> —Bi4—I4 <sup>ix</sup>	94.178 (7)	H10A—C10—H10B	107.9
I4—Bi4—I4 <sup>vii</sup>	85.824 (7)	C10—C11—H11A	109.5
I4—Bi4—I4 <sup>vi</sup>	85.824 (7)	C10—C11—H11B	109.5
I4 <sup>vii</sup> —Bi4—I4 <sup>vi</sup>	85.824 (7)	H11A—C11—H11B	109.5
I4 <sup>ix</sup> —Bi4—I4 <sup>x</sup>	85.824 (7)	C10—C11—H11C	109.5
I4 <sup>viii</sup> —Bi4—I4 <sup>ix</sup>	85.824 (7)	H11A—C11—H11C	109.5
I4 <sup>viii</sup> —Bi4—I4 <sup>x</sup>	85.824 (7)	H11B—C11—H11C	109.5
Bi4—I4—Bi3	81.786 (7)	N3—C12—C13	112.2 (3)
N2—C1—N1	120.5 (3)	N3—C12—H12A	109.2



N2—C1—N3	120.5 (3)	C13—C12—H12A	109.2
N1—C1—N3	119.0 (3)	N3—C12—H12B	109.2
C1—N1—C2	121.8 (3)	C13—C12—H12B	109.2
C1—N1—C4	121.6 (3)	H12A—C12—H12B	107.9
C2—N1—C4	116.6 (3)	C12—C13—H13A	109.5
N1—C2—C3	111.2 (3)	C12—C13—H13B	109.5
N1—C2—H2A	109.4	H13A—C13—H13B	109.5
C3—C2—H2A	109.4	C12—C13—H13C	109.5
N1—C2—H2B	109.4	H13A—C13—H13C	109.5
C3—C2—H2B	109.4	H13B—C13—H13C	109.5
N2—C1—N1—C2	38.7 (4)	N2—C1—N3—C10	-145.5 (3)
N3—C1—N1—C2	-141.6 (3)	N1—C1—N3—C10	34.8 (5)
N2—C1—N1—C4	-137.1 (3)	C1—N1—C4—C5	90.0 (4)
N3—C1—N1—C4	42.6 (4)	C2—N1—C4—C5	-85.9 (3)
C1—N1—C2—C3	103.7 (4)	C1—N2—C6—C7	121.5 (3)
C4—N1—C2—C3	-80.4 (4)	C8—N2—C6—C7	-56.4 (4)
N1—C1—N2—C6	34.8 (4)	C1—N2—C8—C9	129.8 (3)
N3—C1—N2—C6	-144.8 (3)	C6—N2—C8—C9	-52.3 (4)
N1—C1—N2—C8	-147.3 (3)	C1—N3—C10—C11	128.1 (3)
N3—C1—N2—C8	33.0 (4)	C12—N3—C10—C11	-52.8 (4)
N2—C1—N3—C12	35.5 (5)	C1—N3—C12—C13	123.8 (3)
N1—C1—N3—C12	-144.2 (3)	C10—N3—C12—C13	-55.2 (4)

Symmetry codes: (i)  $-y, x-y, z$ ; (ii)  $-x+y, -x, z$ ; (iii)  $-x, -y, -z$ ; (iv)  $y, -x+y, -z$ ; (v)  $x-y, x, -z$ ; (vi)  $-x+y, -x+1, z$ ; (vii)  $-y+1, x-y+1, z$ ; (viii)  $-x+2/3, -y+4/3, -z+1/3$ ; (ix)  $y-1/3, -x+y+1/3, -z+1/3$ ; (x)  $x-y+2/3, x+1/3, -z+1/3$ .