



Crystal structure and Hirshfeld surface analysis of the layered hybrid metal halide poly[bis(2-iodoethylammonium) [di- μ -iodido-diiodidogermanate(II)]]

Olesia I. Kucheriv,^{a*} Mircea-Odin Apostu,^b Olena Prysiashna,^{c,d} Vadim A. Potaskalov^e and Sergey O. Malinkin^a

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^aDepartment of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska St. 64, Kyiv 01601, Ukraine,

^bDepartment of Chemistry, Faculty of Chemistry, Al. I. Cuza University of Iasi, Carol I Blvd. 11, Iasi 700506, Romania,

^cBakul Institute for Superhard Materials, National Academy of Sciences of Ukraine, Avtozavodskaya St. 2, Kyiv 04074, Ukraine,

^dDepartment of Chemistry, Kyiv National University of Construction and Architecture, Povitroflotsky Ave. 31, Kyiv 03680, Ukraine, and

^eDepartment of General and Inorganic Chemistry, National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Beresteyskiy Pr. 37, 03056 Kyiv, Ukraine. *Correspondence e-mail:

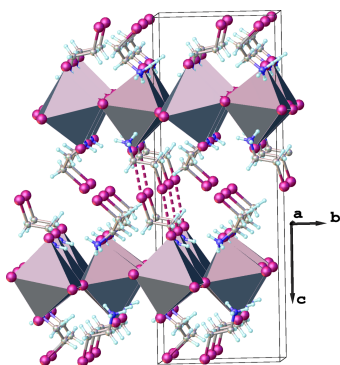
olesia.kucheriv@univ.kiev.ua

The title compound is a germanium-based hybrid metal halide that represents a less-toxic alternative to more popular lead-based analogues in optoelectronic applications. $\{(2\text{-IC}_2\text{H}_4\text{NH}_3)_2[\text{GeI}_4]\}_n$ is composed of infinite inorganic layers that are formed by $[\text{GeI}_6]^{4-}$ octahedra connected in a corner-sharing manner with four equatorial I atoms. The organic $(2\text{-IC}_2\text{H}_4\text{NH}_3)^+$ cations interleave the inorganic layers. There are two types of 2-iodoethylammonium cations, with synclinal and antiperiplanar conformations. The organic cations interact with the inorganic layers through hydrogen bonds and $\text{I}\cdots\text{I}$ contacts. The crystal under investigation was twinned by a 180° rotation around $[100]$.

1. Chemical context

The number of functional materials with exceptional physical properties has been significantly expanded by numerous hybrid organic–inorganic halide perovskites in recent decades. These materials frequently display semiconducting properties that allow their application in various photovoltaic and optoelectronic devices (Zhao & Zhu, 2016). Hybrid perovskites have been shown to form effective active layers in solar cells (Huang *et al.*, 2023), light-emitting diodes (Ngai *et al.*, 2023), photodetectors (Moeini *et al.*, 2022) and thermoelectronic cells (Ngai *et al.*, 2023).

Hybrid halide perovskites are compounds of the ABX_3 type (where A is an organic cation, B is a metal cation and X is a halide anion), which contain fundamental BX_6 octahedra that are organized in all-corner-sharing 3D network (Akkerman & Manna, 2020; Breternitz & Schorr, 2018). Upon development of the field, numerous analogues containing BX_6 octahedra, which are connected in various manners (corner-sharing, edge-sharing and even face-sharing), and organic cations have been developed. Such hybrid metal–halide compounds can form structures in which the inorganic octahedra are connected in very different manners, forming infinite layers (frequently called layered perovskites in the case of corner-to-corner connection; McNulty & Lightfoot, 2021), polymeric chains, discrete moieties and more complicated structures that include double-chains and double-layers. Hybrid metal halides of different structural motifs tend to display distinctive physical properties. For example, 3D perovskites are known to have the narrowest bandgaps and therefore are the most



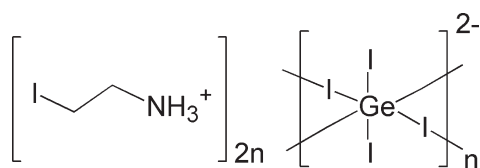
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promising for photovoltaic and optoelectronic applications (Younis *et al.*, 2021). Layered metal halides have bandgaps which are usually *ca.* 1 eV higher than for 3D perovskites with corresponding halogens, but they display enhanced stability (Wong & Yang, 2021). Hybrid metal halides that form inorganic polymeric chains are the most efficient white-light emitters (Yuan *et al.*, 2017), while hybrid metal halides containing discrete inorganic moieties are known to be very efficient emitters with high quantum yields (Zhang *et al.*, 2021).

Importantly, the most applied and studied for today are hybrid perovskites and other metal halides that are formed with lead. However, the significant toxicity of this metal induces efforts towards research into lead-free analogues. Most frequently, lead is substituted with tin or germanium due to the chemical similarity of these elements, which allows retention of the physical properties of the target materials while reducing their toxicity.

Herein we describe the crystal structure of a new layered hybrid metal halide – (2-IC₂H₄NH₃)₂[GeI₄]. The introduction of a 2-iodoethylammonium cation, which is able to create I⋯I contacts, ensures additional structural stability of the framework.



2. Structural commentary

The title compound (2-IC₂H₄NH₃)₂[GeI₄] crystallizes in the centrosymmetric monoclinic *P*2₁/*n* space group. In its crystal

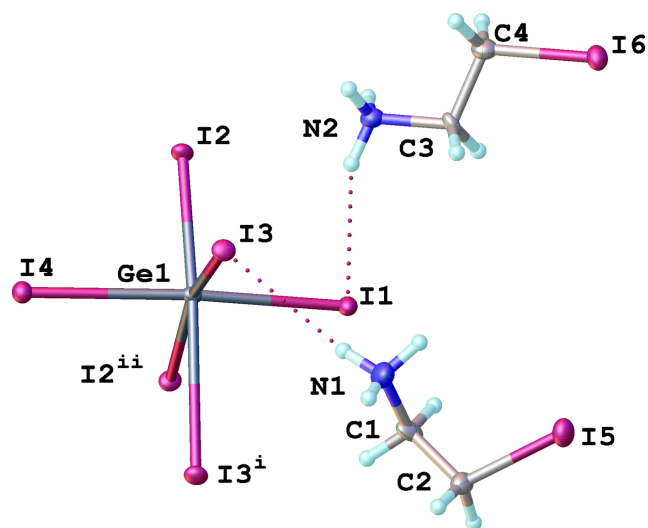


Figure 1
Expanded asymmetric unit of the title compound showing the atom-labeling scheme. Hydrogen bonds between organic and inorganic parts are shown as dotted lines. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $\frac{5}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.]

structure, the Ge²⁺ cation has a significantly distorted octahedral coordination environment provided by six iodide anions (Fig. 1). The Ge—I bond lengths range from 2.7732 (12) to 3.3646 (11) Å, resulting in an octahedral distortion, which can be quantified by the quadratic elongation parameter: $\langle \lambda_{\text{oct}} \rangle = \Sigma(l_i/l_0)^2/6 = 1.0065$, where l_i is the individual Ge—I bond length and l is average Ge—I bond length (Robinson *et al.*, 1971). The *cis*-I—Ge—I angles are in the range of 75.23 (3)–95.46 (4)°, leading to a significant bond angle variance: $\sigma_{\theta}^2 = \Sigma(\theta_i - 90^\circ)^2/11 = 34.047$, where θ_i are the twelve individual *cis*-I—Ge—I angles in the coordination octahedron (Robinson *et al.*, 1971). Such large distortion parameters are quite common for germanium halides. For example, in a series of layered (CIMBA)₂GeI₄ (CIMBA = 4-chloro-methylbenzylamine) with either enantiopure or racemic cations, bond-angle variances were in the 34.52–55.16° range, while the quadratic elongation parameter was almost the same for these materials (1.029; Coccia *et al.*, 2024). In comparison with lead, germanium has a more active lone pair, which results in significantly larger distortions.

The negative charge of the inorganic coordination octahedra in this structure is compensated for by the 2-iodoethylammonium cations. There are two types of crystallographically independent cations in the structure: one of them adopts a synclinal conformation, while the other one is antiperiplanar. Torsion angles in these cations are –65.4 (11)° and 176.7 (7)°, respectively. The I—C, C—C and C—N bond lengths in the organic cations fall within the expected ranges (Allen *et al.*, 1987).

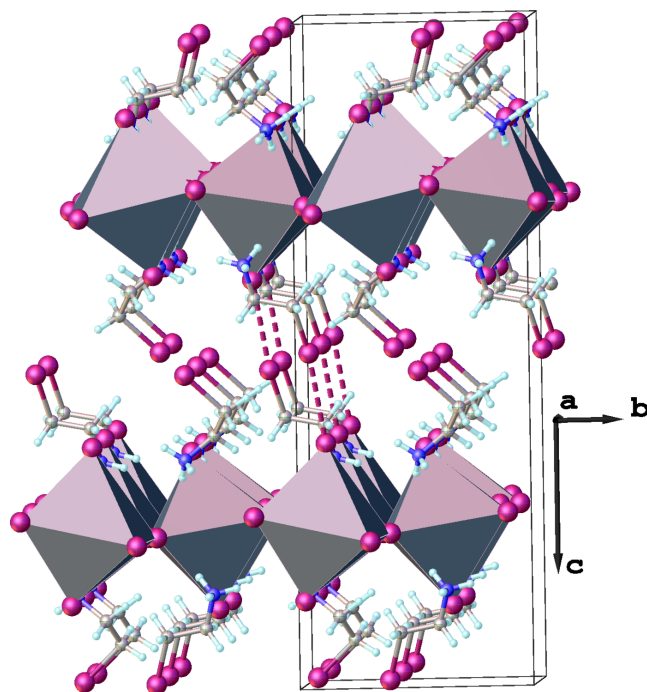


Figure 2
Fragment of the title compound showing the propagation of infinite two-dimensional inorganic layers along the *ab* plane. I⋯I contacts between the organic cations and the inorganic layers are shown as pink dashed lines.

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1A\cdots I4^i$	0.91	2.74	3.544 (11)	147
$N1-H1B\cdots I2^{ii}$	0.91	3.11	3.782 (11)	133
$N1-H1C\cdots I3$	0.91	2.86	3.735 (10)	162
$N2-H2A\cdots I4^{iii}$	0.91	2.70	3.588 (9)	166
$N2-H2B\cdots I3^i$	0.91	2.87	3.744 (9)	160
$N2-H2C\cdots I1$	0.91	2.65	3.496 (9)	154
$C4-H4A\cdots I1^{iv}$	0.99	3.13	3.790 (10)	125

Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + \frac{5}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x, y - 1, z$.

The inorganic $[\text{GeI}_6]^{4-}$ octahedra connect with each other in the corner-sharing mode, creating infinite 2D layers that propagate in the ab plane (Fig. 2). In this type of architecture, the four equatorial iodide anions are bridging (I_b) while two axial iodide anions are terminal (I_t). The coordination octahedra undergo out-of-plane tilting with respect to the ab plane with the $I-\text{Ge}-I$ angles being $161.15 (3)^\circ$, thus the layers are slightly corrugated. The organic cations are located between the inorganic layers.

3. Supramolecular features

There is an extensive network of hydrogen bonds in the title structure. The 2-iodoethylammonium cation in a synclinal conformation forms three hydrogen bonds of the $N-H\cdots I$ type with inorganic layers: two of these hydrogen bonds involve bridging iodine atoms, while the remaining one is with a terminal iodine (Fig. 3). Detailed information about the hydrogen-bonding geometry is given in Table 1. The organic cations with an antiperiplanar conformation make four hydrogen bonds with the inorganic layers: three of them are also of the $N-H\cdots I$ type (one with a bridging iodine atom and two with terminal ones) while the fourth is of the $C-H\cdots I$ type (Fig. 2, Table 1). The cations with synclinal and antiperiplanar conformations are arranged in an alternating manner (Fig. 4). In addition, the iodine atoms of the antiperiplanar cations make $I\cdots I$ contacts with the terminal iodine atoms of neighboring inorganic layers, thus creating an infinite 3D supramolecular framework (Fig. 2). The presence

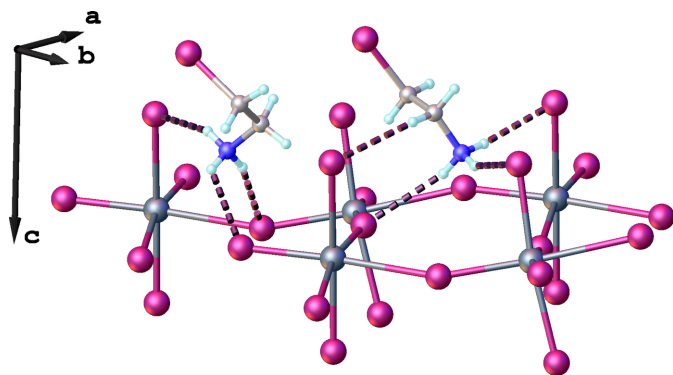


Figure 3

Detail of the hydrogen bonds created between the 2-iodoethylammonium cations and the inorganic layer.

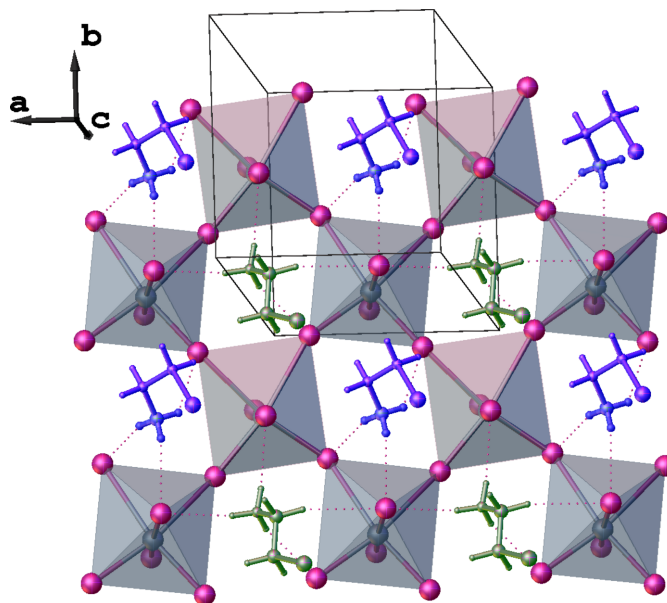


Figure 4

Alternating organic cations in synclinal (blue) and antiperiplanar (green) conformations within a layer.

of such $I\cdots I$ contacts has previously been shown to have a significant impact on the physical properties of hybrid metal halides. For example, the presence of a very similar organic cation, 4-iodobutylammonium, in the layered metal halide $[\text{I}-(\text{CH}_2)_4\text{NH}_3]_2\text{PbI}_4$ was found to suppress phase transitions in this material in contrast to the very similar $[\text{H}-(\text{CH}_2)_4\text{NH}_3]_2\text{PbI}_4$. Phase-transition suppression is associated with the occurrence of $I\cdots I$ interactions between organic cations and the inorganic layers, which restrict the movement of organic cations in space (Chakraborty *et al.*, 2022).

Interestingly, in contrast to the antiperiplanar conformation, the synclinal conformation of an organic cation does not permit the formation of a close $I\cdots I$ contact with the inorganic layers due to steric hindrance. Such an effect has previously been observed for a series of $(\text{ICH}_2\text{CH}_2\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{I}_{3n+1}$ layered perovskites in which the organic cations in different conformations were shown to impact the structural symmetry and electronic band structure of the layered metal halides (Xue *et al.*, 2023).

4. Hirshfeld surface analysis

Hirshfeld surface analysis was performed in order to get a deeper insight into the weak interactions found in the structure (Hirshfeld, 1977). The Hirshfeld surface was plotted with a standard resolution of d_{norm} over a fixed color scale that uses white to depict contacts whose distances are close to the sum of the van der Waals radii, while shorter distances are shown in red and longer in blue. The obtained plot demonstrates the presence of several strong $H\cdots I$ contacts, shown in red in Fig. 5a. The above-mentioned $I\cdots I$ contacts between organic cations in an antiperiplanar conformation with the iodine

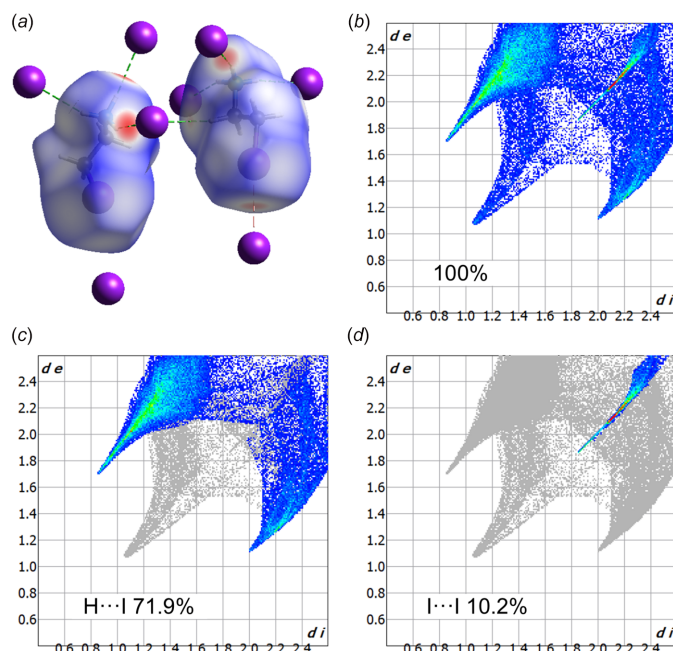


Figure 5

(a) Hirshfeld surface of the title compound plotted over d_{norm} , showing the strongest $\text{H}\cdots\text{I}$ interactions in red; (b)–(d) the two-dimensional fingerprint plots for the title compound.

atoms of the inorganic layers can be observed in pale red. The associated fingerprint plots have also been calculated (Fig. 5b–d). The plots demonstrate that $\text{H}\cdots\text{I}$ contacts are most common and constitute 71.9% of all interactions present in the structure (Fig. 5c). In addition, an important contribution is provided by $\text{I}\cdots\text{I}$ interactions (10.2%), as shown in Fig. 5d.

The prevalence of $\text{H}\cdots\text{I}$ interactions underscores the critical role of hydrogen bonding in stabilizing the structure, while the $\text{I}\cdots\text{I}$ contacts contribute to the three-dimensional supramolecular framework. The remaining $\text{H}\cdots\text{H}$ contacts are statistically frequently observed in the structure due to the terminal positions of the H atoms; they are, however, chemically irrelevant.

It should be mentioned that the color map of the Hirshfeld surface displays the strength of contacts (the strongest contacts are shown in red) while the fingerprint plots indicate how frequently the corresponding contacts are observed in the structure. The Hirshfeld surface analysis was undertaken and the fingerprint plots were generated using *Crystal Explorer 21.45* software (Spackman *et al.*, 2021).

5. Database survey

A survey of the the Cambridge Structural Database (CSD version 5.45, update of September 2024; Groom *et al.*, 2016) showed that the title compound has never been published before. The search revealed 13 previously known structures of hybrid metal halides containing the 2-iodoethylammonium cation. Two of these structures are $(2\text{-IC}_2\text{H}_4\text{NH}_3)\text{SnI}_4$ (Song *et al.*, 2022) and the mixed-cation $[\text{Br}(\text{CH}_2)_2\text{-NH}_3]_{2-x}[\text{I}(\text{CH}_2)_2\text{-NH}_3]_x\text{PbBr}_x\text{I}_{4-x}$ (Sourisseau *et al.*, 2007b), which are isostructural to the title compound.

Table 2

Experimental details.

Crystal data	
Chemical formula	$(\text{C}_2\text{H}_7\text{IN})_2[\text{GeI}_4]$
M_r	924.16
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	8.1431 (2), 8.8362 (2), 25.1787 (7)
β (°)	97.264 (2)
V (Å ³)	1797.16 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ^{−1})	11.99
Crystal size (mm)	0.14 × 0.08 × 0.01
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Analytical (<i>CrysAlis PRO</i> ; Rigaku OD, 2023)
$T_{\text{min}}, T_{\text{max}}$	0.399, 0.852
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5413, 5413, 4967
R_{int}	0.030
$(\sin \theta/\lambda)_{\text{max}}$ (Å ^{−1})	0.708
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.092, 1.19
No. of reflections	5413
No. of parameters	121
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ^{−3})	1.21, −1.27

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXS* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

tural to the title compound. There are four reported structures of $(2\text{-IC}_2\text{H}_4\text{NH}_3)\text{PbI}_4$, which also form inorganic layers; however in contrast to the title compound, in this lead-based analogue all of the organic cations exhibit an antiperiplanar conformation (Sourisseau *et al.*, 2007a,b; Lemmerer & Billing, 2010; Skorokhod *et al.*, 2023). Seven of the found structures contain a second organic cation, methylammonium (MA), and can be described by the general formula $(2\text{-IC}_2\text{H}_4\text{NH}_3)_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 2\text{--}4$). In these compounds there are from two to four consecutive inorganic layers, which are connected into multilayered structures. The methylammonium cations occupy positions in cuboctahedral voids within the multilayers, while the 2-iodoethylammonium cations separate the multilayers. When the number of layers is odd ($n = 3$), the 2-iodoethylammonium cation adopts an antiperiplanar conformation, while in the case of an even number of layers ($n = 2, 4$) this cation is in a synclinal conformation (Xue *et al.*, 2023; Skorokhod *et al.*, 2023).

6. Synthesis and crystallization

The title compound was obtained as a sub-product upon synthesis of (aziridinium) GeI_3 ; the SXRD (single-crystal X-ray diffraction) experiment established the formation of $(2\text{-IC}_2\text{H}_4\text{NH}_3)\text{GeI}_4$ instead of the target perovskite. 63 mg of GeO_2 were mixed with 0.9 ml of an aqueous HI solution (57% w/w) and 0.6 ml of H_3PO_2 (50% w/w). The obtained mixture was heated to 393 K in an oil bath and was kept at this temperature for 20 min upon constant mixing. The obtained transparent orange solution was allowed to cool to room

temperature. 10 mg of aziridine were dissolved in 0.1 ml of water and added dropwise to 0.1 ml of the prior solution. The orange crystals that formed within 1 h were collected immediately and kept in Paratone[®] oil prior to measurements. SXRD measurements were performed at 100 K.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. 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 CH_2 groups were refined as riding, while H atoms of NH_3^+ groups were refined as rotating. The crystal under investigation was twinned by a 180° rotation around [100] and the intensity data processed into a HKLF5-type file; the twin components refined to a ratio of 0.8495:0.1504.

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Computing details

Poly[bis(2-iodoethylammonium) [di- μ -iodido-diiodidogermanate(II)]]

Crystal data

(C₂H₇IN)₂[GeI₄]

$M_r = 924.16$

Monoclinic, $P2_1/n$

$a = 8.1431(2) \text{ \AA}$

$b = 8.8362(2) \text{ \AA}$

$c = 25.1787(7) \text{ \AA}$

$\beta = 97.264(2)^\circ$

$V = 1797.16(8) \text{ \AA}^3$

$Z = 4$

$F(000) = 1608$

$D_x = 3.416 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 10013 reflections

$\theta = 3.3\text{--}30.5^\circ$

$\mu = 11.99 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Plate, clear intense orange

$0.14 \times 0.08 \times 0.01 \text{ mm}$

Data collection

XtaLAB Synergy, Dualflex, HyPix
diffractometer

Detector resolution: $10.0000 \text{ pixels mm}^{-1}$

ω scans

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

$T_{\min} = 0.399$, $T_{\max} = 0.852$

5413 measured reflections

5413 independent reflections

4967 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 30.2^\circ$, $\theta_{\min} = 2.4^\circ$

$h = -10 \rightarrow 11$

$k = -11 \rightarrow 11$

$l = -31 \rightarrow 31$

Refinement

Refinement on F^2

Least-squares matrix: full

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

$wR(F^2) = 0.092$

$S = 1.19$

5413 reflections

121 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2 + 42.6836P]$

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

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

$\Delta\rho_{\max} = 1.21 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -1.27 \text{ e \AA}^{-3}$

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.

Refinement. Refined as a 2-component twin.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I2	1.22418 (8)	0.35127 (7)	0.76979 (3)	0.01606 (14)
I3	0.72110 (8)	0.41154 (7)	0.76396 (3)	0.01657 (14)
I1	0.95890 (8)	0.55334 (7)	0.63911 (3)	0.01699 (14)
I4	1.06654 (8)	0.65550 (7)	0.87689 (3)	0.01740 (14)
I6	0.77665 (9)	−0.09924 (8)	0.51564 (3)	0.02055 (15)
I5	0.25037 (9)	0.56475 (9)	0.51448 (3)	0.02426 (16)
Ge1	0.99725 (12)	0.58843 (11)	0.75456 (4)	0.0128 (2)
N1	0.4449 (15)	0.5521 (12)	0.6444 (4)	0.035 (3)
H1A	0.423703	0.465891	0.624939	0.042*
H1B	0.352259	0.580595	0.658589	0.042*
H1C	0.528452	0.534821	0.671279	0.042*
C3	0.9157 (12)	0.1243 (11)	0.6000 (4)	0.016 (2)
H3A	0.957632	0.183196	0.571113	0.019*
H3B	0.798169	0.151794	0.600885	0.019*
N2	1.0135 (11)	0.1621 (10)	0.6523 (4)	0.0201 (19)
H2A	1.123115	0.148652	0.649940	0.024*
H2B	0.982275	0.100583	0.678197	0.024*
H2C	0.994867	0.260296	0.660675	0.024*
C2	0.3521 (13)	0.7312 (12)	0.5719 (5)	0.022 (2)
H2D	0.388261	0.820189	0.552453	0.026*
H2E	0.264226	0.765182	0.592961	0.026*
C4	0.9289 (15)	−0.0421 (12)	0.5888 (5)	0.024 (2)
H4A	0.893086	−0.100939	0.618776	0.028*
H4B	1.045603	−0.068378	0.585890	0.028*
C1	0.4942 (13)	0.6745 (12)	0.6091 (5)	0.024 (2)
H1D	0.543005	0.759248	0.631442	0.029*
H1E	0.580109	0.635510	0.588073	0.029*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I2	0.0138 (3)	0.0141 (3)	0.0197 (3)	0.0044 (2)	0.0000 (2)	−0.0016 (2)
I3	0.0131 (3)	0.0153 (3)	0.0213 (3)	−0.0038 (2)	0.0023 (2)	0.0007 (2)
I1	0.0233 (3)	0.0132 (3)	0.0140 (3)	0.0010 (2)	0.0006 (3)	0.0001 (2)
I4	0.0192 (3)	0.0172 (3)	0.0155 (3)	−0.0001 (3)	0.0012 (3)	−0.0008 (2)
I6	0.0244 (3)	0.0201 (3)	0.0170 (3)	−0.0036 (3)	0.0019 (3)	−0.0022 (3)
I5	0.0223 (3)	0.0297 (4)	0.0197 (4)	−0.0009 (3)	−0.0015 (3)	−0.0035 (3)
Ge1	0.0112 (4)	0.0101 (4)	0.0172 (5)	0.0000 (4)	0.0016 (4)	0.0002 (4)

N1	0.056 (7)	0.029 (5)	0.019 (5)	0.011 (5)	−0.003 (5)	0.000 (4)
C3	0.016 (4)	0.017 (5)	0.016 (5)	−0.001 (4)	0.004 (4)	−0.008 (4)
N2	0.025 (5)	0.015 (4)	0.020 (5)	0.002 (3)	0.001 (4)	0.002 (3)
C2	0.024 (5)	0.017 (5)	0.022 (6)	−0.002 (4)	−0.004 (4)	0.000 (4)
C4	0.030 (6)	0.015 (5)	0.025 (6)	−0.001 (4)	0.001 (5)	0.002 (4)
C1	0.021 (5)	0.014 (5)	0.035 (7)	−0.001 (4)	−0.006 (5)	−0.008 (5)

Geometric parameters (Å, °)

I2—Ge1	2.7881 (11)	C3—N2	1.487 (13)
I3—Ge1	2.7732 (12)	C3—C4	1.503 (14)
I1—Ge1	2.9006 (12)	N2—H2A	0.9100
I4—Ge1	3.1172 (12)	N2—H2B	0.9100
I6—C4	2.147 (11)	N2—H2C	0.9100
I5—C2	2.153 (10)	C2—H2D	0.9900
N1—H1A	0.9100	C2—H2E	0.9900
N1—H1B	0.9100	C2—C1	1.481 (14)
N1—H1C	0.9100	C4—H4A	0.9900
N1—C1	1.488 (16)	C4—H4B	0.9900
C3—H3A	0.9900	C1—H1D	0.9900
C3—H3B	0.9900	C1—H1E	0.9900
I2—Ge1—I1	92.47 (4)	H2A—N2—H2B	109.5
I2—Ge1—I4	88.45 (3)	H2A—N2—H2C	109.5
I3—Ge1—I2	95.46 (4)	H2B—N2—H2C	109.5
I3—Ge1—I1	92.27 (3)	I5—C2—H2D	108.9
I3—Ge1—I4	94.03 (4)	I5—C2—H2E	108.9
I1—Ge1—I4	173.52 (4)	H2D—C2—H2E	107.7
H1A—N1—H1B	109.5	C1—C2—I5	113.4 (7)
H1A—N1—H1C	109.5	C1—C2—H2D	108.9
H1B—N1—H1C	109.5	C1—C2—H2E	108.9
C1—N1—H1A	109.5	I6—C4—H4A	109.6
C1—N1—H1B	109.5	I6—C4—H4B	109.6
C1—N1—H1C	109.5	C3—C4—I6	110.1 (7)
H3A—C3—H3B	108.2	C3—C4—H4A	109.6
N2—C3—H3A	109.7	C3—C4—H4B	109.6
N2—C3—H3B	109.7	H4A—C4—H4B	108.2
N2—C3—C4	110.0 (9)	N1—C1—H1D	109.2
C4—C3—H3A	109.7	N1—C1—H1E	109.2
C4—C3—H3B	109.7	C2—C1—N1	112.1 (9)
C3—N2—H2A	109.5	C2—C1—H1D	109.2
C3—N2—H2B	109.5	C2—C1—H1E	109.2
C3—N2—H2C	109.5	H1D—C1—H1E	107.9
I5—C2—C1—N1	−65.4 (11)	N2—C3—C4—I6	176.7 (7)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 <i>A</i> $\cdots$ I4 ⁱ	0.91	2.74	3.544 (11)	147
N1—H1 <i>B</i> $\cdots$ I2 ⁱⁱ	0.91	3.11	3.782 (11)	133
N1—H1 <i>C</i> $\cdots$ I3	0.91	2.86	3.735 (10)	162
N2—H2 <i>A</i> $\cdots$ I4 ⁱⁱⁱ	0.91	2.70	3.588 (9)	166
N2—H2 <i>B</i> $\cdots$ I3 ⁱ	0.91	2.87	3.744 (9)	160
N2—H2 <i>C</i> $\cdots$ I1	0.91	2.65	3.496 (9)	154
C4—H4 <i>A</i> $\cdots$ I1 ^{iv}	0.99	3.13	3.790 (10)	125

Symmetry codes: (i) $-x+3/2, y-1/2, -z+3/2$; (ii) $-x+3/2, y+1/2, -z+3/2$; (iii) $-x+5/2, y-1/2, -z+3/2$; (iv) $x, y-1, z$.