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Crystal structure of bis(β-alaninium) tetrabromidoplumbate

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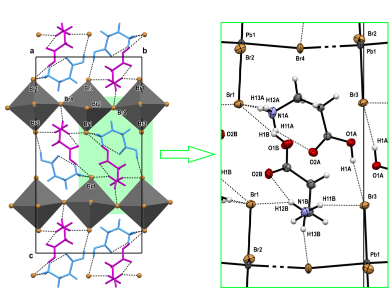
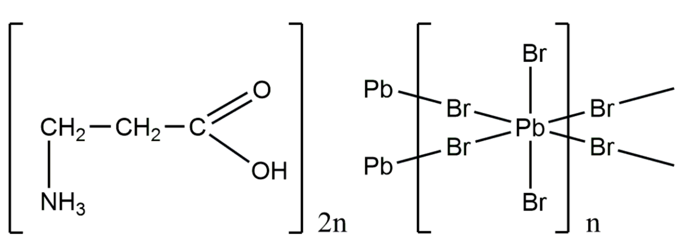
The title compound, poly[bis(β-alaninium) [[dibromidoplumbate]-di-μ-dibromido]] $\{(C_2H_8NO_2)_2[PbBr_4]\}_n$ or (β-AlaH)$_2$PbBr$_4$, crystallizes in the monoclinic space group $P2_1/n$. The $(PbBr_4)^{2-}$ anion is located on a general position and has a two-dimensional polymeric structure. The Pb center is holodirected. The supramolecular network is mainly based on O—H···Br, N—H···Br and N—H···O hydrogen bonds.



1. Chemical context

As plumbiferous compounds are commonly toxic, they are unfavorable for photovoltaic devices. Nonetheless, they have other important applications such as white-light-emitting materials (Peng *et al.*, 2018), luminescent sensing (Wang *et al.*, 2019; Wang, 2020; Martínez-Casado *et al.*, 2012), ferroelectric materials (Gao *et al.*, 2017), non-linear optical materials (Chen *et al.*, 2020) and semiconductors (Terpstra *et al.*, 1997). Lead-containing materials also are attractive from a stereochemical point of view. The Pb^{2+} ion has a $6s^2$ electron pair, which is crucial for the stereochemistry of Pb^{II}. When the $6s^2$ electron pair takes part in hybridization between the *s* and *p* orbitals, the lead atom is stereochemically active and has a hemi-directed coordination, otherwise the lead atom exhibits a regular coordination sphere (Casas *et al.*, 2006; Seth *et al.*, 2018).

Our research group has been studying various amino acid salts for a long time (Fleck & Petrosyan, 2014), and we assumed that amino acids could also be used to synthesize organic–inorganic hybrid materials. After the successful synthesis of (GlyH)PbBr$_3$ (Tonoyan *et al.*, 2024), efforts were focused on obtaining (GlyH)PbI$_3$ and related phases. Later, it was attempted to synthesize salts of β-alanine in the same manner; however, instead of (β-AlaH)PbBr$_3$, crystals of (β-AlaH)$_2$PbBr$_4$ were formed.



In (β-AlaH)$_2$PbBr$_4$ the anion is slightly distorted and the Pb—Br bond lengths range from 2.8952 (3) to 3.2714 (2) Å.

Table 1
Selected geometric parameters (Å, °).

Pb1—Br1	3.0589 (4)	Pb1—Br2^{i}	3.2714 (2)
Pb1—Br3	2.9230 (4)	Pb1—Br4	2.9477 (3)
Pb1—Br2	2.8952 (3)	Pb1—Br4^{ii}	3.0591 (3)
Br1—Pb1—Br2	88.107 (9)	Br2^{i}—Pb1—Br4^{ii}	81.63 (1)
Br1—Pb1—Br2^{i}	80.90 (1)	Br3—Pb1—Br2	87.836 (9)
Br1—Pb1—Br4	87.683 (8)	Br3—Pb1—Br4	92.596 (8)
Br1—Pb1—Br4^{ii}	89.760 (8)	Br3—Pb1—Br4^{ii}	90.472 (8)
Br2—Pb1—Br4	90.568 (9)	Pb1—Br2—Pb1^{iii}	168.87 (1)
Br2—Pb1—Br4^{ii}	96.645 (9)	Pb1—Br2^{i}—Pb1^{i}	168.87 (1)
Br2^{i}—Pb1—Br4	90.75 (1)	Pb1—Br4—Pb1^{iv}	168.90 (1)
O1*A*—C1*A*—C2*A*—C3a	−164.4 (2)	O1*B*—C1*B*—C2*B*—C3*B*	171.4 (2)
C1*A*—C2*A*—C3*A*—N1*A*	−62.9 (3)	C1*B*—C2*B*—C3*B*—N1*B*	59.7 (3)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···Br3^{ii}	0.90 (2)	2.35 (3)	3.241 (2)	171 (4)
N1*A*—H11*A*···O2*A*	0.91	2.18	2.853 (3)	130
N1*A*—H12*A*···Br1^{v}	0.91	2.73	3.619 (2)	166
N1*A*—H13*A*···Br1^{vi}	0.91	2.58	3.445 (2)	159
O1*B*—H1*B*···Br1^{v}	0.88 (2)	2.32 (3)	3.188 (2)	167 (4)
N1*B*—H11*B*···Br3^{vii}	0.91	2.49	3.343 (2)	157
N1*B*—H12*B*···Br1^{iii}	0.91	2.76	3.484 (2)	137
N1*B*—H12*B*···O2*B*	0.91	2.17	2.839 (3)	129
N1*B*—H13*B*···Br4^{vii}	0.91	2.56	3.407 (2)	155

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

This indicates that the Pb^{II} center is not stereochemically active and the anion has holodirected stereochemistry. Recently a paper was published (Zu *et al.*, 2023) in which the authors investigated the relationship between the structures and optoelectronic properties of $[(HOOC_nH_{2n-2}NH_3)_2]PbBr_4$ (n = 3–8) crystals, also including (β-AlaH)$_2$PbBr$_4$ (see also Cazals *et al.*, 2024). In our work, we focused on characterizing the structure from a stereochemical point of view, discussing the Pb^{II} character in a structure solved using XRD data collected at 200 K.

2. Structural commentary

The title compound (β-AlaH)$_2$PbBr$_4$ crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit contains one formula unit. The molecular arrangement is shown in Fig. 1. As can be seen from the dihedral angles (Table 1), both β-alaninium cations have the most common *gauche* conformation (Fleck *et al.*, 2012).

The Pb^{2+} centers of the anion exhibit a holodirected six-coordination with an octahedral geometry. Therefore, for neighboring bromine atoms, the Br—Pb—Br angles are close to right angles, varying from 80.90 (1) to 103.14 (1)° (Table 1). The lead atom forms three partial covalent bonds Pb1—Br2, Pb1—Br3, and Pb1—Br4, and also three coordination bonds with partial covalent character Pb1—Br1, Pb1—Br2^{i} and Pb1—Br4^{ii} (Table 1). Despite the range of Pb1—Br distances, the average value of 3.0259 Å is close to the average value of 3.0310 Å in $PbBr_6$ octahedra, regardless of the anion, for 284 structures in the Cambridge Structural Database (CSD2023.2.0, version 5.45, November update; Groom *et al.*, 2016). The $PbBr_6$ octahedra form a 2D structure with four shared vertices: Br2, Br2^{i}, Br4, and Br4^{ii} (Fig. 2). The octahedra share only vertices, not edges nor faces. The two terminal opposite atoms Br1 and Br3 are located on the surfaces of the layer and the octahedra are arranged in such a way that the angles of the Pb—Br—Pb bridges are close to linear (Table 1), which leads to square-shaped voids between the octahedra.

3. Supramolecular features

The packing in the crystal together with the hydrogen-bond network is shown in Fig. 3. The anionic layers are parallel to the (001) plane, with an interlayer distance of 11.026 (1) Å. The β-alaninium cations are positioned between the anionic layers with the amino and carboxyl groups oriented towards

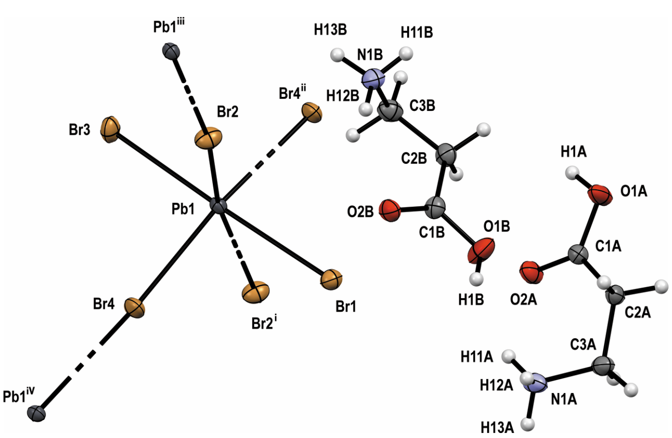


Figure 1
Molecular structure of (β-AlaH)$_2$PbBr$_4$. Displacement ellipsoids are shown at the 50% probability level. Symmetry codes: (i) $x-1, y, z$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x+1, y, z$; (iv) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

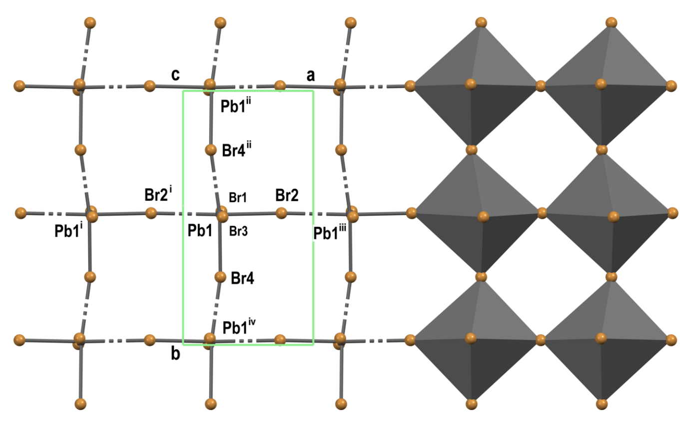


Figure 2
2D structure of the $PbBr_4$ anion viewed along the *c* axis. Part of the anion is shown in an octahedral style. Symmetry codes: (i) $x-1, y, z$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x+1, y, z$; (iv) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

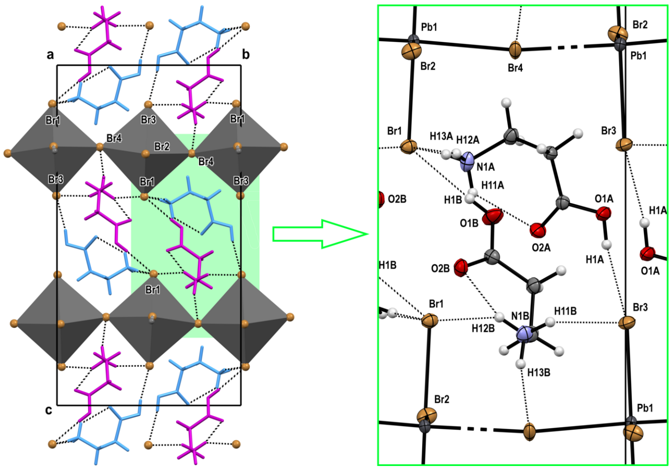


Figure 3
Packing diagram of the structure of $(\beta\text{-AlaH})_2PbBr_4$ viewed along the *a* axis. Hydrogen bonds are shown as dotted lines.

those layers. The β-alaninium cations cross-link neighboring layers of anions through hydrogen bonds between terminal bromine atoms and NH_3^+, and OH groups (Table 2). Each carboxyl group forms one O—H···Br hydrogen bond, while the ammonium groups form two and three N—H···Br hydrogen bonds. Intramolecular N1*A*—H11*A*···O2*A* and N1*B*—H12*B*···O2*B* hydrogen bonds are present in the β-alaninium moieties (Table 2).

4. Database survey

A survey of the Cambridge Structural Database (CSD2023.2.0, version 5.45, November update; Groom *et al.*, 2016) revealed 320 structures containing $PbBr_4$. There were 91 duplicate structures solved at different temperatures, and several inappropriate structures; thus, overall 224 structures were considered. Among them, the title compound was found with refcode YINFIO (Zu *et al.*, 2023), determined at room temperature.

In the structures, the $(PbBr_4)^{2-}$ anion can be in discrete 0D, polymeric 1D, and 2D forms. 0D anions are present in a *pseudotrigonal–bipyramidal geometry* (Fig. 4*a*: ARAJUB, Lin *et al.*, 2019; BOKYAF, Han 2024; YIQPAP, Gröger *et al.*, 2002) and in a *trigonal–pyramidal* geometry (Fig. 4*b*: UVELIT, Gong *et al.*, 2021).

A 1D structure anion may consist of either $PbBr_5$ square-pyramids (3 structures) or $PbBr_6$ octahedra (16 structures). The square-pyramids are alternately connected by a shared bromine atom, with three bromine atoms remaining terminal. Chains can be *linear* (Fig. 4*c*: RUSBUF, Lv *et al.*, 2020) or *zigzag* (Fig. 4*d*: SOHYAS, Li *et al.*, 2019). Octahedral $PbBr_6$ monomers can attach two, three or four adjacent octahedra, have four or three shared bromine atoms, and two or three terminal atoms. Chains can be *linear* (Fig. 4*e*: COKYIO, Zhang *et al.*, 2024), *zigzag* (Fig. 4*f*: CEKYIE, Fu *et al.*, 2022), *V-shaped* (Fig. 4*g*: FERGER, Yuan *et al.*, 2017), and *double* (Fig. 4*h*: HENLAR, Jin *et al.*, 2022).

When each monomer has four adjacent monomers attached, and each pair of adjacent monomers shares one bromine atom, a 2D structure is formed (195 structures). Each lead atom has two terminal bromine atoms in the 2D structure of the anion. There are two main options, depending on the terminal atoms. When terminal atoms are *trans* positioned, a planar arrangement of octahedra is formed. In our case, the Pb—Br—Pb angles are close to linear (Table 1, Fig. 2). An ideal form of this is a rare centrosymmetric anion in the structure of COJKIZ01 (Long *et al.*, 2024) with 180° Pb—Br—Pb angles, and *square*-shaped voids between the octahedra. There are 36 structures with square or near square voids, and this is the second most common geometry at 16%. In other cases, the Pb—Br—Pb angles differ from 180°, and values down to 139° can be encountered, causing *rhombic* voids (Fig. 4*i*: TAKZAK, Zhang, *et al.*, 2020; OBAYAV, Zhang *et al.*, 2021). This geometry is found in the prevailing number of structures, 141, almost 63%. However, in the case of *cis* positioning of terminal atoms, the anion has a zigzag arrangement of octahedra, forming stacked layers. Two-stacked layers can be formed having linear Pb—Br—Pb angles

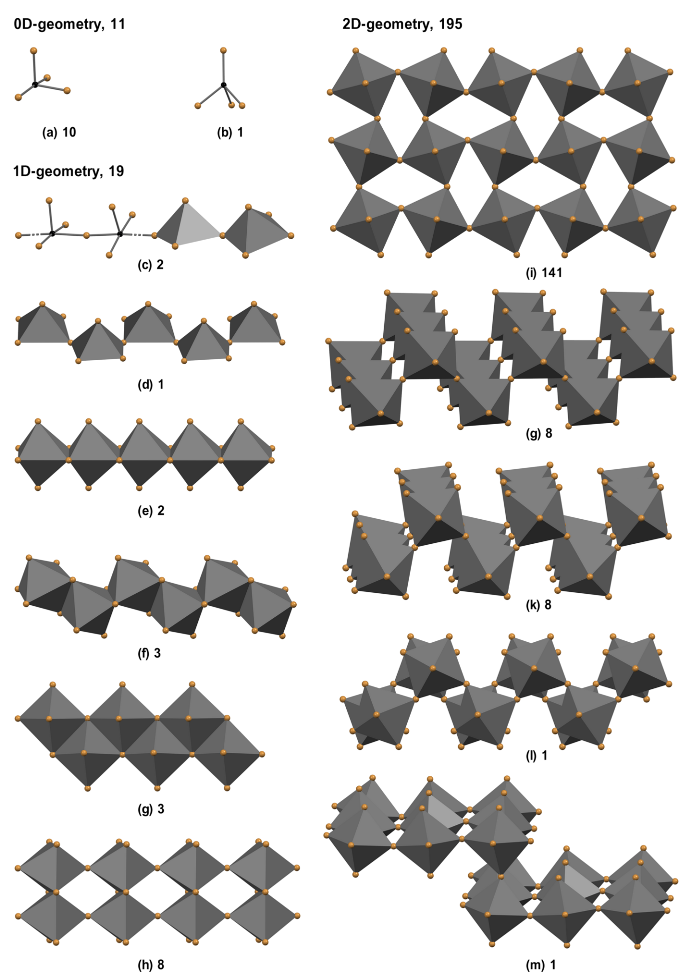


Figure 4
The $(PbBr_4)^{2-}$ anion geometries. Note that one more 2D form is missing here as it is shown in Fig. 2. The numbers of CCD structures for a given type of anion are indicated.

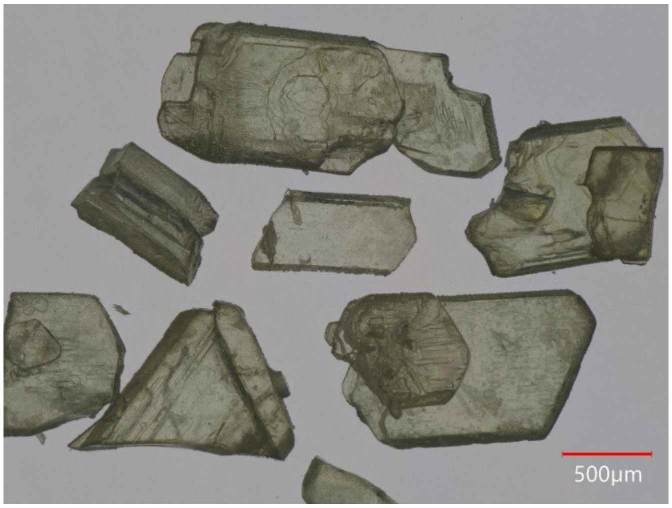


Figure 5
Yellow crystals of (β-AlaH)$_2$PbBr$_4$ under the microscope.

(Fig. 4*g*: SOHYAS01, Li *et al.*, 2019) or obtuse angles in the range of 164–148° (Fig. 4*k*: RICBEO01, RICBEO02, Drozdowski *et al.*, 2023; Fig. 4*l*: NIZQAP, Li *et al.*, 2008). One structure has layers arranged in a zigzag manner that contain octahedra with both *trans*- and *cis*-positioned terminal bromine atoms (Fig. 4*m*: UBUFEG, Guo *et al.*, 2021).

5. Synthesis and crystallization

As initial reagents, we used amino acid β-alanine (99% NT) and hydrobromic acid (48%) purchased from Sigma-Aldrich and lead (reactive grade). Initially, an excess volume of hydrobromic acid was added to a preliminary weighted amount of lead. When the reaction between them was completed (when no H_2 gas is released), the unreacted lead was removed by filtration, dried and weighed. The quantities of lead(II) bromide ($PbBr_2$) obtained and unreacted acid (HBr) in the filtrate were calculated. The appropriate amount of β-alanine was added to it and mixed to achieve a final solution with a 1:1:6 molar ratio of β-Ala, $PbBr_2$ and HBr, respectively. Instead of the desired compound (β-AlaH)-PbBr$_3$, (β-AlaH)$_2$PbBr$_4$ was obtained as yellow crystals (Fig. 5).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms were treated as riding on their parent atoms [C—H = 0.99 Å, N—H = 0.91 Å; U_{iso}(H) = 1.2U$_{eq}$(C) or U_{iso}(H) = 1.5U$_{eq}$(N)] except those of the carboxyl groups, which were refined with the restraint U_{iso}(H) = 1.5U$_{eq}$(C).

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Table 3
Experimental details.

Crystal data	
Chemical formula	(C$_3$H$_8$NO$_2$)$_2$[PbBr$_4$]
M_r	707.04
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	200
a, b, c (Å)	6.1377 (4), 11.9291 (8), 22.1508 (14)
β (°)	95.402 (2)
V (Å^3)	1614.62 (18)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	20.35
Crystal size (mm)	0.20 × 0.18 × 0.08
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.346, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	53070, 6172, 5328
R_{int}	0.046
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.770
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.044, 1.07
No. of reflections	6172
No. of parameters	163
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.51, −1.16

Computer programs: *APEX5* Bruker (2024), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2019/2* (Sheldrick, 2015*b*) and *ShelXle* (Hübschle *et al.*, 2011).

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Crystal structure of bis(*β*-alaninium) tetrabromidoplumbate

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Computing details

Poly[bis(*β*-alaninium) [[dibromidoplumbate]-di-*μ*-dibromido]]

Crystal data

$(C_3H_8NO_2)_2[PbBr_4]$
$M_r = 707.04$
Monoclinic, $P2_1/n$
$a = 6.1377$ (4) Å
$b = 11.9291$ (8) Å
$c = 22.1508$ (14) Å
$\beta = 95.402$ (2)°
$V = 1614.62$ (18) Å^3
$Z = 4$
$F(000) = 1280$
$D_x = 2.909$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9846 reflections
$\theta = 3.4$–32.8°
$\mu = 20.35$ mm^{-1}
$T = 200$ K
Plate, yellow
0.20 × 0.18 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{min} = 0.346$, $T_{max} = 0.747$
53070 measured reflections
6172 independent reflections
5328 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 33.2°$, $\theta_{min} = 1.9°$
$h = -9 \rightarrow 9$
$k = -18 \rightarrow 18$
$l = -33 \rightarrow 33$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.044$
$S = 1.07$
6172 reflections
163 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0092P)^2 + 2.110P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 1.51$ e Å^{-3}
$\Delta\rho_{min} = -1.16$ e Å^{-3}
Extinction correction: *SHELXL2019/2* (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00134 (4)

Special details

Experimental. A selected fragment of a crystal was mounted on a *MiTeGen* loop with silicone grease and examined by single crystal X-ray diffraction at 200 K on a Bruker APEX II diffractometer equipped with a CCD area detector, an Incoatec Microfocus Source IμS (30 W, multilayer mirror, Mo-K_{α}) and an Oxford Cryosystems Cryostream 800 Plus LT device. Several sets of phi- and omega-scans with 2° scanwidth were combined at a crystal-detector distances of 40 mm to achieve respective full sphere data up to 65° 2θ. Data handling with integration and absorption correction by evaluation of multi-scans was done with the Bruker Apex5 suite (Bruker, 2024). The structure was solved by direct methods (Sheldrick, 2015a); subsequent difference Fourier syntheses and least-squares refinements yielded the positions of the remaining atoms using the SHELX software (Sheldrick, 2015b) implemented in the ShelXle GUI tool (Hübschle *et al.* 2011). Non-hydrogen atoms were refined with independent anisotropic displacement parameters.

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Pb1	0.28160 (2)	0.48657 (2)	0.24772 (2)	0.01445 (3)
Br1	0.29433 (4)	0.47456 (2)	0.38595 (2)	0.02132 (6)
Br2	0.75530 (4)	0.48144 (3)	0.26094 (2)	0.02559 (6)
Br3	0.30325 (5)	0.49665 (2)	0.11657 (2)	0.02542 (6)
Br4	0.28669 (5)	0.73272 (2)	0.25942 (2)	0.02607 (7)
O1A	0.3047 (4)	0.05338 (17)	0.52622 (10)	0.0313 (5)
H1A	0.278 (6)	0.046 (3)	0.4858 (11)	0.047*
O2A	0.1232 (3)	0.21235 (17)	0.50427 (9)	0.0269 (4)
C1A	0.2260 (4)	0.1520 (2)	0.54084 (12)	0.0186 (5)
C2A	0.2849 (5)	0.1821 (2)	0.60573 (12)	0.0200 (5)
H21A	0.441345	0.203553	0.611180	0.024*
H22A	0.265866	0.115205	0.631189	0.024*
C3A	0.1492 (5)	0.2771 (2)	0.62751 (14)	0.0239 (6)
H31A	−0.007460	0.256173	0.621905	0.029*
H32A	0.189159	0.289100	0.671382	0.029*
N1A	0.1826 (4)	0.38366 (19)	0.59418 (12)	0.0258 (5)
H11A	0.166295	0.370391	0.553548	0.039*
H12A	0.319688	0.410268	0.604972	0.039*
H13A	0.082103	0.435237	0.603713	0.039*
O1B	0.6103 (4)	0.3217 (2)	0.52220 (10)	0.0340 (5)
H1B	0.658 (6)	0.378 (3)	0.5458 (16)	0.051*
O2B	0.8138 (3)	0.39905 (15)	0.45540 (9)	0.0235 (4)
C1B	0.6963 (4)	0.3238 (2)	0.46965 (13)	0.0204 (5)
C2B	0.6369 (5)	0.2227 (2)	0.43163 (13)	0.0221 (5)
H21B	0.476516	0.211567	0.429550	0.026*
H22B	0.707312	0.156012	0.451675	0.026*
C3B	0.7035 (5)	0.2303 (2)	0.36840 (14)	0.0263 (6)
H31B	0.657467	0.161277	0.345882	0.032*
H32B	0.627841	0.294589	0.347349	0.032*
N1B	0.9441 (4)	0.2447 (2)	0.36811 (12)	0.0269 (5)
H11B	1.013572	0.182729	0.384263	0.040*

H12B	0.987954	0.305927	0.390577	0.040*
H13B	0.977876	0.254316	0.329319	0.040*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.01638 (5)	0.01111 (4)	0.01587 (5)	−0.00006 (3)	0.00157 (3)	0.00083 (3)
Br1	0.02060 (13)	0.02395 (12)	0.01946 (14)	0.00223 (9)	0.00222 (10)	−0.00132 (10)
Br2	0.01714 (12)	0.03413 (15)	0.02531 (15)	0.00159 (10)	0.00106 (11)	−0.00382 (11)
Br3	0.03326 (16)	0.02572 (13)	0.01649 (13)	−0.00212 (11)	−0.00183 (11)	0.00417 (10)
Br4	0.03725 (16)	0.01262 (11)	0.02997 (16)	−0.00035 (10)	0.01171 (12)	−0.00028 (10)
O1A	0.0530 (15)	0.0219 (10)	0.0179 (11)	0.0140 (9)	−0.0025 (10)	−0.0030 (8)
O2A	0.0340 (12)	0.0245 (10)	0.0209 (11)	0.0097 (8)	−0.0045 (9)	0.0011 (8)
C1A	0.0201 (13)	0.0166 (11)	0.0192 (13)	0.0010 (9)	0.0026 (10)	0.0001 (9)
C2A	0.0255 (14)	0.0184 (11)	0.0157 (13)	0.0034 (10)	0.0002 (10)	0.0002 (9)
C3A	0.0269 (14)	0.0203 (12)	0.0255 (15)	0.0000 (10)	0.0086 (12)	−0.0038 (11)
N1A	0.0255 (12)	0.0179 (10)	0.0350 (15)	0.0002 (9)	0.0082 (11)	−0.0043 (10)
O1B	0.0397 (13)	0.0392 (13)	0.0254 (12)	−0.0156 (10)	0.0152 (10)	−0.0090 (9)
O2B	0.0255 (10)	0.0172 (9)	0.0287 (11)	−0.0041 (7)	0.0066 (9)	−0.0009 (8)
C1B	0.0184 (13)	0.0221 (12)	0.0206 (14)	−0.0014 (9)	0.0013 (10)	0.0012 (10)
C2B	0.0222 (13)	0.0199 (12)	0.0244 (15)	−0.0052 (10)	0.0037 (11)	−0.0004 (10)
C3B	0.0283 (15)	0.0244 (13)	0.0254 (15)	0.0026 (11)	−0.0013 (12)	−0.0033 (11)
N1B	0.0305 (13)	0.0235 (11)	0.0283 (14)	0.0017 (10)	0.0111 (11)	−0.0014 (10)

Geometric parameters (Å, º)

Pb1—Br1	3.0589 (4)	N1A—H11A	0.9100
Pb1—Br3	2.9230 (4)	N1A—H12A	0.9100
Pb1—Br2	2.8952 (3)	N1A—H13A	0.9100
Pb1—Br2^{i}	3.2714 (2)	O1B—C1B	1.323 (3)
Pb1—Br4	2.9477 (3)	O1B—H1B	0.88 (2)
Pb1—Br4^{ii}	3.0591 (3)	O2B—C1B	1.212 (3)
O1A—C1A	1.323 (3)	C1B—C2B	1.497 (4)
O1A—H1A	0.90 (2)	C2B—C3B	1.498 (4)
O2A—C1A	1.215 (3)	C2B—H21B	0.9900
C1A—C2A	1.493 (4)	C2B—H22B	0.9900
C2A—C3A	1.512 (4)	C3B—N1B	1.487 (4)
C2A—H21A	0.9900	C3B—H31B	0.9900
C2A—H22A	0.9900	C3B—H32B	0.9900
C3A—N1A	1.494 (4)	N1B—H11B	0.9100
C3A—H31A	0.9900	N1B—H12B	0.9100
C3A—H32A	0.9900	N1B—H13B	0.9100
Br1—Pb1—Br2	88.107 (9)	C2A—C3A—H32A	109.2
Br1—Pb1—Br2^{i}	80.90 (1)	H31A—C3A—H32A	107.9
Br1—Pb1—Br4	87.683 (8)	C3A—N1A—H11A	109.5
Br1—Pb1—Br4^{ii}	89.760 (8)	C3A—N1A—H12A	109.5
Br2—Pb1—Br4	90.568 (9)	H11A—N1A—H12A	109.5

Br2—Pb1—Br4^{ii}	96.645 (9)	C3A—N1A—H13A	109.5
Br2^{i}—Pb1—Br4	90.75 (1)	H11A—N1A—H13A	109.5
Br2^{i}—Pb1—Br4^{ii}	81.63 (1)	H12A—N1A—H13A	109.5
Br3—Pb1—Br2	87.836 (9)	C1B—O1B—H1B	112 (3)
Br3—Pb1—Br4	92.596 (8)	O2B—C1B—O1B	122.7 (3)
Br3—Pb1—Br4^{ii}	90.472 (8)	O2B—C1B—C2B	124.7 (3)
Pb1—Br2—Pb1^{iii}	168.87 (1)	O1B—C1B—C2B	112.5 (2)
Pb1—Br2^{i}—Pb1^{i}	168.87 (1)	C1B—C2B—C3B	113.8 (2)
Pb1—Br4—Pb1^{iv}	168.90 (1)	C1B—C2B—H21B	108.8
Br3—Pb1—Br1	175.936 (9)	C3B—C2B—H21B	108.8
Br4—Pb1—Br4^{ii}	172.266 (4)	C1B—C2B—H22B	108.8
C1A—O1A—H1A	107 (3)	C3B—C2B—H22B	108.8
O2A—C1A—O1A	122.8 (3)	H21B—C2B—H22B	107.7
O2A—C1A—C2A	124.2 (2)	N1B—C3B—C2B	111.7 (2)
O1A—C1A—C2A	112.9 (2)	N1B—C3B—H31B	109.3
C1A—C2A—C3A	113.4 (2)	C2B—C3B—H31B	109.3
C1A—C2A—H21A	108.9	N1B—C3B—H32B	109.3
C3A—C2A—H21A	108.9	C2B—C3B—H32B	109.3
C1A—C2A—H22A	108.9	H31B—C3B—H32B	107.9
C3A—C2A—H22A	108.9	C3B—N1B—H11B	109.5
H21A—C2A—H22A	107.7	C3B—N1B—H12B	109.5
N1A—C3A—C2A	112.0 (2)	H11B—N1B—H12B	109.5
N1A—C3A—H31A	109.2	C3B—N1B—H13B	109.5
C2A—C3A—H31A	109.2	H11B—N1B—H13B	109.5
N1A—C3A—H32A	109.2	H12B—N1B—H13B	109.5

O1A—C1A—C2A—C3a	−164.4 (2)	O1B—C1B—C2B—C3B	171.4 (2)
C1A—C2A—C3A—N1A	−62.9 (3)	C1B—C2B—C3B—N1B	59.7 (3)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···Br3^{ii}	0.90 (2)	2.35 (3)	3.241 (2)	171 (4)
N1*A*—H11*A*···O2*A*	0.91	2.18	2.853 (3)	130
N1*A*—H12*A*···Br1^{v}	0.91	2.73	3.619 (2)	166
N1*A*—H13*A*···Br1^{vi}	0.91	2.58	3.445 (2)	159
O1*B*—H1*B*···Br1^{v}	0.88 (2)	2.32 (3)	3.188 (2)	167 (4)
N1*B*—H11*B*···Br3^{vii}	0.91	2.49	3.343 (2)	157
N1*B*—H12*B*···Br1^{iii}	0.91	2.76	3.484 (2)	137
N1*B*—H12*B*···O2*B*	0.91	2.17	2.839 (3)	129
N1*B*—H13*B*···Br4^{vii}	0.91	2.56	3.407 (2)	155

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

Cation geometry (°)

Torsion angle	Value
O1A-C1A-C2A-C3A	-164.4 (2)
C1A-C2A-C3A-N1A	-62.9 (3)
O1B-C1B-C2B-C3B	171.4 (2)
C1B-C2B-C3B-N1B	59.7 (3)

Anion geometry (Å, °)

Pb1-Br1	3.0589 (3)	Pb1-Br2	2.8952 (3)	Pb1-Br4	2.9477 (3)
Pb1-Br3	2.9230 (4)	Pb1-Br2^{i}	3.2714 (2)	Pb1-Br4^{ii}	3.0591 (3)
Br1-Pb1-Br2	88.11 (1)	Br2-Pb1-Br4	90.57 (1)	Br3-Pb1-Br2	103.14 (1)
Br1-Pb1-Br2^{i}	80.90 (1)	Br2-Pb1-Br4^{ii}	96.64 (1)	Br3-Pb1-Br2^{i}	87.83 (1)
Br1-Pb1-Br4	87.68 (1)	Br2^{i}-Pb1-Br4	90.75 (1)	Br3-Pb1-Br4	92.60 (1)
Br1-Pb1-Br4^{ii}	89.76 (1)	Br2^{i}-Pb1-Br4^{ii}	81.63 (1)	Br3-Pb1-Br4^{ii}	90.47 (1)
Pb1-Br2-Pb1^{iii}	168.87 (1)	Pb1-Br4-Pb1^{iv}	168.90 (1)		
Pb1-Br2^{i}-Pb1^{i}	168.87 (1)	Pb1-Br4^{i}-Pb1^{ii}	168.90 (1)		

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