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Poly[1,4-bis(ammoniomethyl)cyclohexane [di- μ -bromido-dibromido-plumbate(II)]]

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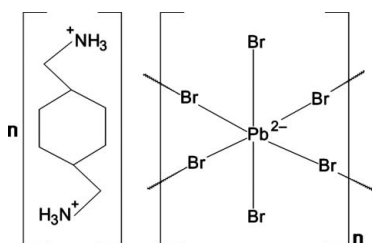
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.021; wR factor = 0.047; data-to-parameter ratio = 28.1.

The title compound, $\{(\text{C}_8\text{H}_{20}\text{N}_2)[\text{PbBr}_4]\}_n$, crystallizes as an inorganic–organic hybrid with alternating layers of diammonium cations and two-dimensional corner-sharing PbBr_6 octahedra extending parallel to the bc plane, which are eclipsed relative to one another. Both PbBr_6 octahedra and the organic cation exhibit $\bar{1}$ symmetry. The cations interact *via* $\text{N}-\text{H}\cdots\text{Br}$ hydrogen bonding in the right-angled halogen sub-type of the terminal halide hydrogen-bonding motif.

Related literature

For hydrogen-bonding nomenclature for inorganic–organic hybrids, see: Mitzi (1999). Hybrid structures containing diammonium cations have been synthesized by Dobrzycki & Woźniak (2008) and Zhu *et al.* (2003). The semiconducting properties of similar hybrids were demonstrated by Mitzi (2004). For the related chloridoplumbate(II), see: Rayner & Billing (2010a) and for the isotypic iodidoplumbate(II), see: Rayner & Billing (2010b).



Experimental

Crystal data

$(\text{C}_8\text{H}_{20}\text{N}_2)[\text{PbBr}_4]$
 $M_r = 671.09$
 Monoclinic, $P2_1/c$
 $a = 12.1042$ (6) Å
 $b = 8.1955$ (4) Å

$c = 8.2160$ (4) Å
 $\beta = 95.693$ (1)°
 $V = 811.01$ (7) Å³
 $Z = 2$
 Mo $K\alpha$ radiation

$\mu = 20.23$ mm⁻¹
 $T = 173$ K

0.20 × 0.14 × 0.02 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: integration (*XPREP*; Bruker, 2005)
 $T_{\min} = 0.091$, $T_{\max} = 0.656$

10495 measured reflections
 1966 independent reflections
 1742 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.063$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.047$
 $S = 0.81$
 1966 reflections

70 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.78$ e Å⁻³
 $\Delta\rho_{\min} = -2.31$ e Å⁻³

Table 1

Selected bond lengths (Å).

| | | | |
|-----------------------|------------|----------------------|------------|
| Pb1—Br2 ⁱ | 2.9821 (3) | Pb1—Br1 ⁱ | 3.0054 (4) |
| Pb1—Br2 ⁱⁱ | 2.9886 (3) | | |

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

Table 2

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|------------------------------------|--------------|--------------------|-------------|----------------------|
| N1—H1C \cdots Br2 ⁱ | 0.91 | 2.54 | 3.387 (3) | 154 |
| N1—H1D \cdots Br1 ⁱⁱ | 0.91 | 2.57 | 3.378 (3) | 148 |
| N1—H1D \cdots Br2 ⁱⁱⁱ | 0.91 | 2.94 | 3.446 (3) | 117 |
| N1—H1E \cdots Br1 | 0.91 | 2.60 | 3.357 (3) | 141 |

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2338).

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supporting information

Acta Cryst. (2010). E66, m658 [https://doi.org/10.1107/S1600536810016806]

Poly[1,4-bis(ammoniomethyl)cyclohexane [di- μ -bromido-dibromidoplumbate(II)]]

Matthew Kyle Rayner and David Gordon Billing

S1. Comment

Inorganic-organic hybrid materials are of interest due to their electronic and fluorescent properties (Mitzi, 2004). The title structure (Fig. 1) is one of three 2-dimensional hybrid structures that we have synthesized incorporating this diammonium cation. The structures differ in terms of their halogen ligands, which include bromide (presented here), chloride (Rayner & Billing, 2010*a*) and iodide (Rayner & Billing, 2010*b*). The bromide and iodide hybrids crystallize in the monoclinic crystal system in space group $P2_1/c$ while the chloride compound crystallizes in the orthorhombic $Pnma$ system.

In the title structure the lead atoms in the $PbBr_6$ octahedra occupy inversion centers, giving the octahedra $\bar{1}$ symmetry. The $PbBr_6$ octahedra share corners to form layers extending parallel to the bc plane. Octahedra from alternate layers are eclipsed relative to one another (Fig. 2). In all three structures only the *trans* form of the cation has been observed giving the cation $\bar{1}$ symmetry (Fig. 3). Very few inorganic-organic hybrid structures incorporating diammonium cations have been reported (Dobrzycki & Woźniak, 2008; Zhu *et al.*, 2003). The ammonium cations interact with the inorganic layer via $N-H\cdots X$ ($X = Br, I$ and Cl) hydrogen bonding in the right-angled halogen subtype of the terminal halide hydrogen bonding motif (Mitzi, 1999).

S2. Experimental

A mixture of 0.050 g (0.14 mmol) $PbBr_2$ and 0.021 g (0.15 mmol) 1,4-bis-(aminomethyl)-cyclohexane (mixture of isomers) was dissolved in 5 ml HBr at 383 K and slowly cooled at a rate of 0.069 K/min to yield colourless, plate-shaped single crystals suitable for X-ray analysis.

S3. Refinement

The H atoms on the diammonium cation were refined using a riding-model, with $C-H = 0.99$ Å, $N-H = 0.91$ Å and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(N)$. The highest residual electron density peak (0.78 e Å⁻³) was 0.923 Å from Pb1.

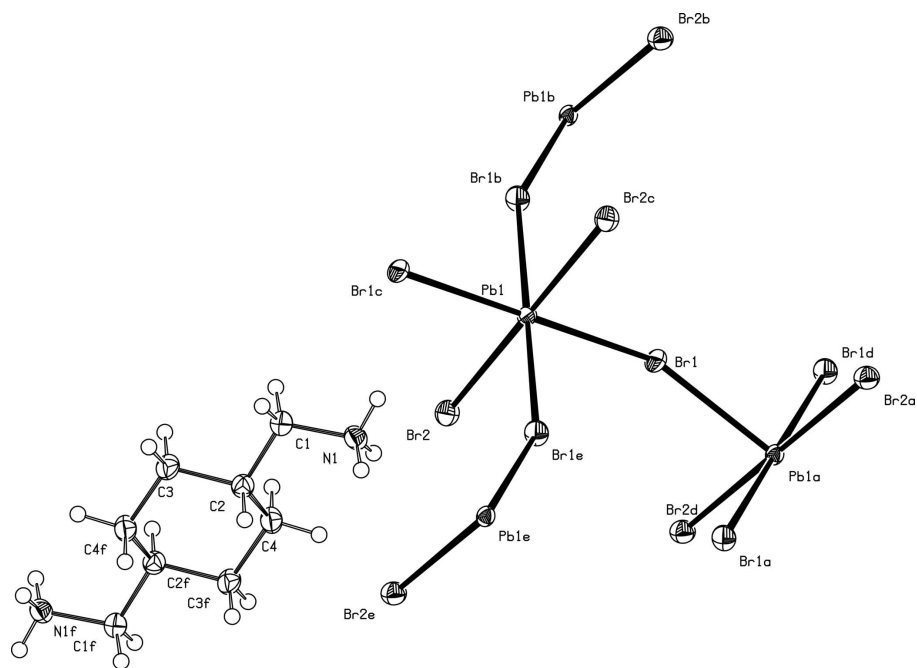


Figure 1

The asymmetric unit of the title compound with atom labels. Displacement ellipsoids were drawn at the 50% probability level. Symmetry codes: (a) $1-x, 1/2+y, 1/2-z$ (b) $1-x, 1-y, 1-z$ (c) $x, 1/2-y, 1/2+z$ (d) $-x, 1-y, 2-z$.

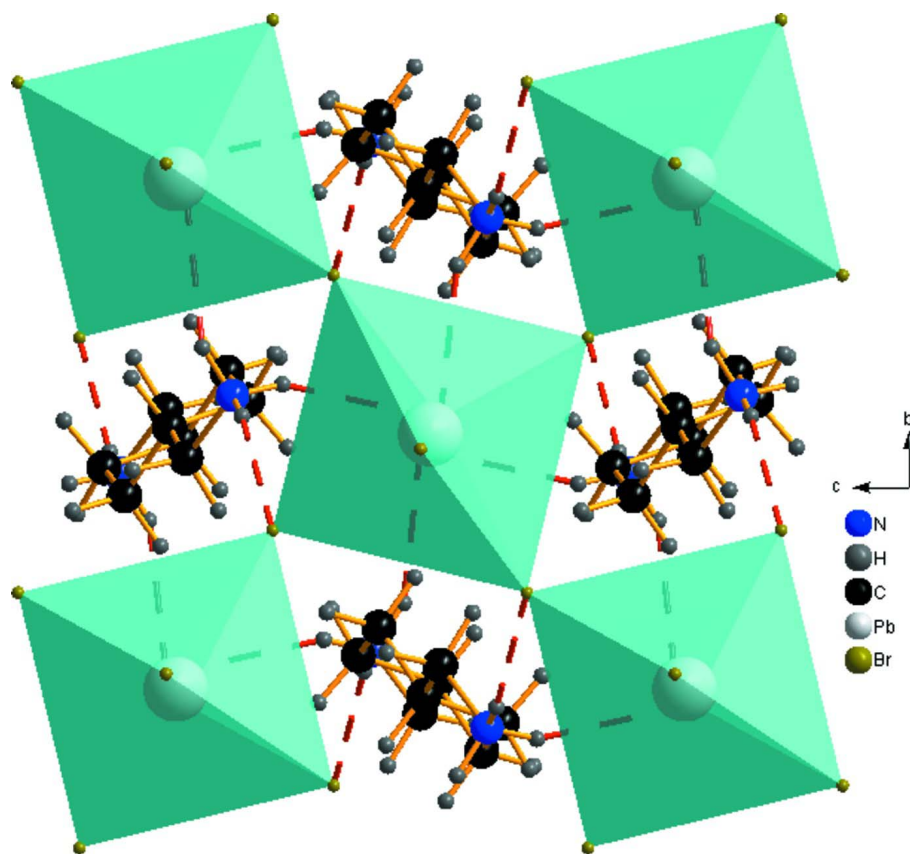


Figure 2

Packing diagram viewed along the *a* axis. Hydrogen bonds are drawn as dashed red lines.

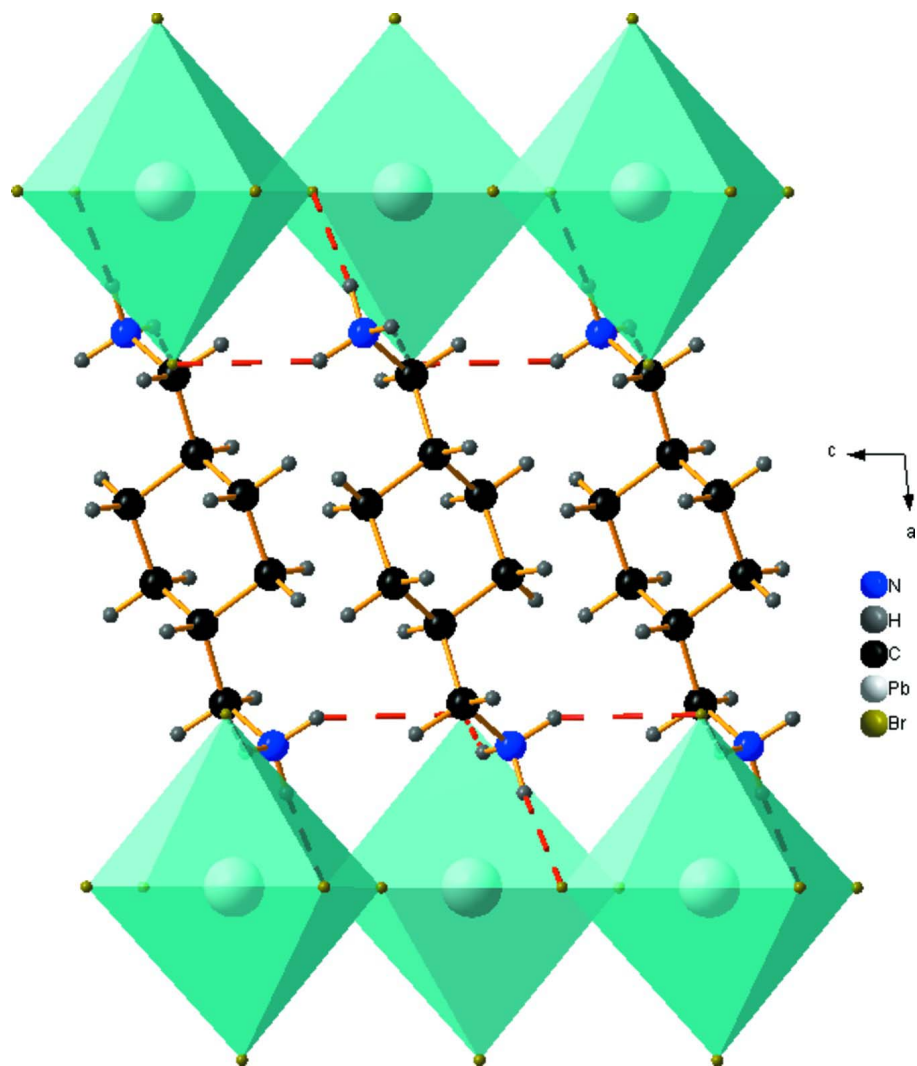


Figure 3

Packing diagram viewed along the b axis. Hydrogen bonds are drawn as dashed red lines.

Poly[1,4-bis(ammoniomethyl)cyclohexane [di- μ -bromido-dibromidoplumbate(II)]]

Crystal data

$(C_8H_{20}N_2)[PbBr_4]$

$M_r = 671.09$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2_1/c$

$a = 12.1042 (6) \text{ \AA}$

$b = 8.1955 (4) \text{ \AA}$

$c = 8.2160 (4) \text{ \AA}$

$\beta = 95.693 (1)^\circ$

$V = 811.01 (7) \text{ \AA}^3$

$Z = 2$

$F(000) = 608$

$D_x = 2.748 \text{ Mg m}^{-3}$

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

Cell parameters from 5293 reflections

$\theta = 3.0\text{--}28.2^\circ$

$\mu = 20.23 \text{ mm}^{-1}$

$T = 173 \text{ K}$

Plate, colourless

$0.20 \times 0.14 \times 0.02 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 φ and ω scans
Absorption correction: integration
(*XPREP*; Bruker, 2005)
 $T_{\min} = 0.091$, $T_{\max} = 0.656$

10495 measured reflections
1966 independent reflections
1742 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.063$
 $\theta_{\max} = 28.0^\circ$, $\theta_{\min} = 1.7^\circ$
 $h = -15 \rightarrow 15$
 $k = -10 \rightarrow 10$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.047$
 $S = 0.81$
1966 reflections
70 parameters
0 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0349P)^2 + 0.0549P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.011$
 $\Delta\rho_{\max} = 0.78 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -2.31 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. Numerical intergration absorption corrections based on indexed crystal faces were applied using the *XPREP* routine (Bruker, 2005)

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. 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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|------------|-------------|------------|----------------------------------|
| C1 | 0.2360 (3) | -0.0472 (4) | 0.4803 (5) | 0.0262 (8) |
| H1A | 0.2798 | -0.0711 | 0.5858 | 0.031* |
| H1B | 0.2282 | -0.1498 | 0.4166 | 0.031* |
| C2 | 0.1224 (3) | 0.0131 (4) | 0.5124 (4) | 0.0216 (8) |
| H2 | 0.1325 | 0.1095 | 0.5871 | 0.026* |
| C3 | 0.0636 (3) | -0.1206 (4) | 0.6011 (4) | 0.0257 (8) |
| H3A | 0.0558 | -0.2192 | 0.5312 | 0.031* |
| H3B | 0.1093 | -0.1499 | 0.7035 | 0.031* |
| C4 | 0.0501 (3) | 0.0661 (5) | 0.3589 (4) | 0.0247 (7) |
| H4A | 0.0869 | 0.1569 | 0.3058 | 0.030* |
| H4B | 0.0419 | -0.0261 | 0.2807 | 0.030* |
| N1 | 0.2966 (2) | 0.0758 (4) | 0.3879 (4) | 0.0230 (6) |
| H1C | 0.3644 | 0.0356 | 0.3700 | 0.035* |
| H1D | 0.3054 | 0.1695 | 0.4473 | 0.035* |

| | | | | |
|-----|-------------|-------------|--------------|-------------|
| H1E | 0.2569 | 0.0972 | 0.2904 | 0.035* |
| Br1 | 0.25157 (3) | 0.02969 (4) | -0.01928 (4) | 0.02426 (9) |
| Br2 | 0.50023 (3) | 0.18890 (4) | -0.31018 (4) | 0.02370 (9) |
| Pb1 | 0.5000 | 0.0000 | 0.0000 | 0.01590 (6) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|--------------|---------------|
| C1 | 0.024 (2) | 0.0232 (17) | 0.0322 (19) | 0.0000 (15) | 0.0076 (16) | 0.0042 (14) |
| C2 | 0.024 (2) | 0.0206 (17) | 0.0210 (17) | -0.0015 (13) | 0.0039 (15) | -0.0010 (12) |
| C3 | 0.0206 (19) | 0.0285 (18) | 0.0277 (18) | 0.0035 (15) | 0.0011 (15) | 0.0101 (14) |
| C4 | 0.0213 (19) | 0.0285 (18) | 0.0246 (17) | -0.0011 (15) | 0.0040 (14) | 0.0042 (14) |
| N1 | 0.0203 (16) | 0.0229 (15) | 0.0267 (15) | -0.0014 (12) | 0.0065 (12) | -0.0019 (12) |
| Br1 | 0.0241 (2) | 0.02380 (17) | 0.02478 (17) | -0.00282 (13) | 0.00175 (14) | -0.00035 (12) |
| Br2 | 0.0311 (2) | 0.02090 (17) | 0.01975 (16) | 0.00481 (13) | 0.00579 (13) | 0.00695 (12) |
| Pb1 | 0.02093 (10) | 0.01395 (9) | 0.01320 (9) | 0.00121 (6) | 0.00358 (6) | 0.00007 (5) |

Geometric parameters (Å, °)

| | | | |
|-------------------------|-----------|---|--------------|
| C1—N1 | 1.497 (4) | C4—H4B | 0.9900 |
| C1—C2 | 1.509 (5) | N1—H1C | 0.9100 |
| C1—H1A | 0.9900 | N1—H1D | 0.9100 |
| C1—H1B | 0.9900 | N1—H1E | 0.9100 |
| C2—C3 | 1.531 (4) | Br1—Pb1 | 3.0054 (4) |
| C2—C4 | 1.526 (5) | Br2—Pb1 | 2.9821 (3) |
| C2—H2 | 1.0000 | Br2—Pb1 ⁱⁱ | 2.9886 (3) |
| C3—C4 ⁱ | 1.514 (5) | Pb1—Br2 ⁱⁱⁱ | 2.9821 (3) |
| C3—H3A | 0.9900 | Pb1—Br2 ^{iv} | 2.9886 (3) |
| C3—H3B | 0.9900 | Pb1—Br2 ^v | 2.9886 (3) |
| C4—C3 ⁱ | 1.514 (5) | Pb1—Br1 ⁱⁱⁱ | 3.0054 (4) |
| C4—H4A | 0.9900 | | |
| N1—C1—C2 | 111.7 (3) | H4A—C4—H4B | 108.0 |
| N1—C1—H1A | 109.3 | C1—N1—H1C | 109.5 |
| C2—C1—H1A | 109.3 | C1—N1—H1D | 109.5 |
| N1—C1—H1B | 109.3 | H1C—N1—H1D | 109.5 |
| C2—C1—H1B | 109.3 | C1—N1—H1E | 109.5 |
| H1A—C1—H1B | 108.0 | H1C—N1—H1E | 109.5 |
| C1—C2—C3 | 108.9 (3) | H1D—N1—H1E | 109.5 |
| C1—C2—C4 | 114.0 (3) | Pb1—Br2—Pb1 ⁱⁱ | 152.724 (12) |
| C3—C2—C4 | 110.0 (3) | Br2 ⁱⁱⁱ —Pb1—Br2 | 180.000 (11) |
| C1—C2—H2 | 107.9 | Br2 ⁱⁱⁱ —Pb1—Br2 ^{iv} | 89.827 (4) |
| C3—C2—H2 | 107.9 | Br2—Pb1—Br2 ^{iv} | 90.173 (4) |
| C4—C2—H2 | 107.9 | Br2 ⁱⁱⁱ —Pb1—Br2 ^v | 90.173 (4) |
| C4 ⁱ —C3—C2 | 111.6 (3) | Br2—Pb1—Br2 ^v | 89.827 (4) |
| C4 ⁱ —C3—H3A | 109.3 | Br2 ^{iv} —Pb1—Br2 ^v | 180.000 (15) |
| C2—C3—H3A | 109.3 | Br2 ⁱⁱⁱ —Pb1—Br1 | 90.075 (10) |
| C4 ⁱ —C3—H3B | 109.3 | Br2—Pb1—Br1 | 89.925 (10) |

| | | | |
|--------------------------|-----------|---|--------------|
| C2—C3—H3B | 109.3 | Br2 ^{iv} —Pb1—Br1 | 84.697 (10) |
| H3A—C3—H3B | 108.0 | Br2 ^v —Pb1—Br1 | 95.303 (10) |
| C3 ⁱ —C4—C2 | 111.3 (3) | Br2 ⁱⁱⁱ —Pb1—Br1 ⁱⁱⁱ | 89.925 (10) |
| C3 ⁱ —C4—H4A | 109.4 | Br2—Pb1—Br1 ⁱⁱⁱ | 90.075 (10) |
| C2—C4—H4A | 109.4 | Br2 ^{iv} —Pb1—Br1 ⁱⁱⁱ | 95.303 (10) |
| C3 ⁱ —C4—H4B | 109.4 | Br2 ^v —Pb1—Br1 ⁱⁱⁱ | 84.697 (10) |
| C2—C4—H4B | 109.4 | Br1—Pb1—Br1 ⁱⁱⁱ | 180.000 (13) |
| N1—C1—C2—C3 | 177.9 (3) | C3—C2—C4—C3 ⁱ | 55.8 (4) |
| N1—C1—C2—C4 | 54.7 (4) | Pb1 ⁱⁱ —Br2—Pb1—Br2 ^{iv} | -0.28 (4) |
| C1—C2—C3—C4 ⁱ | 178.5 (3) | Pb1 ⁱⁱ —Br2—Pb1—Br2 ^v | 179.72 (4) |
| C4—C2—C3—C4 ⁱ | -56.0 (4) | Pb1 ⁱⁱ —Br2—Pb1—Br1 | 84.42 (3) |
| C1—C2—C4—C3 ⁱ | 178.4 (3) | Pb1 ⁱⁱ —Br2—Pb1—Br1 ⁱⁱⁱ | -95.58 (3) |

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

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—H1C \cdots Br2 ⁱⁱⁱ | 0.91 | 2.54 | 3.387 (3) | 154 |
| N1—H1D \cdots Br1 ^{iv} | 0.91 | 2.57 | 3.378 (3) | 148 |
| N1—H1D \cdots Br2 ^{vi} | 0.91 | 2.94 | 3.446 (3) | 117 |
| N1—H1E \cdots Br1 | 0.91 | 2.60 | 3.357 (3) | 141 |

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