

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

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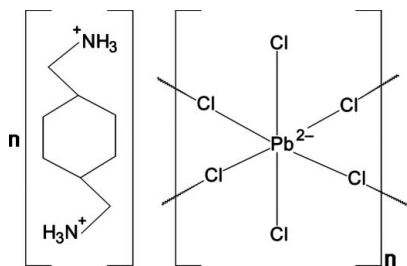
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 Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.009$ Å; R factor = 0.031; wR factor = 0.067; data-to-parameter ratio = 25.3.

The title compound, $\{(\text{C}_8\text{H}_{20}\text{N}_2)[\text{PbCl}_4]\}_n$, crystallizes as an layered inorganic–organic hybrid perovskite-type structure. Corner-sharing PbCl_6 octahedra extend parallel to the ac plane. Adjacent layers are staggered relative to one another, with diammonium cations separating these layers. The cations exhibit $\bar{1}$ symmetry and interact with the inorganic sheets *via* $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonding in the right-angled halogen sub-type of the terminal halide hydrogen-bonding motif.

Related literature

Similar structures have been reported by Billing & Lemmerer (2006) and Dobrzycki & Woźniak (2009). Structure–properties relation experiments have been performed by Mitzi *et al.* (2001). For hydrogen-bonding nomenclature for inorganic–organic hybrids, see: Mitzi (1999). For the bromido- and iodidoplumbate(II) analogues of the title compound, see: Rayner & Billing (2010*a,b*).



Experimental

Crystal data

 $(\text{C}_8\text{H}_{20}\text{N}_2)[\text{PbCl}_4]$
 $M_r = 493.25$

 Orthorhombic, $Pnma$
 $a = 7.7990$ (2) Å

 $b = 24.0666$ (6) Å

 $c = 7.9348$ (2) Å

 $V = 1489.33$ (7) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 12.02$ mm⁻¹
 $T = 173$ K

 $0.54 \times 0.41 \times 0.04$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer

 Absorption correction: integration (*XPREP*; Bruker, 2005)

 $T_{\min} = 0.032$, $T_{\max} = 0.685$

13290 measured reflections

1850 independent reflections

 1654 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.067$
 $S = 1.16$

1850 reflections

73 parameters

H-atom parameters constrained

 $\Delta\rho_{\max} = 1.47$ e Å⁻³
 $\Delta\rho_{\min} = -3.53$ e Å⁻³
Table 1

Selected bond lengths (Å).

Pb1—Cl1 ⁱ	2.834 (2)	Pb1—Cl2 ⁱⁱⁱ	2.900 (2)
Pb1—Cl1 ⁱⁱ	2.8723 (15)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1C}\cdots\text{Cl3}^{\text{iv}}$	0.91	2.40	3.249 (5)	156
$\text{N1}-\text{H1D}\cdots\text{Cl1}^{\text{v}}$	0.91	2.44	3.196 (6)	141
$\text{N1}-\text{H1E}\cdots\text{Cl1}^{\text{iii}}$	0.91	2.39	3.212 (5)	150
$\text{N1}-\text{H1E}\cdots\text{Cl2}^{\text{iii}}$	0.91	2.84	3.337 (5)	115

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

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: WM2339).

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supporting information

Acta Cryst. (2010). E66, m659 [https://doi.org/10.1107/S1600536810016818]

Poly[1,4-bis(ammoniomethyl)cyclohexane [di- μ -chlorido-dichloridoplumbate(II)]]

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S1. Comment

Inorganic-organic hybrid compounds have been investigated for their semiconducting and electronic properties (Mitzi *et al.*, 2001). For literature regarding hydrogen bonding nomenclature for inorganic-organic hybrids, see: Mitzi (1999). 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 chloride (presented here), bromide (Rayner & Billing, 2010*a*) and iodide (Rayner & Billing, 2010*b*). The bromide and iodide hybrids crystallize in the monoclinic system with space group $P2_1/c$ while the chloride hybrid crystallizes in the orthorhombic, $Pnma$ system.

In the title structure the lead-chloride octahedra from alternate layers that are staggered 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). The ammonium cations interact with the inorganic layer via N—H \cdots X ($X = \text{Br, I and Cl}$) hydrogen bonding in the right-angled halogen subtype of the terminal halide hydrogen bonding motif (Mitzi, 1999). Similar inorganic-organic hybrid structures have been reported (Billing & Lemmerer, 2006; Dobrzycki & Woźniak, 2009), however very few hybrids incorporating diammonium cations have been synthesized.

S2. Experimental

A mixture of 0.052 g (0.19 mmol) PbCl_2 and 0.030 g (0.21 mmol) 1,4-bis-(aminomethyl)-cyclohexane (mixture of isomers) was dissolved in 5 ml HCl at 383 K and slow 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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{N})$. The highest residual electron density peak (1.47 e Å⁻³) was 0.822 Å from Pb1.

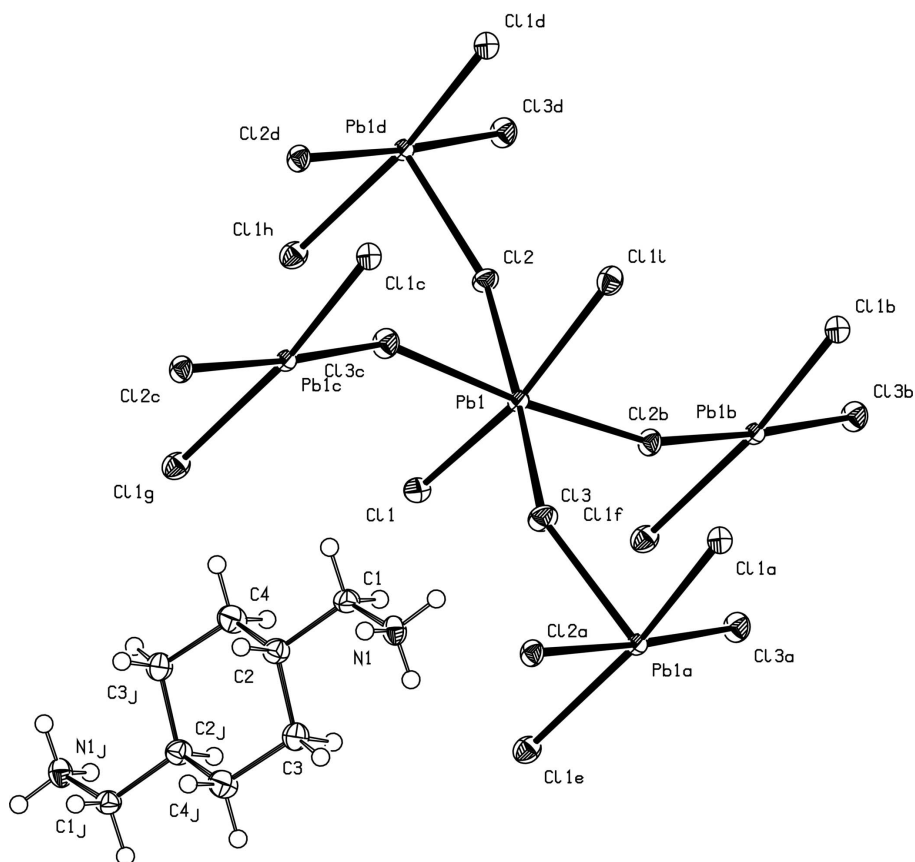


Figure 1

The asymmetric unit of the title compound with atom labels. Displacement ellipsoids were drawn at the 50% probability level. Symmetry codes: (a) $-1/2+x, 1/2-y, 3/2-z$ (b) $1/2+x, 1/2-y, 1/2-z$ (c) $x, 1/2-y, z$ (d) $1-x, -y, -z$.

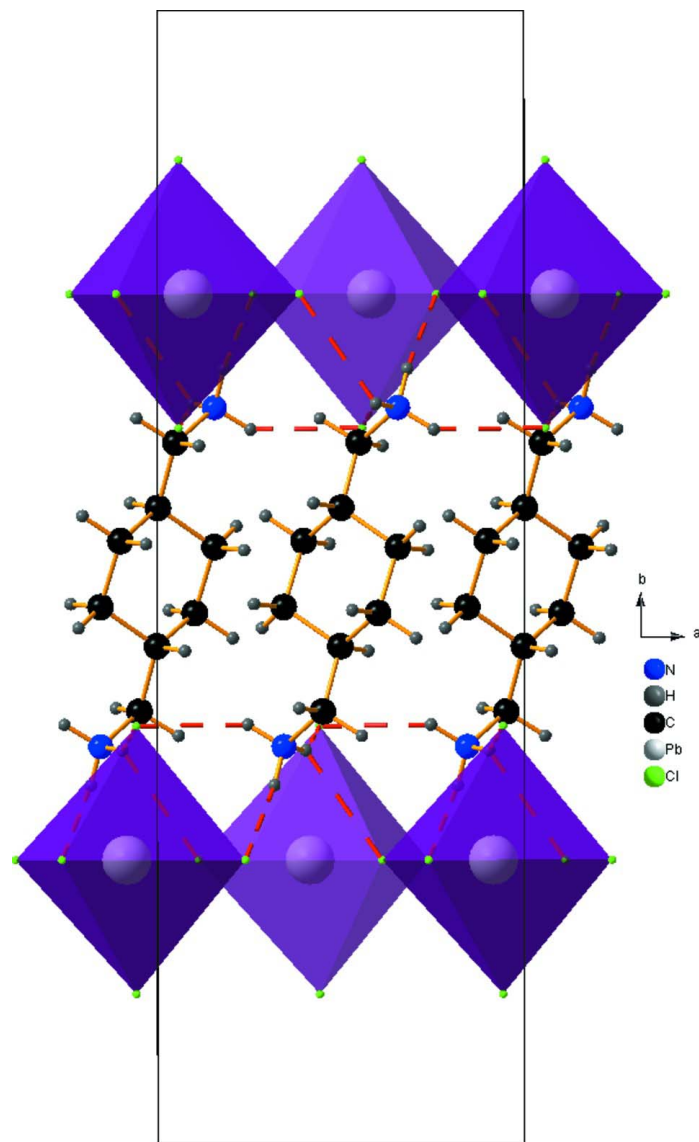


Figure 2

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

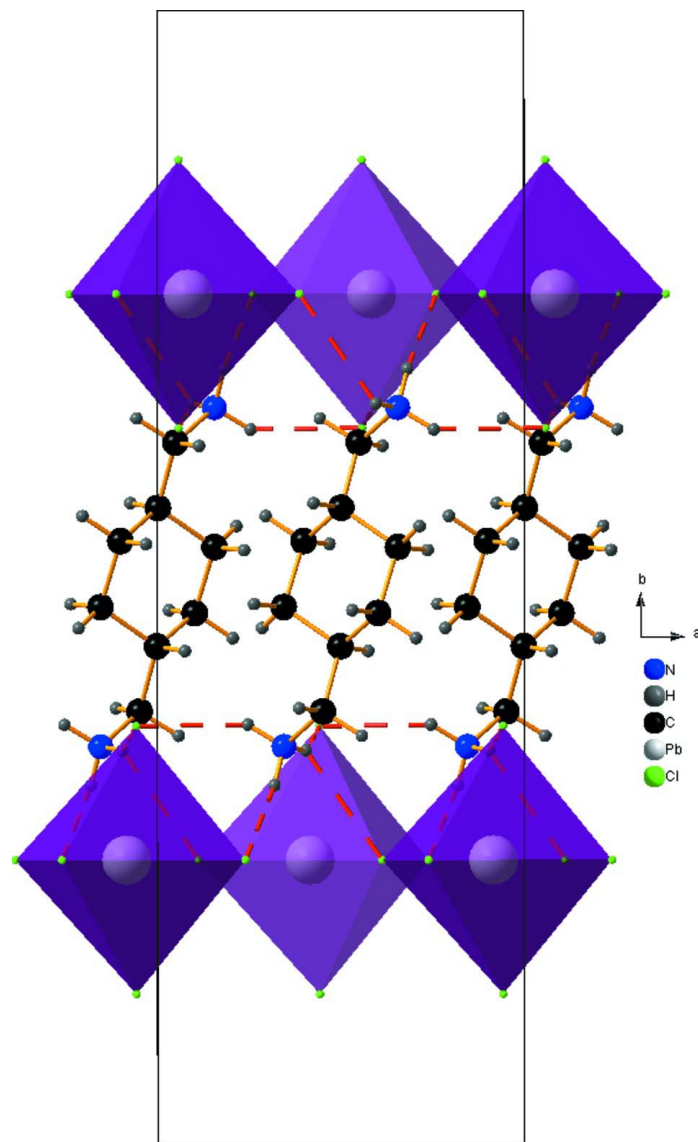


Figure 3

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

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Crystal data

(C₈H₂₀N₂)[PbCl₄]

M_r = 493.25

Orthorhombic, *Pnma*

Hall symbol: -P 2ac 2n

a = 7.7990 (2) Å

b = 24.0666 (6) Å

c = 7.9348 (2) Å

V = 1489.33 (7) Å³

Z = 4

F(000) = 928

D_x = 2.200 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 6650 reflections

θ = 2.7–28.3°

μ = 12.02 mm⁻¹

T = 173 K

Plate, colourless

0.54 × 0.41 × 0.04 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)
 $T_{\min} = 0.032$, $T_{\max} = 0.685$

13290 measured reflections
1850 independent reflections
1654 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$
 $\theta_{\text{max}} = 28.0^\circ$, $\theta_{\text{min}} = 1.7^\circ$
 $h = -10 \rightarrow 10$
 $k = -31 \rightarrow 31$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.067$
 $S = 1.16$
1850 reflections
73 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
 $w = 1/[\sigma^2(F_o^2) + (0.003P)^2 + 19.9694P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.007$
 $\Delta\rho_{\text{max}} = 1.47 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -3.53 \text{ e } \text{\AA}^{-3}$

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	0.5490 (8)	0.6188 (2)	0.9551 (8)	0.0201 (12)
H1A	0.6135	0.6159	0.8480	0.024*
H1B	0.4429	0.6401	0.9326	0.024*
C2	0.5016 (8)	0.5612 (2)	1.0147 (8)	0.0201 (12)
H2	0.4256	0.5654	1.1154	0.024*
C3	0.3984 (9)	0.5318 (3)	0.8783 (8)	0.0256 (13)
H3A	0.4683	0.5293	0.7744	0.031*
H3B	0.2948	0.5540	0.8521	0.031*
C4	0.6555 (8)	0.5265 (3)	1.0676 (8)	0.0239 (13)
H4A	0.7150	0.5451	1.1623	0.029*
H4B	0.7369	0.5238	0.9723	0.029*
N1	0.6553 (7)	0.6496 (2)	1.0812 (7)	0.0213 (11)
H1C	0.6816	0.6838	1.0400	0.032*
H1D	0.7537	0.6303	1.1013	0.032*

H1E	0.5954	0.6532	1.1789	0.032*
Cl1	0.05791 (19)	0.63163 (6)	1.02923 (19)	0.0229 (3)
Cl2	-0.1125 (3)	0.7500	1.2974 (2)	0.0194 (4)
Cl3	0.2609 (3)	0.7500	0.6719 (3)	0.0238 (4)
Pb1	0.08434 (4)	0.7500	0.99093 (4)	0.01374 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.019 (3)	0.018 (3)	0.023 (3)	0.002 (2)	-0.002 (2)	0.001 (2)
C2	0.020 (3)	0.021 (3)	0.019 (3)	0.000 (2)	-0.003 (2)	-0.001 (3)
C3	0.031 (4)	0.020 (3)	0.026 (3)	-0.004 (3)	-0.009 (3)	0.000 (2)
C4	0.023 (3)	0.021 (3)	0.028 (3)	-0.004 (3)	-0.005 (3)	-0.001 (3)
N1	0.023 (3)	0.018 (2)	0.023 (2)	-0.003 (2)	0.002 (2)	-0.003 (2)
Cl1	0.0202 (7)	0.0229 (7)	0.0257 (7)	0.0021 (5)	0.0001 (6)	-0.0037 (6)
Cl2	0.0170 (10)	0.0221 (9)	0.0192 (9)	0.000	0.0049 (7)	0.000
Cl3	0.0222 (10)	0.0297 (11)	0.0197 (9)	0.000	0.0056 (8)	0.000
Pb1	0.01269 (14)	0.01657 (14)	0.01196 (13)	0.000	0.00002 (12)	0.000

Geometric parameters (Å, °)

C1—N1	1.495 (8)	C4—H4B	0.9900
C1—C2	1.512 (8)	N1—H1C	0.9100
C1—H1A	0.9900	N1—H1D	0.9100
C1—H1B	0.9900	N1—H1E	0.9100
C2—C3	1.523 (8)	Cl1—Pb1	2.8723 (15)
C2—C4	1.521 (9)	Cl2—Pb1	2.8759 (19)
C2—H2	1.0000	Cl2—Pb1 ⁱⁱ	2.9002 (19)
C3—C4 ⁱ	1.525 (9)	Cl3—Pb1 ⁱⁱⁱ	2.834 (2)
C3—H3A	0.9900	Cl3—Pb1	2.882 (2)
C3—H3B	0.9900	Pb1—Cl3 ^{iv}	2.834 (2)
C4—C3 ⁱ	1.525 (9)	Pb1—Cl1 ^v	2.8723 (15)
C4—H4A	0.9900	Pb1—Cl2 ^{vi}	2.900 (2)
N1—C1—C2	112.4 (5)	C1—N1—H1C	109.5
N1—C1—H1A	109.1	C1—N1—H1D	109.5
C2—C1—H1A	109.1	H1C—N1—H1D	109.5
N1—C1—H1B	109.1	C1—N1—H1E	109.5
C2—C1—H1B	109.1	H1C—N1—H1E	109.5
H1A—C1—H1B	107.9	H1D—N1—H1E	109.5
C1—C2—C3	109.5 (5)	Pb1—Cl2—Pb1 ⁱⁱ	157.64 (8)
C1—C2—C4	113.4 (5)	Pb1 ⁱⁱⁱ —Cl3—Pb1	145.68 (9)
C3—C2—C4	111.0 (5)	Cl3 ^{iv} —Pb1—Cl1 ^v	89.10 (3)
C1—C2—H2	107.6	Cl3 ^{iv} —Pb1—Cl1	89.10 (3)
C3—C2—H2	107.6	Cl1 ^v —Pb1—Cl1	165.31 (6)
C4—C2—H2	107.6	Cl3 ^{iv} —Pb1—Cl2	84.87 (6)
C2—C3—C4 ⁱ	111.8 (5)	Cl1 ^v —Pb1—Cl2	82.66 (3)
C2—C3—H3A	109.2	Cl1—Pb1—Cl2	82.66 (3)

C4 ⁱ —C3—H3A	109.2	Cl3 ^{iv} —Pb1—Cl3	91.42 (3)
C2—C3—H3B	109.2	Cl1 ^v —Pb1—Cl3	97.31 (3)
C4 ⁱ —C3—H3B	109.2	Cl1—Pb1—Cl3	97.31 (3)
H3A—C3—H3B	107.9	Cl2—Pb1—Cl3	176.29 (6)
C2—C4—C3 ⁱ	111.4 (5)	Cl3 ^{iv} —Pb1—Cl2 ^{vi}	171.75 (6)
C2—C4—H4A	109.3	Cl1 ^v —Pb1—Cl2 ^{vi}	89.84 (3)
C3 ⁱ —C4—H4A	109.3	Cl1—Pb1—Cl2 ^{vi}	89.84 (3)
C2—C4—H4B	109.3	Cl2—Pb1—Cl2 ^{vi}	86.875 (17)
C3 ⁱ —C4—H4B	109.3	Cl3—Pb1—Cl2 ^{vi}	96.83 (6)
H4A—C4—H4B	108.0		
N1—C1—C2—C3	-178.3 (5)	Pb1 ⁱⁱ —Cl2—Pb1—Cl1 ^v	89.76 (3)
N1—C1—C2—C4	-53.7 (7)	Pb1 ⁱⁱ —Cl2—Pb1—Cl1	-89.76 (3)
C1—C2—C3—C4 ⁱ	-179.2 (5)	Pb1 ⁱⁱ —Cl2—Pb1—Cl2 ^{vi}	180.0
C4—C2—C3—C4 ⁱ	54.9 (8)	Pb1 ⁱⁱⁱ —Cl3—Pb1—Cl3 ^{iv}	180.0
C1—C2—C4—C3 ⁱ	-178.3 (5)	Pb1 ⁱⁱⁱ —Cl3—Pb1—Cl1 ^v	90.72 (3)
C3—C2—C4—C3 ⁱ	-54.6 (8)	Pb1 ⁱⁱⁱ —Cl3—Pb1—Cl1	-90.72 (3)
Pb1 ⁱⁱ —Cl2—Pb1—Cl3 ^{iv}	0.0	Pb1 ⁱⁱⁱ —Cl3—Pb1—Cl2 ^{vi}	0.0

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

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—H1C...Cl3 ⁱⁱⁱ	0.91	2.40	3.249 (5)	156
N1—H1D...Cl1 ^{vii}	0.91	2.44	3.196 (6)	141
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