research communications

Hybrid organic–inorganic crystal structure of 4-(dimethylamino)pyridinium dimethylammonium tetrachloridolead(II)

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The title compound, $(C_2H_8N)(C_7H_{11}N_2)[PbCl_4]$, is a hybrid organic–inorganic material. It crystallizes in the space group $C2/c$ and contains one half of a molecule of lead chloride, 4-(dimethylamino)pyridinium, and dimethyl-ammonium in the asymmetric unit. The crystal structure exhibits chains of lead chloride capped by 4-(dimethylamino)pyridinium and dimethylammoium by hydrogen bonding. This creates a one-dimensional zipper-like structure down the a axis. The crystal structure is examined and compared to a similar structure containing lead chloride and dimethylbenzene-1,4-diaminium.

1. Chemical context

Hybrid organic–inorganic materials have been gaining attention due to their interesting optical properties and for their applications as semiconductors (Dobrzycki & Woźniak, 2008). Early materials such as lead halogen perovskites have been identified as having intrinsic white-light emission (Dohner *et al.*, 2014) and as an inexpensive and high conversion material for solar cells (Baikie *et al.*, 2013; Zhao & Zhu, 2014). By changing the size and structure of the organic portions of these materials, one can begin to assess the impact of these groups on the resulting crystal structures (Gillon *et al.*, 2000). For organic cations containing groups capable of hydrogen bonding, these interactions may form the basis for deliberate crystal engineering of next generation materials. Herein we report the structure of a new hybrid organic–inorganic material that contains 1-D lead chloride chains capped by dimethylammonium (DMA) and 4-(dimethylamino)-pyridinium (4DAP) groups through extensive hydrogen-bonding interactions.
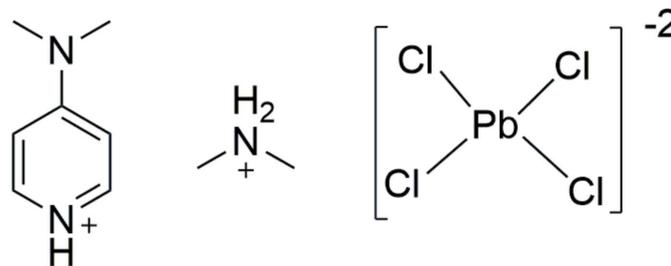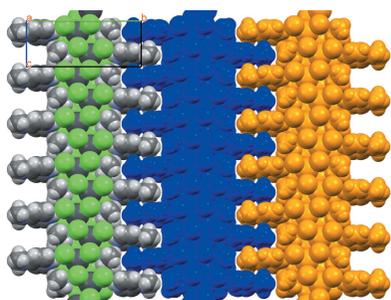
2. Structural commentary

This structure crystallizes in the centrosymmetric space group $C2/c$ with half of a molecule of DMA, half of a $[PbCl_4]^{2-}$ anion,
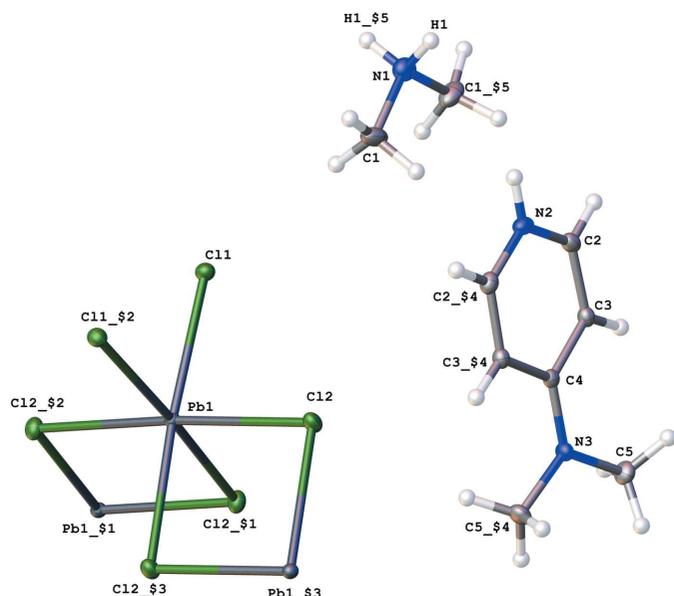
Figure 1
The expanded asymmetric unit of the title crystal structure, showing the naming scheme. The asymmetric unit contains half of each component: dimethylammonium, 4-(dimethylamino)pyridinium, and $[PbCl_4]^{2-}$. Displacement ellipsoids are drawn at the 50% probability level. Atom colors: carbon (gray), nitrogen (blue), hydrogen (white), lead (dark blue) and chlorine (green). [Symmetry operators: ($1) x, $1 - y$, $-\frac{1}{2} + z$; ($2) $2 - x$, y, $\frac{1}{2} - z$; ($3) $2 - x$, $1 - y$, $1 - z$; ($4) $1 - x$, y, $\frac{3}{2} - z$; ($5) $1 - x$, y, $\frac{1}{2} - z$.]

Figure 2
Hydrogen-bonding network in a single $PbCl_4$ chain viewed down [100]. Displacement ellipsoids are drawn at the 50% probability level. Atom colors: carbon (gray), nitrogen (blue), hydrogen (white), lead (dark blue) and chlorine (green).

and half of a molecule of 4DAP in the asymmetric unit, shown in Fig. 1. The point groups of the two cations are C_2. The lead metal center, with its six chloride ligands, exhibits a slightly distorted octahedral coordination geometry (formally C_2 symmetry). Of the two crystallographically unique Cl atoms, Cl1 and its symmetry equivalent produced through a C_2 rotation are the two terminal atoms [Pb—Cl = 2.8499 (4) Å]. The other crystallographically unique Cl atom, Cl2, produces the four bridging atoms through a C_2 rotation and inversion operation that results in an additional two unique Pb—Cl bonds [2.9015 (5) and 2.9041 (5) Å]. These bridging ligands form one-dimensional chains of $[PbCl_4]^{2-}$ anions which extend approximately along the [001] direction. The net negative two charge of the lead chloride anion is balanced by the positive charges of the DMA and 4DAP cations.

3. Supramolecular features

The one-dimensional lead chloride chains are capped in the [010] direction by 4DAP and DMA molecules via hydrogen bonds (Table 1), which form between the NH groups on the 4DAP and DMA molecules and the terminal chloride ligands on each lead atom. The hydrogen-bond donor on the 4DAP forms a hydrogen bond with each of the two terminal chlorides on the nearest Pb atom, while each donor on the DMA forms a hydrogen bond with one terminal chloride on Pb atoms that are separated in the chain by one additional Pb. The hydrogen-bonding network of the title structure is shown in

Fig. 2. The chains are packed together along the [010] direction by intercalation of the peripheral 4DAP ligands, as shown in Fig. 3, to form sheets which lie in the (100) plane. These sheets are held together primarily by weak intermolecular interactions, although one CH···Cl contact (2.788 Å) does exist that is 0.162 Å less than the sum of the van der Waals radii for these atoms.
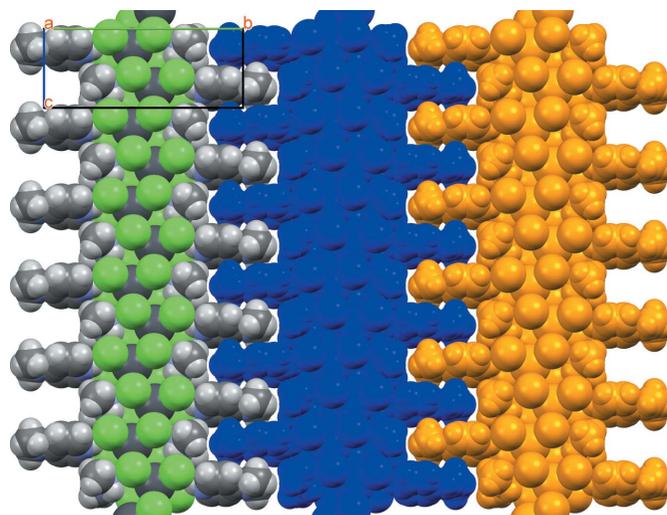
Figure 3
Space-filling model of intercalated $PbCl_4$ chains viewed down [100]. (Left) $PbCl_4$ chain colored by element. (Center and right) Intercalation illustrated by chains coloured in blue and orange..

4. Database survey

The crystal structure of $[PbCl_4]^{2-}$ and dimethylbenzene-1,4 diaminium was reported in 2008 (Dobrzycki & Woźniak, 2008). This compound crystallizes in the centrosymmetric space group $P2_1/n$, and the structure contains two-dimensional lead chloride sheets that run parallel to [001]. Like in the title structure, each Pb center possesses approximately octahedral symmetry (formally C_1) and is coordinated to two terminal and four bridging chloride atoms. Two of the bridging atoms are crystallographically unique and each give rise to a symmetry-related atom to yield four bonds to the Pb center (Pb—Cl2 = 2.945 and 2.927 Å; Pb—Cl3 = 3.095 and 2.765 Å). In this compound, hydrogen bonding occurs between the terminal chloride ligands and the protons on the diaminium groups of the organic cation, as shown in Fig. 4. Both structures are similarly charge-balanced in that the respective anionic $PbCl_4$ sheet or chain is balanced by the positive charge from organic cation molecules. The major difference between these two compounds is that the title structure contains one-dimensional chains while this structure contains two-dimensional sheets.

5. Synthesis and crystallization

To a 20 mL scintillation vial was added 4DAP (1.008 g, 8.25×10^{-3} mol) and concentrated hydrochloric acid (2 ml) creating an acidic solution. To a 23 mL screw-top thick-walled vial was added $PbCl_2$ (0.5040 g, 1.81×10^{-3} mol), DMF (1 ml), and the 4DAP acid solution (1 ml). The thick-walled vial was placed in the oven for 11 days at 373 K. Clear, colorless crystals of the title compound that were suitable for single-crystal X-ray diffraction were obtained. The DMA is present in the lattice due to the *in situ* degradation of DMF, which can occur at the reaction temperature (Burrows *et al.*, 2008).
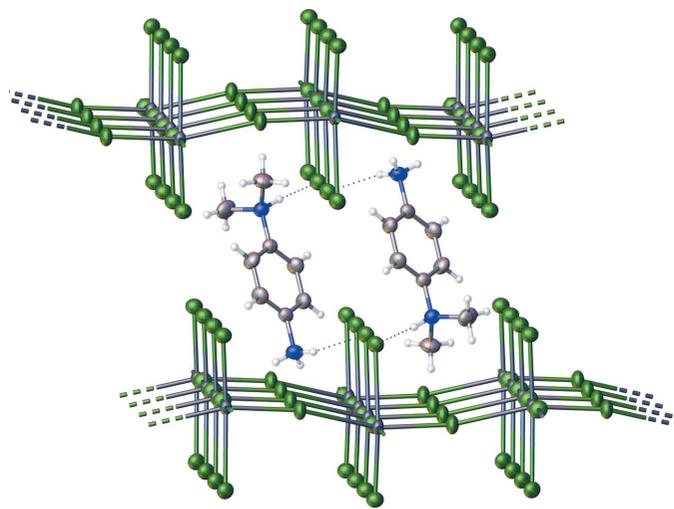
Figure 4
Hydrogen-bonding network in $[PbCl_4]^{2-}$·dimethylbenzene-1,4-diaminium. Displacement ellipsoids are drawn at the 50% probability level. Atom colors: carbon (gray), nitrogen (blue), hydrogen (white), lead (dark blue) and chlorine (green).

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl1^i	0.87 (2)	2.47 (1)	3.1844 (6)	139 (2)
N2—H2···Cl1^i	0.88	2.63	3.2901 (18)	133
N2—H2···Cl1^{ii}	0.88	2.63	3.2901 (18)	133

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

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The position of the ammonium hydrogen atom was determined from the difference-Fourier map, and all other hydrogen atoms were placed in idealized positions with bond lengths set to 0.98 Å for alkyl C—H protons, 0.95 Å for aliphatic C—H protons, and 0.88 Å for the pyridinium proton. These hydrogen atoms were refined using a riding model with $U_{iso}(H) = 1.2\ U_{eq}(N,C)$ for all N—H and aliphatic protons and $1.5\ U_{eq}(C)$ for methyl group protons. To appropriately model the ammonium hydrogen atom, which is complicated by the site of symmetry on which the nitrogen atom resides, the distance between the hydrogen atom and its symmetry-equivalent was restrained to 1.4 (2) Å. No other constraints were applied to the refinement model.

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_2H_8N)(C_7H_{11}N_2)[PbCl_4]$
M_r	518.26
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	90
a, b, c (Å)	11.0965 (11), 19.120 (2), 7.5453 (8)
β (°)	91.0813 (19)
V (Å^3)	1600.6 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	11.19
Crystal size (mm)	$0.12 \times 0.10 \times 0.04$
Data collection	
Diffractometer	Bruker SMART APEXII area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.291, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14318, 2461, 2398
R_{int}	0.030
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.716
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.013, 0.034, 1.04
No. of reflections	2461
No. of parameters	85
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.68, −0.76

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *olex2.solve* (Bourhis *et al.*, 2015), *SHELXL2016* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

References

Baikie, T., Fang, Y., Kadro, J. M., Schreyer, M., Wei, F., Mhaisalkar, S. G., Graetzel, M. & White, T. J. (2013). *J. Mater. Chem. A*, **1**, 5628–5641.

Bourhis, L. J., Dolomanov, O. V., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2015). *Acta Cryst.* A**71**, 59–75.

Bruker (2016). *APEX3*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Burrows, A. D., Cassar, K., Düren, T., Friend, R. M. W., Mahon, M. F., Rigby, S. P. & Savarese, T. L. (2008). *Dalton Trans.* pp. 2465–2474.

Dobrzycki, L. & Woźniak, K. (2008). *CrystEngComm*, **10**, 577–589.

Dohner, E. R., Jaffe, A., Bradshaw, L. R. & Karunadasa, H. I. (2014). *J. Am. Chem. Soc.* **136**, 13154–13157.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Gillon, A. L., Lewis, G. R., Orpen, A. G., Rotter, S., Starbuck, J., Wang, X.-M., Rodríguez-Martín, Y. & Ruiz-Pérez, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3897–3905.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Zhao, Y. & Zhu, K. (2014). *J. Phys. Chem. C*, **118**, 9412–9418.

supporting information

Hybrid organic–inorganic crystal structure of 4-(dimethylamino)pyridinium di-methylammonium tetrachloridolead(II)

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Computing details

Data collection: *APEX2* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: *olex2.solve* (Bourhis *et al.*, 2015); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

4-Dimethylaminopyridinium dimethylammonium tetrachloridolead(II)

Crystal data

$(C_2H_8N)(C_7H_{11}N_2)[PbCl_4]$	$F(000) = 976$
$M_r = 518.26$	$D_x = 2.151$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 11.0965\,(11)$ Å	Cell parameters from 9977 reflections
$b = 19.120\,(2)$ Å	$\theta = 3.4$–$30.6°$
$c = 7.5453\,(8)$ Å	$\mu = 11.19$ mm^{-1}
$\beta = 91.0813\,(19)°$	$T = 90$ K
$V = 1600.6\,(3)$ Å^3	Plate, colourless
$Z = 4$	$0.12 \times 0.10 \times 0.04$ mm

Data collection

Bruker SMART APEXII area detector diffractometer	$T_{min} = 0.291$, $T_{max} = 0.746$
Radiation source: microfocus rotating anode, Incoatec Iμs	14318 measured reflections
	2461 independent reflections
Mirror optics monochromator	2398 reflections with $I > 2\sigma(I)$
Detector resolution: 7.9 pixels mm^{-1}	$R_{int} = 0.030$
ω and φ scans	$\theta_{max} = 30.6°$, $\theta_{min} = 2.1°$
Absorption correction: multi-scan	$h = -15 \rightarrow 15$
(SADABS; Bruker, 2016)	$k = -27 \rightarrow 27$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent
$R[F^2 > 2\sigma(F^2)] = 0.013$	and constrained refinement
$wR(F^2) = 0.034$	$w = 1/[\sigma^2(F_o^2) + (0.0197P)^2 + 0.6272P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
2461 reflections	$(\Delta/\sigma)_{max} = 0.001$
85 parameters	$\Delta\rho_{max} = 1.68$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.76$ e Å^{-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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Pb1	1.000000	0.44266 (2)	0.250000	0.00845 (3)
Cl2	0.86249 (4)	0.44764 (2)	0.57303 (6)	0.01412 (8)
Cl1	0.85512 (3)	0.33250 (2)	0.10684 (5)	0.01280 (7)
N1	0.500000	0.18730 (13)	0.250000	0.0181 (4)
H1	0.4713 (19)	0.1598 (13)	0.3311 (18)	0.022*
N3	0.500000	0.52247 (11)	0.750000	0.0121 (4)
N2	0.500000	0.30724 (11)	0.750000	0.0138 (4)
H2	0.499998	0.261213	0.750000	0.017*
C4	0.500000	0.45287 (12)	0.750000	0.0103 (4)
C2	0.40384 (16)	0.34254 (9)	0.6811 (2)	0.0138 (3)
H2A	0.337557	0.317062	0.632503	0.017*
C3	0.40049 (14)	0.41371 (9)	0.6802 (2)	0.0121 (3)
H3	0.331759	0.437346	0.633026	0.015*
C5	0.39118 (18)	0.56252 (9)	0.7039 (3)	0.0165 (4)
H5A	0.320144	0.537848	0.747178	0.025*
H5B	0.384567	0.567587	0.574804	0.025*
H5C	0.396086	0.608909	0.758791	0.025*
C1	0.5973 (2)	0.23118 (11)	0.3336 (3)	0.0238 (4)
H1A	0.641230	0.255783	0.240978	0.036*
H1B	0.653055	0.201124	0.400987	0.036*
H1C	0.561169	0.265369	0.413504	0.036*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.00920 (5)	0.00796 (5)	0.00818 (5)	0.000	0.00013 (3)	0.000
Cl2	0.01194 (18)	0.01588 (19)	0.01458 (19)	−0.00345 (13)	0.00121 (15)	−0.00144 (13)
Cl1	0.01214 (16)	0.01147 (16)	0.01476 (17)	−0.00031 (13)	−0.00059 (13)	−0.00139 (13)
N1	0.0206 (11)	0.0187 (11)	0.0151 (10)	0.000	0.0012 (8)	0.000
N3	0.0089 (8)	0.0123 (9)	0.0149 (9)	0.000	−0.0014 (7)	0.000
N2	0.0176 (10)	0.0103 (9)	0.0136 (9)	0.000	0.0019 (7)	0.000
C4	0.0102 (10)	0.0123 (10)	0.0085 (10)	0.000	0.0009 (8)	0.000
C2	0.0132 (7)	0.0152 (8)	0.0131 (7)	−0.0030 (6)	0.0011 (6)	−0.0018 (6)
C3	0.0098 (6)	0.0143 (7)	0.0121 (7)	−0.0003 (6)	0.0002 (5)	−0.0003 (6)
C5	0.0131 (8)	0.0165 (8)	0.0200 (9)	0.0044 (6)	−0.0016 (7)	0.0015 (6)
C1	0.0315 (10)	0.0156 (8)	0.0247 (9)	−0.0080 (7)	0.0084 (8)	−0.0049 (7)

Geometric parameters (Å, º)

Pb1—Cl2	2.9015 (5)	N2—C2	1.358 (2)
Pb1—Cl2ⁱ	2.9041 (5)	N2—C2^v	1.358 (2)
Pb1—Cl2ⁱⁱ	2.9015 (5)	C4—C3^v	1.427 (2)
Pb1—Cl2ⁱⁱⁱ	2.9041 (5)	C4—C3	1.427 (2)
Pb1—Cl1ⁱⁱ	2.8500 (4)	C2—H2A	0.9500
Pb1—Cl1	2.8499 (4)	C2—C3	1.361 (2)
N1—H1^{iv}	0.872 (17)	C3—H3	0.9500
N1—H1	0.872 (17)	C5—H5A	0.9800
N1—C1^{iv}	1.497 (2)	C5—H5B	0.9800
N1—C1	1.497 (2)	C5—H5C	0.9800
N3—C4	1.331 (3)	C1—H1A	0.9800
N3—C5^v	1.466 (2)	C1—H1B	0.9800
N3—C5	1.466 (2)	C1—H1C	0.9800
N2—H2	0.8800		
Cl2—Pb1—Cl2ⁱⁱ	176.237 (16)	C2—N2—H2	119.8
Cl2ⁱⁱ—Pb1—Cl2ⁱⁱⁱ	94.728 (14)	C2^v—N2—H2	119.8
Cl2—Pb1—Cl2ⁱⁱⁱ	82.538 (14)	C2^v—N2—C2	120.4 (2)
Cl2—Pb1—Cl2ⁱ	94.728 (14)	N3—C4—C3^v	121.65 (10)
Cl2ⁱⁱⁱ—Pb1—Cl2ⁱ	87.519 (19)	N3—C4—C3	121.66 (10)
Cl2ⁱⁱ—Pb1—Cl2ⁱ	82.539 (14)	C3^v—C4—C3	116.7 (2)
Cl1—Pb1—Cl2ⁱⁱ	90.441 (13)	N2—C2—H2A	119.3
Cl1ⁱⁱ—Pb1—Cl2	90.442 (13)	N2—C2—C3	121.33 (16)
Cl1—Pb1—Cl2ⁱ	94.115 (15)	C3—C2—H2A	119.3
Cl1ⁱⁱ—Pb1—Cl2ⁱⁱ	92.339 (12)	C4—C3—H3	119.9
Cl1—Pb1—Cl2	92.340 (13)	C2—C3—C4	120.13 (16)
Cl1—Pb1—Cl2ⁱⁱⁱ	174.742 (12)	C2—C3—H3	119.9
Cl1ⁱⁱ—Pb1—Cl2ⁱⁱⁱ	94.116 (15)	N3—C5—H5A	109.5
Cl1ⁱⁱ—Pb1—Cl2ⁱ	174.741 (12)	N3—C5—H5B	109.5
Cl1—Pb1—Cl1ⁱⁱ	84.698 (18)	N3—C5—H5C	109.5
Pb1—Cl2—Pb1ⁱⁱⁱ	97.462 (14)	H5A—C5—H5B	109.5
H1—N1—H1^{iv}	106 (3)	H5A—C5—H5C	109.5
C1^{iv}—N1—H1^{iv}	108.2 (15)	H5B—C5—H5C	109.5
C1—N1—H1^{iv}	111.3 (15)	N1—C1—H1A	109.5
C1^{iv}—N1—H1	111.3 (15)	N1—C1—H1B	109.5
C1—N1—H1	108.2 (15)	N1—C1—H1C	109.5
C1^{iv}—N1—C1	111.8 (2)	H1A—C1—H1B	109.5
C4—N3—C5	121.49 (10)	H1A—C1—H1C	109.5
C4—N3—C5^v	121.49 (10)	H1B—C1—H1C	109.5
C5^v—N3—C5	117.0 (2)		
N3—C4—C3—C2	179.51 (11)	C5—N3—C4—C3^v	−170.46 (13)
N2—C2—C3—C4	1.0 (2)	C5^v—N3—C4—C3^v	9.54 (13)

C2ᵛ—N2—C2—C3	−0.51 (12)	C5ᵛ—N3—C4—C3	−170.46 (13)
C3ᵛ—C4—C3—C2	−0.49 (11)	C5—N3—C4—C3	9.54 (13)

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

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl1ᵛⁱ	0.87 (2)	2.47 (1)	3.1844 (6)	139 (2)
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N2—H2···Cl1ᵛⁱⁱ	0.88	2.63	3.2901 (18)	133

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