

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

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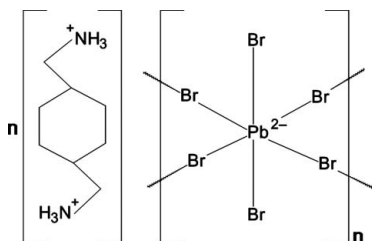
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 Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.021; wR factor = 0.047; data-to-parameter ratio = 28.1.

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 (2010*a*) and for the isotypic iodidoplumbate(II), see: Rayner & Billing (2010*b*).



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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supplementary materials

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

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

M. K. Rayner and D. G. Billing

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 $\text{N—H}\cdots\text{X}$ ($\text{X} = \text{Br}, \text{I}$ and Cl) hydrogen bonding in the right-angled halogen subtype of the terminal halide hydrogen bonding motif (Mitzi, 1999).

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.

Refinement

The H atoms on the diammonium cation were refined using a riding-model, with $\text{C—H} = 0.99 \text{ \AA}$, $\text{N—H} = 0.91 \text{ \AA}$ 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 (0.78 e \AA^{-3}) was 0.923 \AA from Pb1 .

Figures

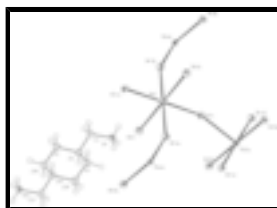


Fig. 1. The asymmetric unit of the title compound with atom labels. Displacement ellipsoids were drawn at the 50% probability level. Symmetry codes: (a) $1-x, 1/2+y, 1/2-z$ (b) $1-x, 1-y, 1-z$ (c) $x, 1/2-y, 1/2+z$ (d) $-x, 1-y, 2-z$.

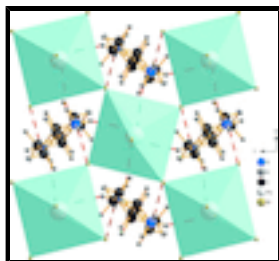


Fig. 2. Packing diagram viewed along the *a* axis. Hydrogen bonds are drawn as dashed red lines.

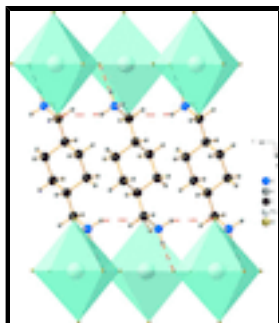


Fig. 3. Packing diagram viewed along the *b* axis. Hydrogen bonds are drawn as dashed red lines.

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

Crystal data

(C₈H₂₀N₂)[PbBr₄]

$M_r = 671.09$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

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$b = 8.1955$ (4) Å

$c = 8.2160$ (4) Å

$\beta = 95.693$ (1)°

$V = 811.01$ (7) Å³

$Z = 2$

$F(000) = 608$

$D_x = 2.748$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5293 reflections

$\theta = 3.0$ – 28.2 °

$\mu = 20.23$ mm⁻¹

$T = 173$ K

Plate, colourless

$0.20 \times 0.14 \times 0.02$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

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 $I > 2\sigma(I)$

$R_{\text{int}} = 0.063$

$\theta_{\max} = 28.0$ °, $\theta_{\min} = 1.7$ °

$h = -15$ → 15

$k = -10$ → 10

$l = -10$ → 10

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.021$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.047$	H-atom parameters constrained
$S = 0.81$	$w = 1/[\sigma^2(F_o^2) + (0.0349P)^2 + 0.0549P]$
1966 reflections	where $P = (F_o^2 + 2F_c^2)/3$
70 parameters	$(\Delta/\sigma)_{\max} = 0.011$
0 restraints	$\Delta\rho_{\max} = 0.78 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -2.31 \text{ e } \text{\AA}^{-3}$

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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)

supplementary materials

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 (\AA^2)

	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 (\AA , $^\circ$)

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 ($\text{\AA}, ^\circ$)

<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) $x, y, z+1$.

Fig. 1

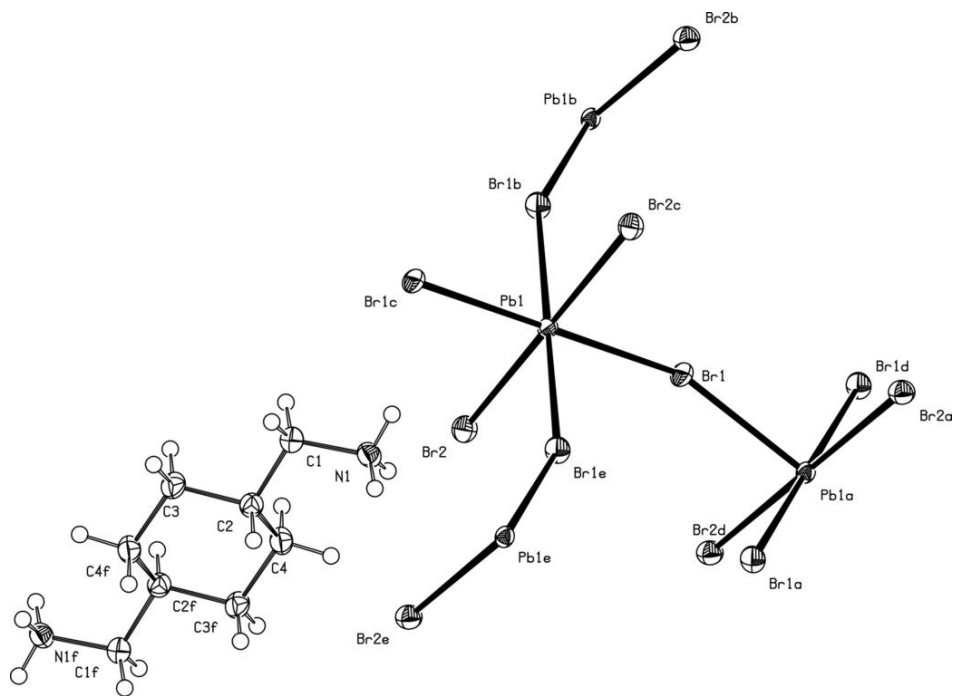


Fig. 2

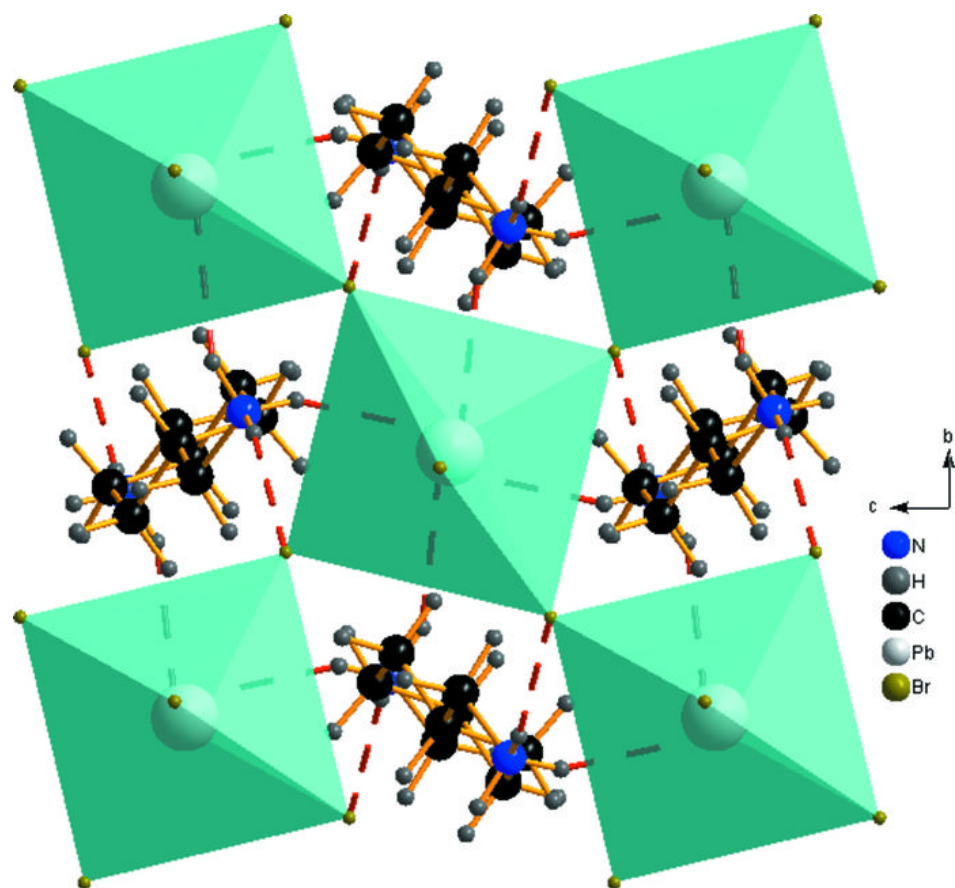


Fig. 3

