

## Poly[1,4-bis(ammoniomethyl)cyclohexane [di- $\mu$ -iodido-diiodido-plumbate(II)]]

Matthew Kyle Rayner and David Gordon Billing\*

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, PO Wits 2050, South Africa

Correspondence e-mail: david.billing@wits.ac.za

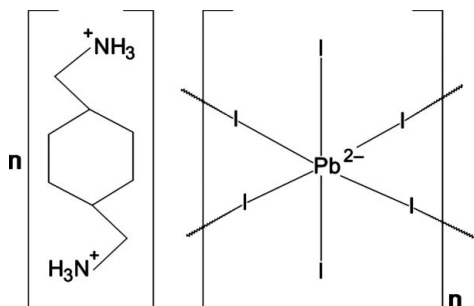
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 Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{C}-\text{C}) = 0.010$  Å;  $R$  factor = 0.033;  $wR$  factor = 0.093; data-to-parameter ratio = 32.3.

The title compound,  $\{(\text{C}_8\text{H}_{20}\text{N}_2)[\text{PbI}_4]\}_n$ , is an inorganic-organic hybrid. The structure is composed of alternate layers of two-dimensional corner-sharing  $\text{PbI}_6$  octahedra ( $\bar{1}$  symmetry) and 1,4-bis(ammoniomethyl)cyclohexane cations ( $\bar{1}$  symmetry) extending parallel to the  $bc$  plane. The cations interact with the inorganic layer via  $\text{N}-\text{H}\cdots\text{I}$  hydrogen bonding in the right-angled halogen sub-type of the terminal halide hydrogen-bonding motif.

### Related literature

For other examples of inorganic-organic hybrid structures incorporating cyclic ammonium cations, see: Billing & Lemmerer (2006). For hydrogen-bonding nomenclature for inorganic-organic hybrids, see: Mitzi (1999). For the related chloridoplumbate(II), see: Rayner & Billing (2010a) and for the isotopic bromidoplumbate(II), see: Rayner & Billing (2010b).



### Experimental

#### Crystal data

$(\text{C}_8\text{H}_{20}\text{N}_2)[\text{PbI}_4]$   
 $M_r = 859.05$   
 Monoclinic,  $P2_1/c$   
 $a = 12.2793$  (17) Å

$b = 8.7413$  (12) Å  
 $c = 8.7829$  (13) Å  
 $\beta = 95.922$  (3)°  
 $V = 937.7$  (2) Å<sup>3</sup>

$Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 15.56$  mm<sup>-1</sup>

$T = 173$  K  
 $0.36 \times 0.26 \times 0.08$  mm

#### Data collection

Bruker APEXII CCD area-detector diffractometer  
 Absorption correction: integration (*XPREP*; Bruker, 2005)  
 $T_{\min} = 0.043$ ,  $T_{\max} = 0.288$   
 5435 measured reflections  
 2264 independent reflections  
 2085 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.080$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.093$   
 $S = 1.08$   
 2264 reflections  
 70 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 1.76$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -2.79$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

Pb1—I2 <sup>i</sup>	3.1824 (5)	Pb1—I1 <sup>i</sup>	3.2243 (6)
Pb1—I2 <sup>ii</sup>	3.1875 (5)		

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

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1D}\cdots\text{I1}^i$	0.91	2.88	3.598 (5)	137
$\text{N1}-\text{H1E}\cdots\text{I1}^{iii}$	0.91	2.84	3.619 (6)	144
$\text{N1}-\text{H1E}\cdots\text{I2}^{iv}$	0.91	3.12	3.672 (6)	121
$\text{N1}-\text{H1C}\cdots\text{I2}$	0.91	2.78	3.611 (6)	152

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

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).

The University of the Witwatersrand and the National Research Fund (GUN: 2069064) are acknowledged for the funding and infrastructure required to perform the experiment.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2340).

### References

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**supplementary materials**

*Acta Cryst.* (2010). E66, m660 [ doi:10.1107/S160053681001682X ]

**Poly[1,4-bis(ammoniomethyl)cyclohexane [di- $\mu$ -iodido-diiodidoplumbate(II)]]**

**M. K. Rayner and D. G. Billing**

**Comment**

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 iodide (presented here), the bromide (Rayner & Billing, 2010*b*) and chloride (Rayner & Billing, 2010*a*). The bromide and iodide hybrids are isotypic and crystallize in the monoclinic system with space group  $P2_1/c$  while the chloride hybrid crystallizes in the orthorhombic,  $Pnma$  system.

In the structure of the title compound the lead atoms in the  $PbI_6$  octahedra occupy inversion centers, giving the octahedra  $\bar{1}$  symmetry. The  $PbI_6$  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). 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). Billing & Lemmerer (2006) reported a series of inorganic-organic hybrids incorporating cyclic ammonium cations, however no diammonium cations were synthesized.

**Experimental**

A mixture of 0.050 g (0.11 mmol)  $PbI_2$  and 0.017 g (0.17 mmol) 1,4-bis-(aminomethyl)-cyclohexane (mixture of isomers) was dissolved in 5 ml HI at 383 K and slow cooled at a rate of 0.069 K/min to yield yellow, plate-shaped single crystals suitable for X-ray analysis.

**Refinement**

The H atoms on the diammonium cation were refined using a riding-model, with  $C-H = 0.99 \text{ \AA}$ ,  $N-H = 0.91 \text{ \AA}$  and with  $U_{iso}(H)=1.2U_{eq}(C)$  or  $1.5U_{eq}(N)$ . The highest residual electron density peak ( $1.76 e \text{ \AA}^{-3}$ ) was  $0.955 \text{ \AA}$  from  $Pb1$ .

**Figures**

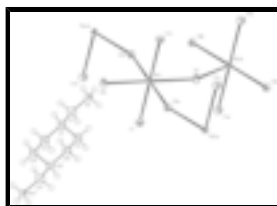


Fig. 1. The extended asymmetric unit of the title compound with atom labels. Displacement ellipsoids were drawn at the 50% probability level. Symmetry codes: (a)  $-x, -1/2+y, 3/2-z$  (b)  $-x, 1-y, 1-z$  (c)  $x, 3/2-y, -1/2+z$  (d)  $1-x, 1-y, -z$ .

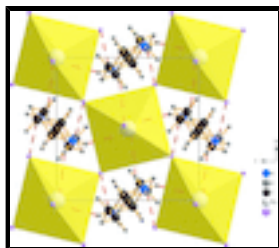


Fig. 2. Packing diagram viewed along the *a* axis. Hydrogen bonds are drawn as dashed red lines.

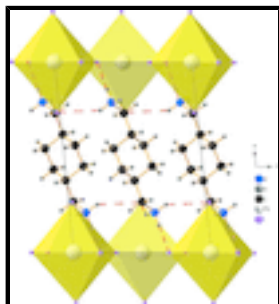


Fig. 3. Packing diagram viewed along the *b* axis. Hydrogen bonds are drawn as dashed red lines.

**Poly[1,4-bis(ammoniomethyl)cyclohexane [di- $\mu$ -iodido-diiodidoplumbate(II)]]**

*Crystal data*

(C<sub>8</sub>H<sub>20</sub>N<sub>2</sub>)[PbI<sub>4</sub>]

$M_r = 859.05$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 12.2793$  (17) Å

$b = 8.7413$  (12) Å

$c = 8.7829$  (13) Å

$\beta = 95.922$  (3)°

$V = 937.7$  (2) Å<sup>3</sup>

$Z = 2$

$F(000) = 752$

$D_x = 3.043$  Mg m<sup>-3</sup>

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

Cell parameters from 6011 reflections

$\theta = 3.0$ – $28.2$ °

$\mu = 15.56$  mm<sup>-1</sup>

$T = 173$  K

Plate, orange

$0.36 \times 0.26 \times 0.08$  mm

*Data collection*

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

$\varphi$  and  $\omega$  scans

Absorption correction: integration (XPREP; Bruker, 2005)

$T_{\min} = 0.043$ ,  $T_{\max} = 0.288$

5435 measured reflections

2264 independent reflections

2085 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.080$

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

$h = -16 \rightarrow 16$

$k = -11 \rightarrow 10$

$l = -9 \rightarrow 11$

*Refinement*

Refinement on  $F^2$

Primary atom site location: structure-invariant direct methods

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.033$$

$$wR(F^2) = 0.093$$

$$S = 1.08$$

2264 reflections

70 parameters

0 restraints

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 1.0393P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.009$$

$$\Delta\rho_{\max} = 1.76 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -2.79 \text{ e } \text{\AA}^{-3}$$

### 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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2676 (6)	0.0434 (9)	-0.4667 (9)	0.0333 (15)
H1A	0.2773	0.1355	-0.4011	0.040*
H1B	0.2216	0.0719	-0.5617	0.040*
C2	0.3794 (6)	-0.0123 (8)	-0.5065 (8)	0.0273 (15)
H2	0.3672	-0.0991	-0.5804	0.033*
C3	0.4366 (6)	0.1194 (9)	-0.5867 (8)	0.0306 (14)
H3A	0.3890	0.1529	-0.6785	0.037*
H3B	0.4475	0.2077	-0.5162	0.037*
C4	0.4542 (6)	-0.0685 (9)	-0.3667 (8)	0.0299 (14)
H4A	0.4654	0.0151	-0.2906	0.036*
H4B	0.4187	-0.1550	-0.3183	0.036*
N1	0.2111 (5)	-0.0797 (7)	-0.3841 (6)	0.0274 (12)
H1C	0.1450	-0.0448	-0.3610	0.041*
H1D	0.2531	-0.1050	-0.2962	0.041*
H1E	0.2012	-0.1637	-0.4451	0.041*
I1	-0.26315 (4)	0.02539 (5)	-0.02301 (5)	0.02714 (13)
I2	0.00031 (4)	0.18981 (5)	-0.30914 (4)	0.02605 (14)
Pb1	0.0000	0.0000	0.0000	0.01915 (11)

## supplementary materials

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.036 (4)	0.026 (3)	0.039 (4)	0.002 (3)	0.005 (3)	0.004 (3)
C2	0.027 (4)	0.027 (4)	0.028 (3)	-0.003 (3)	0.003 (3)	-0.001 (2)
C3	0.028 (3)	0.030 (3)	0.034 (3)	0.000 (3)	0.001 (3)	0.010 (3)
C4	0.023 (3)	0.035 (4)	0.031 (3)	-0.003 (3)	0.002 (3)	0.008 (3)
N1	0.025 (3)	0.031 (3)	0.026 (3)	-0.004 (2)	0.003 (2)	-0.001 (2)
I1	0.0262 (2)	0.0257 (2)	0.0288 (2)	-0.00327 (17)	-0.00048 (18)	-0.00028 (16)
I2	0.0356 (2)	0.0218 (2)	0.0212 (2)	0.00569 (16)	0.00513 (16)	0.00779 (14)
Pb1	0.02537 (19)	0.01599 (17)	0.01602 (16)	0.00087 (11)	0.00182 (12)	0.00032 (10)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

C1—N1	1.507 (9)	C4—H4B	0.9900
C1—C2	1.530 (10)	N1—H1C	0.9100
C1—H1A	0.9900	N1—H1D	0.9100
C1—H1B	0.9900	N1—H1E	0.9100
C2—C4	1.536 (10)	I1—Pb1	3.2243 (6)
C2—C3	1.554 (9)	I2—Pb1	3.1824 (5)
C2—H2	1.0000	I2—Pb1 <sup>ii</sup>	3.1875 (5)
C3—C4 <sup>i</sup>	1.510 (10)	Pb1—I2 <sup>iii</sup>	3.1824 (5)
C3—H3A	0.9900	Pb1—I2 <sup>iv</sup>	3.1875 (5)
C3—H3B	0.9900	Pb1—I2 <sup>v</sup>	3.1875 (5)
C4—C3 <sup>i</sup>	1.510 (10)	Pb1—I1 <sup>iii</sup>	3.2243 (6)
C4—H4A	0.9900		
N1—C1—C2	110.5 (6)	H4A—C4—H4B	108.1
N1—C1—H1A	109.5	C1—N1—H1C	109.5
C2—C1—H1A	109.5	C1—N1—H1D	109.5
N1—C1—H1B	109.5	H1C—N1—H1D	109.5
C2—C1—H1B	109.5	C1—N1—H1E	109.5
H1A—C1—H1B	108.1	H1C—N1—H1E	109.5
C4—C2—C1	113.3 (6)	H1D—N1—H1E	109.5
C4—C2—C3	109.8 (6)	Pb1—I2—Pb1 <sup>ii</sup>	153.144 (15)
C1—C2—C3	109.0 (6)	I2—Pb1—I2 <sup>iii</sup>	180.00 (2)
C4—C2—H2	108.2	I2—Pb1—I2 <sup>iv</sup>	90.294 (11)
C1—C2—H2	108.2	I2 <sup>iii</sup> —Pb1—I2 <sup>iv</sup>	89.706 (11)
C3—C2—H2	108.2	I2—Pb1—I2 <sup>v</sup>	89.706 (11)
C4 <sup>i</sup> —C3—C2	111.1 (6)	I2 <sup>iii</sup> —Pb1—I2 <sup>v</sup>	90.294 (11)
C4 <sup>i</sup> —C3—H3A	109.4	I2 <sup>iv</sup> —Pb1—I2 <sup>v</sup>	180.0
C2—C3—H3A	109.4	I2—Pb1—I1 <sup>iii</sup>	89.999 (12)
C4 <sup>i</sup> —C3—H3B	109.4	I2 <sup>iii</sup> —Pb1—I1 <sup>iii</sup>	90.001 (12)
C2—C3—H3B	109.4	I2 <sup>iv</sup> —Pb1—I1 <sup>iii</sup>	94.518 (12)
H3A—C3—H3B	108.0	I2 <sup>v</sup> —Pb1—I1 <sup>iii</sup>	85.482 (12)

C3 <sup>i</sup> —C4—C2	110.6 (6)	I2—Pb1—I1	90.001 (12)
C3 <sup>i</sup> —C4—H4A	109.5	I2 <sup>iii</sup> —Pb1—I1	89.999 (12)
C2—C4—H4A	109.5	I2 <sup>iv</sup> —Pb1—I1	85.482 (12)
C3 <sup>i</sup> —C4—H4B	109.5	I2 <sup>v</sup> —Pb1—I1	94.518 (12)
C2—C4—H4B	109.5	I1 <sup>iii</sup> —Pb1—I1	180.0
N1—C1—C2—C4	-55.7 (8)	C3—C2—C4—C3 <sup>i</sup>	-57.0 (9)
N1—C1—C2—C3	-178.2 (6)	Pb1 <sup>ii</sup> —I2—Pb1—I2 <sup>iv</sup>	-0.35 (4)
C4—C2—C3—C4 <sup>i</sup>	57.3 (8)	Pb1 <sup>ii</sup> —I2—Pb1—I2 <sup>v</sup>	179.65 (4)
C1—C2—C3—C4 <sup>i</sup>	-178.1 (6)	Pb1 <sup>ii</sup> —I2—Pb1—I1 <sup>iii</sup>	-94.87 (4)
C1—C2—C4—C3 <sup>i</sup>	-179.1 (6)	Pb1 <sup>ii</sup> —I2—Pb1—I1	85.13 (4)

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

*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1D $\cdots$ I1 <sup>iii</sup>	0.91	2.88	3.598 (5)	137
N1—H1E $\cdots$ I1 <sup>v</sup>	0.91	2.84	3.619 (6)	144
N1—H1E $\cdots$ I2 <sup>vi</sup>	0.91	3.12	3.672 (6)	121
N1—H1C $\cdots$ I2	0.91	2.78	3.611 (6)	152

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

Fig. 1

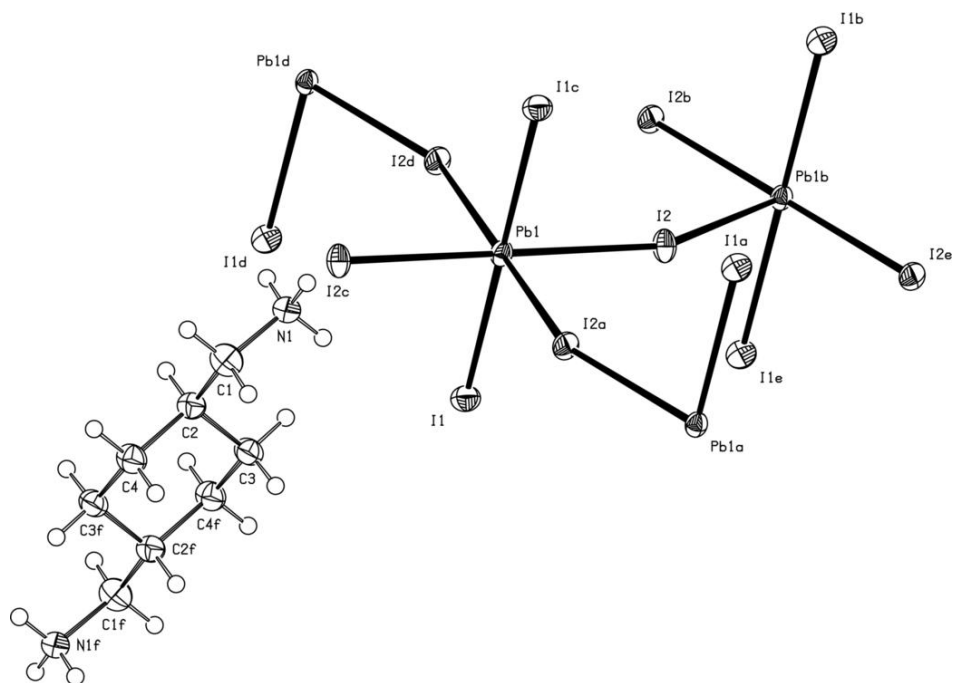




Fig. 2

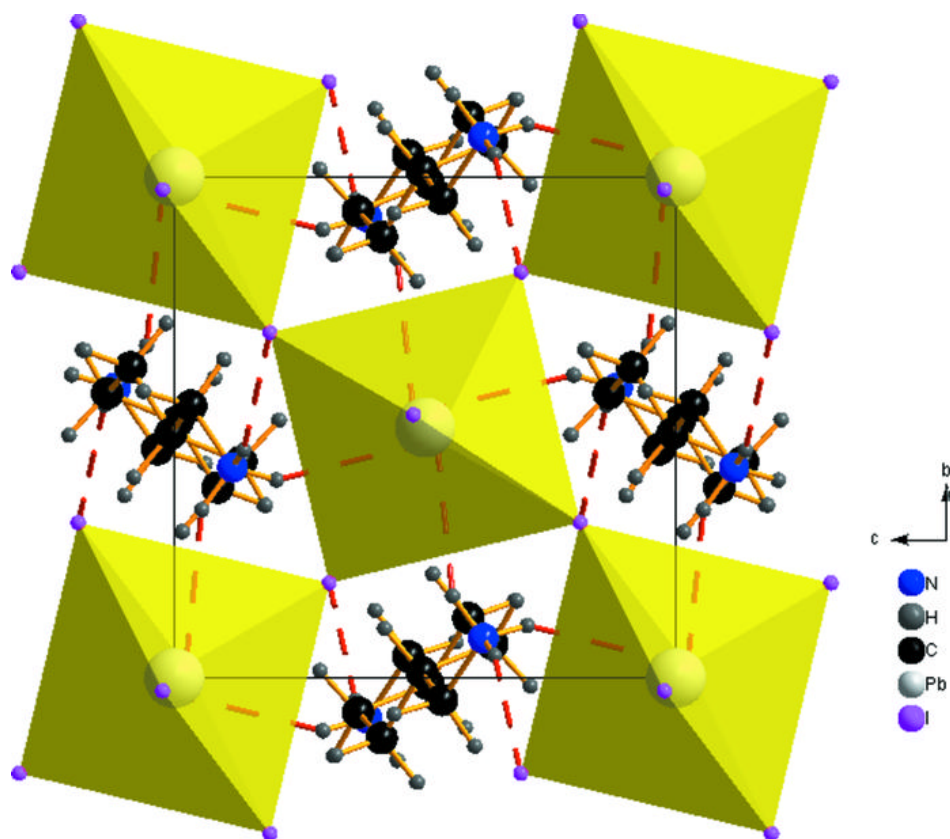


Fig. 3

