

The one-dimensional organic inorganic hybrid compound poly[(diethylene-triamine)tetra- μ -iodido-dilead(II)]

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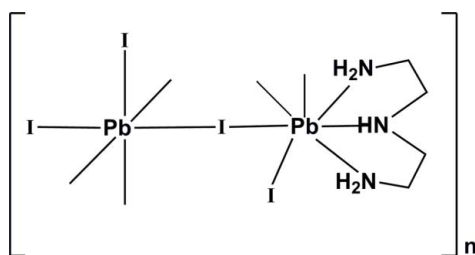
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.020$ Å; R factor = 0.041; wR factor = 0.100; data-to-parameter ratio = 29.8.

A new organic–inorganic hybrid, $[\text{Pb}_2\text{I}_4(\text{C}_4\text{H}_{13}\text{N}_3)]_n$, was obtained by the reaction of $\text{C}_4\text{N}_3\text{H}_{10}$ and PbI_2 at room temperature. The structure is a three-dimensional polymer resulting from the association of PbI_6 octahedra and a mixed lead organic–inorganic $\text{PbI}_4(\text{C}_4\text{N}_3\text{H}_{13})$ coordination polyhedron. Both Pb atoms, two I atoms and one N atom lie on a mirror plane. $\text{N}-\text{H}\cdots\text{I}$ hydrogen bonds further connect the organic unit and some I atoms.

Related literature

For related literature, see: Lode & Krautscheild (2001); Krautscheild *et al.* (2001); Papavassiliou *et al.* (1999); Wang *et al.* (1995); Zhu *et al.* (2004).



Experimental

Crystal data

$[\text{Pb}_2\text{I}_4(\text{C}_4\text{H}_{13}\text{N}_3)]$
 $M_r = 1025.15$

Orthorhombic, $Pnma$
 $a = 17.034$ (6) Å

$b = 9.218$ (3) Å
 $c = 11.092$ (4) Å
 $V = 1741.6$ (10) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 26.38$ mm⁻¹
 $T = 293$ (2) K
 $0.2 \times 0.05 \times 0.05$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.095$, $T_{\max} = 0.268$
2906 measured reflections

1998 independent reflections
1202 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
2 standard reflections
frequency: 120 min
intensity decay: 5%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.099$
 $S = 1.00$
1998 reflections

67 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 1.57$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.58$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1A}\cdots\text{I1}^{\text{i}}$	0.90	2.93	3.791 (12)	160
$\text{N1}-\text{H1B}\cdots\text{I2}^{\text{ii}}$	0.90	2.88	3.746 (12)	163
$\text{N2}-\text{H2}\cdots\text{I2}^{\text{iii}}$	0.91	3.19	3.731 (17)	121

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

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2346).

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supplementary materials

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The one-dimensional organic inorganic hybrid compound poly[(diethylenetriamine)tetra- μ -iodido-dilead(II)]

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Comment

The basic structure building block of this compound is made up of lead iodide octahedral [PbI₆] and a mixed lead organic-inorganic PbI₄(C₄N₃H₁₃) coordination polyhedron (Fig 1). Both Pb atoms, two I atoms and one N atom lie on a mirror plane. Atom Pb1 is located in the octahedral cavity of the inorganic chains while Pb2 is responsible of the connectivity between organic moiety and inorganic chains. To our knowledge, this is the first report of an organic-inorganic hybrid exhibiting this kind of lead connectivity.

A part of the inorganic back bone is staked as single chains of edge sharing PbI₆ octahedra, as shown in Fig 2. The halide atoms I3 are responsible for the edge sharing between PbI₆ neighboring octahedron to join infinite one dimensional chain (parallel to *b* axis). Within the octahedra the bond lengths around Pb1 range from 3.182 (2) to 3.319 (2) Å which indicate the dominant ionic character of the Pb—I bonds in the inorganic chains. The bond angles I—Pb1—I deviate slightly from ideal octahedral value of 90° and 180°, ranging from 88.39 (4)° to 92.98 (5)° for the adjacent iodides and from 176.76 (3)° to 179.59 (4)° for the opposite ones. This ideal octahedron indicates the unstereochemical activity of lead (II) lone pair electrons (Wang *et al.* 1995). Note that the regular octahedrons are a characteristic feature often encountered in the low dimensional lead iodide structures (Zhu *et al.*, 2004).

As mentioned above, C₄N₃H₁₃ is in combination with inorganic moiety by three Pb2—N non covalent interaction and hydrogen bonds. The non centrosymmetric organic molecule is slightly twisted around the C—C bond as reflected by a torsion angle of 25.1 (14)°. Bond distances and angles appear to be within normal range.

It is note worthy that the yellow color observed for the title compound is in good accordance with a low dimensional network of lead octahedral (Lode *et al.*, 2001; Krautscheild *et al.*, 2001; Papavassiliou *et al.*, 1999).

Experimental

An aqueous solution of HI was added to the diethylenetriamin to synthesis C₄H₁₃N₃I₃ salts. Under ambient conditions, stoichiometric amounts of C₄H₁₃N₃I₃ and PbI₂ with excess HI (to improve PbI₂ solubility), were sailed in DMF. The resulting solution was kept at room temperature. Yellow needle-like crystals are obtained five weeks later.

Refinement

All H atoms attached to C atoms and N atom were fixed geometrically and treated as riding with C—H = 0.97 Å (CH₂) and N—H = 0.90 Å (NH₂) or 0.91 Å (NH) 0.86 Å with U_{iso}(H) = 1.2U_{eq} (C or N).

Figures

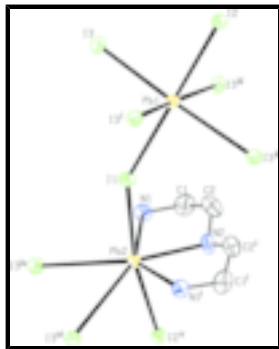


Fig. 1. : View of the $C_4N_3H_{13}Pb_2I_4$ with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $x, 1/2 - y, z$; (ii) $1 - x, 1/2 + y, 1 - z$; (iii) $1 - x, -y, 1 - z$; (iv) $1/2 - x, -y, 1/2 + z$; (v) $x - 1/2, 1/2 - y, 3/2 - z$; (vi) $1/2 - x, 1/2 + y, 1/2 + z$

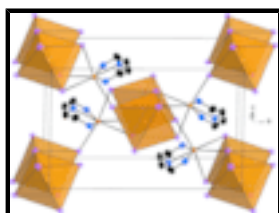


Fig. 2. : Packing view of $C_4N_3H_{13}Pb_2I_4$ viewed along $[010]$ direction. H atoms have been omitted for clarity.

poly[(diethylenetriamine)tetra- μ -iodido-dilead(II)]

Crystal data

$[Pb_2I_4(C_4H_{13}N_3)]$

$M_r = 1025.15$

Orthorhombic, $Pnma$

Hall symbol: $-P\ 2ac\ 2n$

$a = 17.034\ (6)\ \text{\AA}$

$b = 9.218\ (3)\ \text{\AA}$

$c = 11.092\ (4)\ \text{\AA}$

$V = 1741.6\ (10)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1736$

$D_x = 3.910\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 10.7\text{--}13.8^\circ$

$\mu = 26.38\ \text{mm}^{-1}$

$T = 293\ (2)\ \text{K}$

Needle, yellow

$0.2 \times 0.05 \times 0.05\ \text{mm}$

Data collection

Enraf-Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293\ (2)\ \text{K}$

Non-profiled $\omega/2\theta$ scans

Absorption correction: ψ scan
(North *et al.*, 1968)

$T_{\min} = 0.095, T_{\max} = 0.268$

2906 measured reflections

1998 independent reflections

$R_{\text{int}} = 0.045$

$\theta_{\max} = 27.0^\circ$

$\theta_{\min} = 2.2^\circ$

$h = -1 \rightarrow 21$

$k = -11 \rightarrow 3$

$l = -1 \rightarrow 14$

2 standard reflections

every 120 min

intensity decay: 5%

1202 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.040$	H-atom parameters constrained
$wR(F^2) = 0.099$	$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2]$
$S = 1.00$	where $P = (F_o^2 + 2F_c^2)/3$
1998 reflections	$(\Delta/\sigma)_{\max} < 0.001$
67 parameters	$\Delta\rho_{\max} = 1.57 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -1.58 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Experimental. Number of psi-scan sets used was 4 Theta correction was applied. Averaged transmission function was used. No Fourier smoothing was applied (North *et al.*, 1968).

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	$U_{\text{iso}}^*/U_{\text{eq}}$
Pb1	0.49490 (3)	0.2500	0.49379 (7)	0.0376 (2)
Pb2	0.23035 (4)	0.2500	0.86880 (7)	0.0361 (2)
I1	0.32678 (7)	0.2500	0.61874 (12)	0.0482 (4)
I2	0.66724 (7)	0.2500	0.36339 (11)	0.0441 (3)
I3	0.43945 (5)	-0.00127 (10)	0.31479 (9)	0.0458 (3)
N1	0.2835 (7)	-0.0102 (10)	0.8986 (11)	0.049 (3)
H1A	0.2469	-0.0639	0.9365	0.059*
H1B	0.2922	-0.0506	0.8260	0.059*
N2	0.3598 (9)	0.2500	0.9763 (17)	0.055 (5)
H2	0.3467	0.2500	1.0558	0.066*
C2	0.4032 (8)	0.113 (2)	0.9595 (18)	0.079 (6)
H2C	0.4281	0.1143	0.8807	0.094*
H2D	0.4445	0.1075	1.0195	0.094*
C1	0.3559 (10)	-0.0133 (16)	0.9684 (18)	0.076 (6)
H1C	0.3426	-0.0282	1.0525	0.091*

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H1D 0.3867 -0.0961 0.9425 0.091*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.0375 (4)	0.0355 (4)	0.0399 (4)	0.000	0.0008 (3)	0.000
Pb2	0.0285 (3)	0.0402 (4)	0.0397 (4)	0.000	0.0006 (3)	0.000
I1	0.0465 (7)	0.0557 (8)	0.0425 (8)	0.000	0.0098 (7)	0.000
I2	0.0429 (7)	0.0507 (8)	0.0388 (7)	0.000	0.0023 (6)	0.000
I3	0.0484 (5)	0.0472 (6)	0.0419 (5)	-0.0063 (4)	-0.0028 (4)	-0.0008 (5)
N1	0.060 (7)	0.025 (6)	0.062 (9)	0.006 (5)	0.010 (6)	0.001 (6)
N2	0.043 (8)	0.062 (12)	0.059 (12)	0.000	-0.015 (9)	0.000
C2	0.048 (9)	0.084 (14)	0.103 (16)	0.013 (10)	-0.007 (10)	0.011 (13)
C1	0.088 (12)	0.043 (10)	0.096 (16)	0.017 (9)	-0.023 (12)	0.001 (11)

Geometric parameters (\AA , $^\circ$)

Pb1—I1	3.1816 (17)	N1—H1A	0.9000
Pb1—I3	3.1936 (13)	N1—H1B	0.9000
Pb1—I2	3.2725 (16)	N2—C2	1.476 (18)
Pb1—I3 ⁱ	3.3190 (13)	N2—H2	0.9100
Pb2—N2	2.506 (15)	C2—C1	1.42 (2)
Pb2—N1	2.585 (10)	C2—H2C	0.9700
Pb2—I2 ⁱⁱ	3.1591 (18)	C2—H2D	0.9700
Pb2—I1	3.2236 (17)	C1—H1C	0.9700
Pb2—I3 ⁱⁱⁱ	3.7392 (17)	C1—H1D	0.9700
N1—C1	1.457 (19)		
I1—Pb1—I3	90.26 (3)	Pb1 ^{ix} —I3—Pb2 ^{viii}	74.61 (2)
I3—Pb1—I3 ^{iv}	92.98 (5)	Pb1—I1—Pb2	146.46 (5)
I1—Pb1—I2	179.59 (4)	Pb2 ^x —I2—Pb1	83.66 (4)
I3—Pb1—I2	89.46 (3)	Pb1—I3—Pb1 ^{ix}	90.21 (4)
I1—Pb1—I3 ⁱ	91.41 (3)	C1—N1—Pb2	112.5 (8)
I3—Pb1—I3 ⁱ	176.76 (3)	C1—N1—H1A	109.1
I3 ^{iv} —Pb1—I3 ⁱ	89.79 (4)	Pb2—N1—H1A	109.1
I2—Pb1—I3 ⁱ	88.88 (3)	C1—N1—H1B	109.1
I3—Pb1—I3 ^v	89.79 (4)	Pb2—N1—H1B	109.1
I3 ^{iv} —Pb1—I3 ^v	176.76 (3)	H1A—N1—H1B	107.8
I3 ⁱ —Pb1—I3 ^v	87.39 (4)	C2—N2—C2 ^{iv}	117.7 (17)
N2—Pb2—N1	68.4 (3)	C2—N2—Pb2	112.4 (9)
N1 ^{iv} —Pb2—N1	136.3 (5)	C2—N2—H2	104.2
N2—Pb2—I2 ⁱⁱ	81.5 (4)	Pb2—N2—H2	104.2
N1—Pb2—I2 ⁱⁱ	89.9 (3)	C1—C2—N2	114.1 (12)
N2—Pb2—I1	87.8 (4)	C1—C2—H2C	108.7
N1—Pb2—I1	86.1 (3)	N2—C2—H2C	108.7
I2 ⁱⁱ —Pb2—I1	169.26 (4)	C1—C2—H2D	108.7

I3 ⁱⁱⁱ —Pb2—N1	73.9 (3)	N2—C2—H2D	108.7
I1—Pb2—I3 ⁱⁱⁱ	104.85 (3)	H2C—C2—H2D	107.6
I3 ⁱⁱⁱ —Pb2—N2	139.17 (15)	C2—C1—N1	115.4 (13)
I3 ⁱⁱⁱ —Pb2—I3 ^{vi}	75.64 (2)	C2—C1—H1C	108.4
I2 ^{vii} —Pb2—I3 ⁱⁱⁱ	83.54 (3)	N1—C1—H1C	108.4
I3 ^{vi} —Pb2—N1	149.3 (3)	C2—C1—H1D	108.4
I3 ^{vi} —Pb2—N1 ^{iv}	73.8 (3)	N1—C1—H1D	108.4
Pb1—I3—Pb2 ^{viii}	125.02 (3)	H1C—C1—H1D	107.5
C1—N1—N2—C2	25.1 (14)		

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

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—H1A \cdots I1 ^{xi}	0.90	2.93	3.791 (12)	160
N1—H1B \cdots I2 ^v	0.90	2.88	3.746 (12)	163
N2—H2 \cdots I2 ⁱⁱ	0.91	3.19	3.731 (17)	121

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

Fig. 1

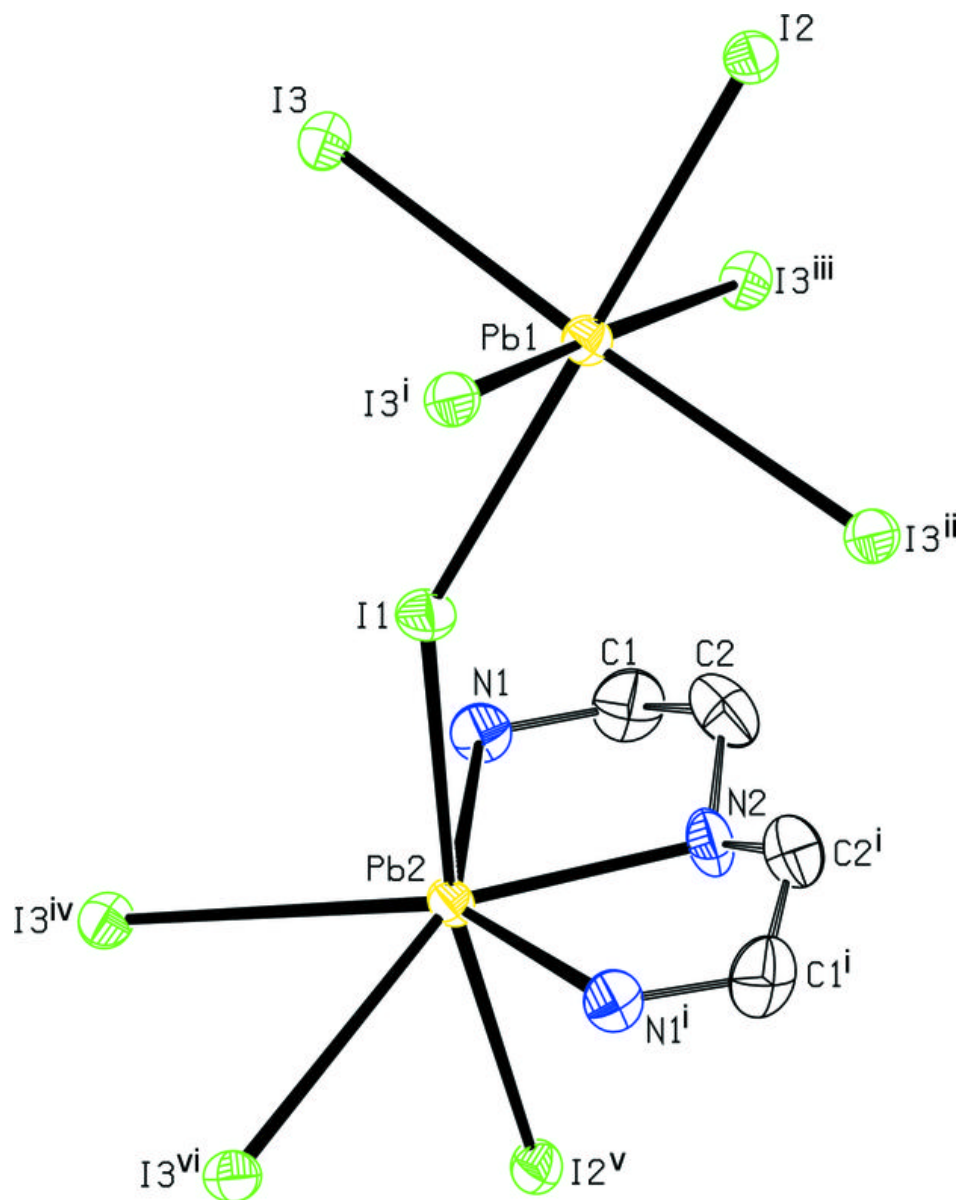


Fig. 2

