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Key indicators

Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(\text{C}-\text{C}) = 0.012 \text{ \AA}$
 R factor = 0.035
 wR factor = 0.092
 Data-to-parameter ratio = 16.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Tetrakis[(9-oxo-10-thiaxanthen-2-yl-oxyethyl)ammonium] decaiodotriplumbate(II)

The structure of the title compound, $(\text{AETO})_4[\text{Pb}_3\text{I}_{10}]$ or $(\text{C}_{15}\text{H}_{14}\text{NO}_2\text{S})_4[\text{Pb}_3\text{I}_{10}]$, contains chains of octahedrally coordinated PbI_6 species along with two crystallographically independent AETO cations that hydrogen bond to these chains. Individual $(\text{Pb}_3\text{I}_{10})_n^{4n-}$ chains are linked into layers *via* hydrogen bonds. The cations sheath each layer of chains, forming cation–chain–cation triple layers. Cations on adjacent triple layers interdigitate, forming stacks running parallel to [110]. There is a range of hydrogen bonding interactions between each cation and the $(\text{Pb}_3\text{I}_{10})_n^{4n-}$ chains.

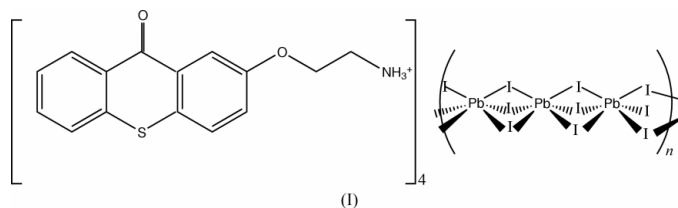
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Comment

The title structure, (I), consists of $(\text{Pb}_3\text{I}_{10})_n^{4n-}$ chains running parallel to [010] and stacks of AETO cations running parallel to [110]. The chains, illustrated in Fig. 1, can be viewed as centrosymmetric sets of three face-sharing octahedra, joined together into chains *via* edge-sharing between terminal octahedra on adjacent trinuclear units. The extended inorganic anion may thus be viewed as a mixed face-shared/edge-shared chain, with a repeat pattern $(f_2e)_n$, where *f* denotes the face-sharing of adjacent octahedra and *e* denotes edge-sharing. Similar chains are observed in several other lead(II) and tin(II) halide salts, both as $(f_2e)_n$ (Krautscheid & Vielsack, 1997; Corradi *et al.*, 1999; Corradi *et al.*, 2001; Gröger *et al.*, 2002; Lode & Krautscheid, 2001) and $(fe)_n$ chains (Krautscheid *et al.*, 2001). A longer face-sharing sequence is found in $(\text{C}_6\text{H}_9\text{N}_2)\text{Ni}_5\text{Cl}_{14}(\text{CH}_3\text{CN})_2$ (Bond & Willett, 1993), where an $(f_4e)_n$ repeat pattern is observed. These structures represent a variation of the parent hexagonal CsNiCl_3 structure type that contains chains of face-shared octahedra (Gmelin, 1966). The replacement of selected face-sharing linkages by edge-sharing units is one structural motif whereby a halide ion (or other ligand) can be incorporated into the parent structure.



The coordination of the central lead(II) ion (Pb1) within the trinuclear unit is relatively symmetrical [$\text{Pb}\cdots\text{I}$ distances of 3.1683 (9), 3.2479 (14) and 3.2649 (11) Å, and bond angles ranging from 83.57 (2) to 94.05 (3)°]. The terminal lead(II) (Pb2) ions are much more distorted, with $\text{Pb}\cdots\text{I}$ distances ranging from 3.0700 (14) to 3.4471 (7) Å and angles from 77.22 (2) to 101.32 (2)°. This distortion is likely due to the asymmetric nature of the environment of the iodide ions

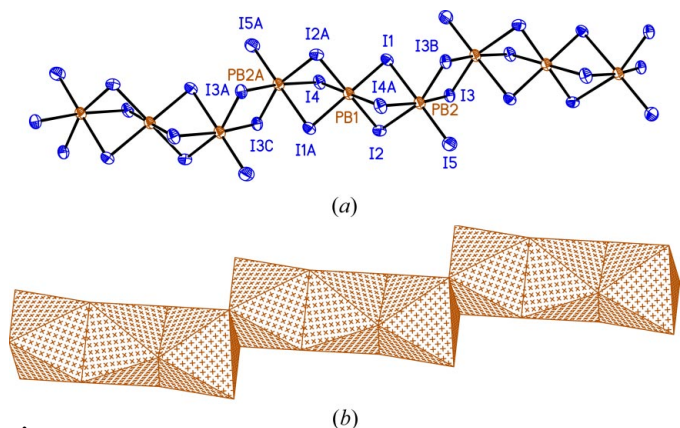


Figure 1
(a) Illustration of the $(\text{Pb}_3\text{I}_{10})_n^{4n-}$ chain. Displacement ellipsoids are drawn at the 50% probability level. (b) Polyhedral representation of the chain.

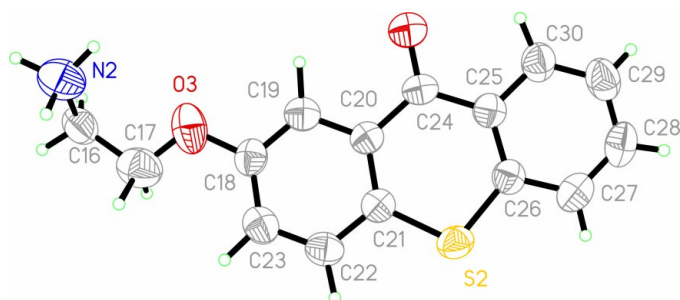


Figure 2
Illustration of cation 2.

coordinated to Pb2. Average values for octahedrally coordinated $\text{Pb}^{\text{II}}\text{I}_6$ species from the Cambridge Structural Database (Version 5.24; Allen, 2002), are $\text{Pb}\cdots\text{I}$ ca 3.10–3.34 Å and angles in the range 77.69–97.25°.

The compound contains two crystallographically independent cations (labeled cat1 for the cation containing N1 and cat2 for the cation containing N2). Fig. 2 illustrates cat2. In both cations, the ethoxyammonium arm has a *gauche* configuration. The cations form stacks parallel to the [110] direction, as shown in Fig. 3. The sequence in these stacks is (cat1, cat1, cat2, cat2, ...). The (cat1, cat1) and (cat2, cat2) pairs are related by centers of inversion, so within each pair the keto C=O groups lie on opposite sides of the stacks. In contrast, for the (cat1, cat2) pairs, the keto C=O groups lie on the same sides of the stacks.

Hydrogen bonding from the ammonium ion on cat1 forms $\text{N}-\text{H}\cdots\text{I}$ bonds bridging pairs of chains. This ties the chains of $(\text{Pb}_3\text{I}_{10})_n^{4n-}$ ions together into sheets parallel to (110), as seen in Fig. 3. In contrast, the $\text{N}-\text{H}\cdots\text{I}$ hydrogen bonds from cat2 involve iodide ions on a single chain. This hydrogen-bonding geometry is presented in Table 1. $\text{N1}-\text{H1C}$ forms a bifurcated hydrogen bond between I2^{ii} and I5^{ii} (for symmetry codes see Table 1). There is also an intramolecular hydrogen bond between N1 and O1. The other cation forms hydrogen bonds to the same chain with a bifurcated hydrogen bond $\text{N2}-\text{H2D}$ to both I2 and I4. In addition, there is both inter- and intramolecular hydrogen bonding between N2 and O2/O3.

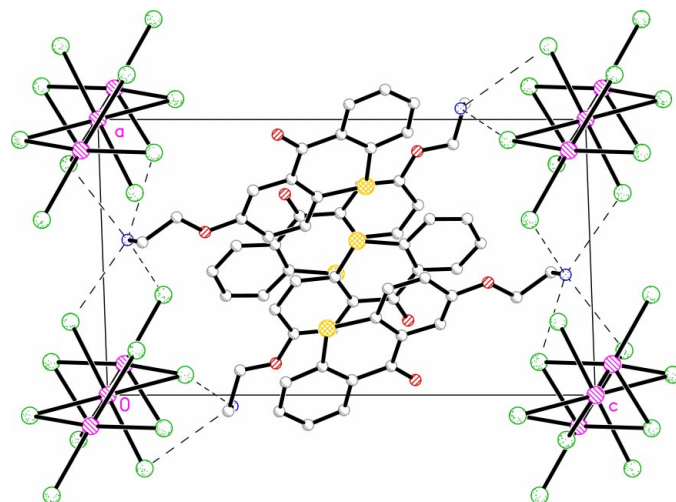


Figure 3
Packing diagram, illustrating the stacking of the cations parallel to [110]. H atoms have been omitted for clarity.

Experimental

Under ambient conditions, stoichiometric amounts of (AETO)I (6.72×10^{-5} mol) and PbI_2 (5.04×10^{-5} mol) were sealed in a large test tube. Under flowing N_2 gas, 5 ml of concentrated hydroiodic acid and 5 ml of 2-propanol were added. The reaction was sealed and heated to 343 K, resulting in a yellow solution. The solution was cooled to 263 K over 24 h. Yellow needle-like crystals were collected and one was selected for structural investigation.

Crystal data

$(\text{C}_{15}\text{H}_{14}\text{NO}_2\text{S})_4[\text{Pb}_3\text{I}_{10}]$
 $M_r = 2979.90$
 Triclinic, $P\bar{1}$
 $a = 9.793$ (2) Å
 $b = 11.704$ (2) Å
 $c = 18.061$ (4) Å
 $\alpha = 71.72$ (3)°
 $\beta = 89.45$ (3)°
 $\gamma = 82.09$ (3)°
 $V = 1945.7$ (8) Å³

$Z = 1$
 $D_x = 2.543$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 8192 reflections
 $\theta = 1.9$ – 24.7 °
 $\mu = 10.60$ mm⁻¹
 $T = 293$ (2) K
 Needle, yellow
 $0.16 \times 0.10 \times 0.08$ mm

Data collection

Bruker SMART 1000 diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1999)
 $T_{\text{min}} = 0.249$, $T_{\text{max}} = 0.428$
 18436 measured reflections

6618 independent reflections
 5205 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.084$
 $\theta_{\text{max}} = 24.7$ °
 $h = -11 \rightarrow 11$
 $k = -13 \rightarrow 13$
 $l = -21 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.092$
 $S = 0.97$
 6618 reflections
 403 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0469P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.93$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.73$ e Å⁻³

Table 1

Hydrogen-bonding 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—H1 <i>B</i> ···I1 ⁱ	0.89	2.92	3.576 (7)	132
N1—H1 <i>C</i> ···I2 ⁱⁱ	0.89	3.21	3.653 (6)	113
N1—H1 <i>A</i> ···I3 ⁱⁱⁱ	0.89	2.88	3.689 (7)	152
N1—H1 <i>C</i> ···I5 ⁱⁱ	0.89	2.94	3.635 (7)	136
N1—H1 <i>A</i> ···O1	0.89	2.53	2.831 (8)	100
N2—H2 <i>D</i> ···I2	0.89	3.10	3.786 (9)	136
N2—H2 <i>D</i> ···I4	0.89	3.24	3.832 (9)	126
N2—H2 <i>E</i> ···O2 ^{iv}	0.89	2.21	2.780 (10)	121
N2—H2 <i>C</i> ···O3	0.89	2.36	2.745 (11)	107

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

H atoms were positioned geometrically and refined using a riding model, with U_{iso} values constrained to be $1.2U_{\text{eq}}$ of the carrier atom. There is a large residual of $1.93 \text{ e } \text{Å}^{-3}$ *ca* 0.96 Å from I5. Please give location of deepest hole.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *XS* in *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in

SHELXTL; software used to prepare material for publication: *XCIF* in *SHELXTL*.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bond, M. R. & Willett, R. D. (1993). *Acta Cryst.* **C49**, 861–865.
- Bruker (1998). *SMART*. Version 5.059. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *SAINT-Plus*. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
- Corradi, A. B., Ferrari, A. M., Pellacani, G. C., Saccani, A., Sandrolini, F. & Sgaraboto, P. (1999). *Inorg. Chem.* **38**, 716–721.
- Corradi, A. B., Ferrari, A. M., Righi, L. & Sgaraboto, P. (2001). *Inorg. Chem.* **40**, 218–223.
- Gmelins Handbuch der Anorganischen Chemie (1966). *Nickel Compounds*, B-3, 8th ed. New York: Springer-Verlag.
- Gröger, H., Lode, C., Vollmer, H., Krautscheid, H. & Lebedkin, S. (2002). *Z. Anorg. Allg. Chem.* **628**, 57–62.
- Krautscheid, H., Lode, C., Vielsack, F. & Vollmer, H. (2001). *J. Chem. Soc. Dalton Trans.* pp. 1099–1104.
- Krautscheid, H. & Vielsack, F. (1997). *Z. Anorg. Allg. Chem.* **623**, 259–265.
- Lode, C. & Krautscheid, H. (2001). *Z. Anorg. Allg. Chem.* **627**, 1454.
- Sheldrick, G. M. (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1999). *SADABS*. Version 2.01. Bruker AXS Inc., Madison, Wisconsin, USA.