

Bis[(*S*)- β -phenethylammonium] tribromoplumbate(II)

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.010\text{ \AA}$

R factor = 0.033

wR factor = 0.065

Data-to-parameter ratio = 27.5

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

The title compound, [(*S*)- $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3^+$][PbBr_3^-], crystallizes as an organic–inorganic hybrid. As such, the structure consists of extended chains of [PbBr_3] $^-$ units running along the a axis. Each Pb atom is octahedrally coordinated by six bromides, arranged as chains of face-sharing octahedra. These inorganic chains are separated by the isolated organic cations.

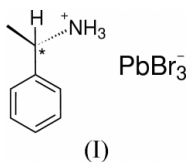
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Comment

In recent years, a significant number of organic–inorganic hybrid materials, based on metal halide units, have been prepared and studied; for reviews, see Papavassiliou (1997) and Mitzi (2001). Haloplumbates, in particular, have demonstrated a propensity for forming a great variety of crystalline structures by self-assembling from suitable solution mixtures. It has been shown that their structures can vary considerably, ranging from systems based on isolated molecules to ones containing extended chains as in [Me_4N][PbI_3] (Contreras *et al.*, 1983) and up to two- or three-dimensional networks (Mitzi, 1999). For systems containing extended chains, the extended chains may be formed by one, two or three bridging halides. Very few examples of the last kind, also described in terms of face-sharing octahedra, involving bromide are known, for example, [Et_4N][PbBr_3] and [Bu_4N][PbBr_3] (Vanek *et al.*, 1992). A search of the Cambridge Structural Database (Version 5.24, February 2003 release; Allen, 2002) for amine-containing compounds yielded only one similar case involving bromide, [PhMe_3N] $_4$ [$\text{Pb}_3\text{Br}_{10}$] (Wiest *et al.*, 1999), consisting of face-sharing trinuclear [$\text{Pb}_3\text{Br}_{10}$] units connected by the sharing of a vertex.



Having previously reported the structure of organic–inorganic hybrid perovskite containing a racemic mixture of the cation 1-phenylethylammonium (Billing, 2002), we present here the room temperature structure of the title compound, ((*S*)- $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3^+$)[PbBr_3^-], (I). This is the first report of an inorganic–organic hybrid with only a single enantiomer of a chiral amine as the counterion.

Fig. 1 shows the asymmetric unit of the title compound, with its atomic numbering scheme. The bromide Br1 is axial and Br2 and Br3 are equatorial. The inorganic chains of distorted face-sharing octahedra orientated along the a axis, separated by isolated amides, are clearly visible in the packing diagrams

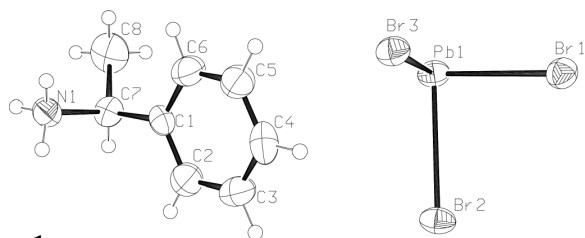


Figure 1
View of the asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level.

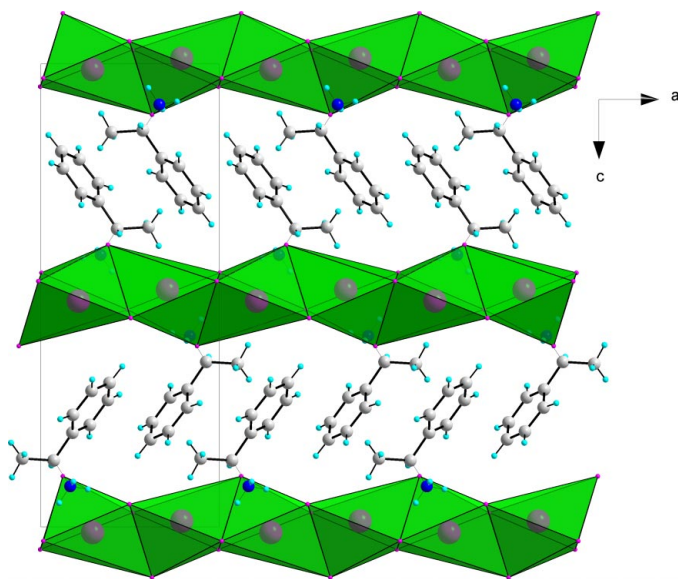


Figure 2
Packing diagram of (I), viewed along the *b* axis.

(Fig. 2 and Fig. 3). Within the chain, the shared face consists of two equatorial bromides and one axial bromide. The octahedra are severely distorted with all lead–bromide distances different, ranging from 2.8576 (11) Å to 3.3253 (17) Å (Table 1). The bond angles between *cis* ligands vary from 75.56 (4)° to 93.49 (5)° and *trans* angles from 154.83 (3)° to 167.54(2)°.

There is extensive hydrogen bonding, with the large ionic radius of bromine enabling contact with four different H atoms (Table 2). The hydrogen bonds are similar in length to the average lengths reported by Steiner (1998) for hydrogen bonds involving halide ions. The bifurcated Br2⋯H1A⋯Br3 distances are 2.76 Å and 2.88 Å, whereas the lengths in the simpler Br⋯H1B and Br⋯H1C are both 2.68 Å. Within the organic section, adjacent aromatic rings are separated by a centroid-to-centroid distance of 5.373 Å, which is probably too large to be considered as representing π -stacking interactions.

Experimental

Crystals of ((*S*)-C₆H₅C₂H₄NH₂)[PbBr₃] were grown at room temperature by first dissolving 0.204 g PbBr₂ (0.556 mmol) in 5 ml HBr and 5 ml of ethanol. 0.120 g (*S*)-C₆H₅C₂H₄NH₂(I) (0.990 mmol) was then added dropwise. The needle-shaped colourless crystals were harvested after seven days. Analysis calculated for C₈H₁₂N₁PbBr₃: C 16.89, H 2.13, N 2.46%; found: C 16.95, H 2.20, N 2.43%.

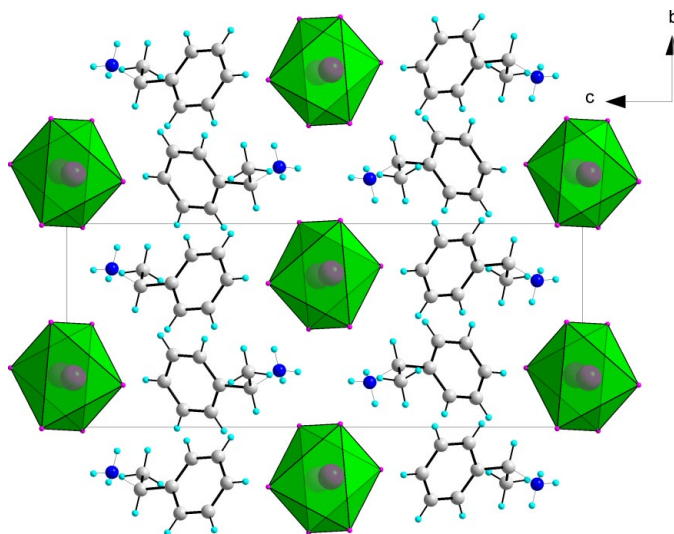


Figure 3
Packing diagram of (I), viewed along the *a* axis.

Crystal data

(C₈H₁₂N)[PbBr₃]
M_r = 569.11
 Orthorhombic, *P*2₁2₁2₁
a = 7.930 (5) Å
b = 8.147 (5) Å
c = 20.580 (5) Å
V = 1329.6 (12) Å³
Z = 4
D_x = 2.843 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 840 reflections
 θ = 7.8–55.7°
 μ = 21.67 mm⁻¹
T = 293 (2) K
 Plate, colourless
 0.22 × 0.16 × 0.03 mm

Data collection

Bruker CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: by integration (*XPREP*; Bruker, 1999)
T_{min} = 0.056, *T_{max}* = 0.485
 9328 measured reflections

3268 independent reflections
 2587 reflections with *I* > 2σ(*I*)
R_{int} = 0.062
 θ_{max} = 28.3°
h = −10 → 6
k = −10 → 10
l = −27 → 26

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.033
wR(*F*²) = 0.065
S = 1.01
 3268 reflections
 119 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0222P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} = 0.001
 $\Delta\rho_{max}$ = 1.21 e Å⁻³
 $\Delta\rho_{min}$ = −0.71 e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0118 (3)
 Absolute structure: Flack (1983)
 Flack parameter = −0.032 (12)

Table 1

Selected geometric parameters (Å, °).

Pb1–Br1	2.8576 (11)	Pb1–Br2	3.0716 (16)
Pb1–Br3 ⁱ	2.8981 (14)	Pb1–Br3	3.2566 (16)
Pb1–Br2 ⁱ	2.9880 (15)	Pb1–Br1 ⁱ	3.3253 (17)
Br1–Pb1–Br3 ⁱ	88.80 (3)	Br3 ⁱ –Pb1–Br3	165.20 (2)
Br1–Pb1–Br2 ⁱ	84.84 (4)	Br2 ⁱ –Pb1–Br3	90.07 (5)
Br3 ⁱ –Pb1–Br2 ⁱ	93.49 (5)	Br2–Pb1–Br3	85.25 (5)
Br1–Pb1–Br2	82.86 (4)	Pb1 ⁱⁱ –Br2–Pb1	82.58 (5)
Br3 ⁱ –Pb1–Br2	88.28 (5)	Pb1 ⁱⁱ –Br3–Pb1	80.81 (5)
Br2 ⁱ –Pb1–Br2	167.54 (2)	Br1–Pb1–Br1 ⁱ	154.83 (3)
Br1–Pb1–Br3	77.21 (3)	Br3 ⁱ –Pb1–Br1 ⁱ	75.56 (4)

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

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1A \cdots Br2^i$	0.89	2.76	3.452 (7)	136
$N1-H1A \cdots Br3^{ii}$	0.89	2.88	3.567 (7)	135
$N1-H1B \cdots Br1^{ii}$	0.89	2.68	3.532 (7)	162
$N1-H1C \cdots Br3^{iii}$	0.89	2.68	3.532 (7)	160

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

All H atoms were refined in idealized positions in the riding model approximation and with their isotropic displacement parameters fixed to 1.2 of the equivalent isotropic displacement parameter of the atom to which they are bonded. The highest residual peak is located 0.99 Å from Pb1.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *XPREP* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); 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, 2003).

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